# Diagenesis of mudrocks, illite 'crystallinity' and the effects on engineering properties.

**Mourice Andrew Czerewko**

Submitted in fulfilment of the
requirements for the degree of Doctor of
Philosophy

Department of Earth Sciences
University of Sheffield

May 1997

# Diagenesis of mudrocks, illite ‘crystallinity’ and the effects on engineering properties.

## Abstract.

This study deals with the changes in mineralogy and fabric of a suite of mudrocks due to increased induration caused by diagenetic history, and the subsequent controls on geotechnical properties. Burial diagenesis of mudrocks has important implications on their engineering behaviour, in particular the liberation of Si and Ca during illitisation of smectite and mixed layer clay minerals leading to cementation. The objective of the research has been to provide a means of predicting engineering performance of mudrocks from mineralogical composition. A suite of 41 mudrock samples ranging from Cambrian slates to Carboniferous Coal Measures in age and variable diagenetic rank has been sampled and tested.

A detailed mineralogical evaluation of the samples was conducted and it was found that the proportion of mixed layer clays and kaolinite decreased with an increase in diagenetic rank of the material, but not necessarily with increasing ages of the samples.

The diagenetic histories of the samples was assessed using illite ‘crystalinity’ and vitrinite reflectance measurement, which indicated that the samples ranged low diagenetic to epizonal in rank.

The textures of the samples was studied using back-scattered scanning electron microscope imagery. The novel application of this technique to textural analysis in the field of engineering geology resulted in the diagenetic rank parameter classification scheme being devised. The classification parameter consists of a systematic approach to the evaluation of pore and microfracture distribution, clay mineral orientation and degree of recrystallization, degree of contact of clastic mineral constituent and the degree of cementation.

The physical properties of the mudrocks were assessed in terms of bulk index properties, swelling, slaking and strength.

In evaluating the test data, it was found that that the principal controls on the durability of indurated mudrocks was the distribution of microfractures and the mixed layer clay content. With increasing diagenetic rank measured by illite 'crystallinity' determination, the durability of the samples increased due to the development of a more mature rock fabric as seen by the use of back-scatter scanning electron microscope imagery. With increasing diagenetic rank there is a decrease in microfracture distribution due to recrystallization of clay mineral species and subsequent recementation of the sample also due to release of Ca and Si from the conversion of clay mineral species. This process reduces void space, eliminates microfractures and creates a non expansive clay mineral suite resulting in a durable mudrock less susceptable to swelling and slaking effects.

An additional controlling factor on mudrock durability was found to be the presence of calcareous and organic carbon cements. These controls were found to be short term, as seen in natural weathering experiments, where samples of high calcareous and carbonate contents were found to start slaking after a period of 6 to 8 months of exposure, and samples of low carbonate and calcareous content began to degenerate almost instantaneously. The controls of cementation on the durability of mudrocks are eventually broken down due to the effects of air breakage in voids and swelling stress resulting from the expansive clay mineral species present.

A range of simple index tests were used to physically characterise the mudrock samples and their potential in determining mudrock durability was evaluated. A mudrock rank durability classification approach is presented which is based on the modified jar slake test, methylene blue adsorption and moisture absorption determination. These index tests were found to correlate strongly with void and microfracture distributions and proportions of mixed layer clays within the samples. This classification approach was tested on the samples in the study and found to be effective in distinguishing between non-durable, moderately durable, and durable mudrocks.

## Acknowledgements.

I would like firstly to express my gratitude to my supervisor, Dr. John Cripps for his support, advice and patience during this work. I would like to thank The University of Sheffield for providing me with the 'Farmy' scholarship which funded the research. All the individuals and organisations who provided access to sites for sample collection.

I would like like to thank all the staff within the Department of Earth Sciences for their assistance along the way, especially Dr. R. Soutiriou for help with XRD and XRF analysis, Dr. C. Booth and Mr. S. Ellin for assistance in sample preparation and determination of vitrinite reflectance, Mr. B. Piggot for help with the photography and Pat Mellor, Gill Thompson and Paul Higham for generally helping out and keeping me in line. In other departments within the University I would like to thank Miss. D. Bussy in assisting with the electron microscope work and Miss. B. Lane in assisting with the mercury porosimetry.

On a more personal note I would like to thank my mother for her patience and support during the course of my research, to my house-mates M. Snooks, R.Burgess and G. Foran I would like to appologise for making their life a misery when writing up. To P. Manning, M. Snook and P. Jeremias, I would like to offer my thanks for endless hours of discussion on a topic they once knew little about and now know too much about.

On a final note I would like to thank all my friends who have helped me through a difficult period especially Mr. O. Tkachuk, Miss. A. Hunder, the brothers P. and R Greshko, and Mr. T. Ciuriak for pestering me to complete this study and Mr. M. Babinsky for convincing me to do this research, I hope he is happy for all the misery he has brought me !.

# Contents

## Appendices

## List of figures

**A2: Whole rock XRD plots**

**A3: Clay mineralogy plots**

**B3: PSD plots for the slake durability test debris**

**B4: Triaxial swelling test plots**

**C2: Roof weathering experiment ICP-AES data plots**

## List of tables

## List of plates

**Plate No.** ........ **Following page.**

**Standard petrographic and back-scattered scanning electron microscopy.**

**Roof weathering experiment.**

# Chapter 1.

# Introduction.

## 1.1. Outline of previous research

The aim of the study is to investigate the controls that diagenetic rank exerts upon the mineralogy, texture and geotechnical properties of mudrocks. The measurement of illite 'crystallinity' in mudrocks by X-ray diffraction provides a means of determining the diagenetic rank and also is indicative of engineering properties. Along with other rank indicators, such as vitrinite reflectance, illite 'crystallinity' was measured to investigate the relationship with respect to swelling, slaking, textural and porosity changes in unweathered mudrocks.

Mudrocks are defined as very fine grained argillaceous sedimentary rocks. As noted by Dick and Shakoor (1992), the term encompasses a wide variety of lithotypes ranging from poorly indurated low durability soil type deposits to low grade slates and argillites. Mudrocks are the most common type of sedimentary rocks, making up approximately two thirds of the sedimentary stratigraphic column (Blatt, 1982). Due to their abundance, mudrocks are unavoidably encountered in all types of engineering projects. As the range of mudrock lithotypes is large, so is their engineering behaviour, since slates and argillites will generally tend to behave favourably in an engineering environment, whilst low durability mudrocks tend to decay over relatively short periods of time.

The fundamental engineering problem with some mudrocks is their physical disintegration when exposed to atmospheric conditions. The prediction of the response to weathering of mudrocks in the field has been investigated in detail since the 1950's. Unfortunately, the majority of the research has been conducted to solve particular problems or in connection with individual projects or formations, leading to the development of engineering classification schemes for mudrocks, which have proved to be site specific, and not generally applicable. Few existing studies on the behaviour of mudrocks contain sufficient information about the mineralogy and texture of the material.

The mainstay of mudrock research in the field of engineering geology and mining has been into the measurement of durability. This primarily is controlled by the related slaking and swelling tendencies of the mudrocks and the constituent clay minerals. The slaking properties of mudrocks were of concern to the British coal mining industry, which established the 'Shales Panel' in 1953 (Taylor, 1988). Their research established a basic understanding of abrasive and breakdown behaviour of mudrocks (Badger et al, 1956; Berkovitch et al, 1959). The Shales Panel designed the 'end-over-end' slaking test, which was the forerunner of the ISRM slake durability test (Franklin and Chandra, 1972), which is the accepted standard test for durability classification of mudrocks. The extensive research on the slaking behaviour of mudrocks has produced a catalogue of geodurability classification schemes, such as those of Gamble (1971), Morgenstern and Eigenbrod (1974), Olivier (1980), Deen (1981), and Taylor (1988). Additional research has provided recommendations for the engineering descriptions of mudrocks, such as those of Taylor and Spears (1981), Grainger (1984), Hawkins and Pinches (1992),and Spink and Norbury (1993).

The engineering properties of mudrocks, especially durability have been found to relate to their composition, geological history (i.e. diagenetic rank) and degree of weathering (Cripps and Taylor, 1981; Steward and Cripps, 1983; Shakoor and Brock, 1987; and Taylor 1988). Research has been carried out by many workers in an attempt to relate weathering properties, composition and geological histories of mudrocks to each other. Many of these studies such as those by Okagbue (1984), Seedsman (1980), Russell (1982) and Bell and Coulthard (1993), have been restricted to particular geographical localities. Additionally research has been restricted to a wide range of samples but from a specific formations, such as the Carboniferous Coal Measures by Badger et al (1956), Spears and Taylor (1974) and Taylor (1988), or Jurassic clays by Chandler (1974) and Campbell (1993). In addition a limited number of studies such as those by Gamble (1971), Smith (1978) and Dick (1992) have been carried out on a suite of mudrocks of varying geological ages from a range of geographical localities. In summary, these latter research projects, have shown that the principal processes for mudrock degradation are:

- Stress relief upon exhumation forming or opening existing microdiscontinuities (Dick and Shakoor, 1992; Dick, 1992).
- Physical disintegration which occurs on contact with water (Taylor, 1988).
- Chemical weathering involving pyrite breakdown (Steward and Cripps, 1983).
- The expansion of mixed layer clays (Taylor and Smith, 1986).

The latter process has been shown to have less control on geologically older, more mature mudrocks due to the diagenetic conversion of expansive clays to a more stable clay suite. Processes of maturation due to diagenetic changes include recrystallization and bonding of clay mineral phases, cementation and the changes to sedimentary structures and discontinuities.

The effects of geological history in terms of diagenetic heating and compression upon the engineering behaviour of mudrocks has received less attention than other controlling parameters, although a few studies have been attempted on less indurated mudrocks (Smith, 1978; Campbell, 1993). In attempts to investigate the effects of geological history and burial upon mudrock durabilities, Smith (1978) and Campbell (1993) employed standard consolidation tests as would be used for estimating the maximum depth of burial of consolidated sediments. However, with increasing burial it was not possible to determine the burial depth, the results became meaningless as recrystallization and cementation of the rock obliterated the consolidation effects. In order to overcome these difficulties Campbell (1993) also employed vitrinite reflectance as a measure of diagenetic changes in his samples of Jurassic mudrocks, but he encountered problems in the interpretation of the results due to a large scatter of readings caused by the presence of reworked older organic phytoclasts being present within the samples. Grainger (1984) suggested that illite ‘crystallinity’ could be a useful parameter for classification of indurated mudrocks, but unfortunately the usefulness has never been investigated with respect to engineering classification. Taylor (1984) showed that mudrock durability increased with increasing coal rank in Carboniferous Coal Measures material, and many workers including Foscolus and Kodama (1974), Gill et al. (1977) and Bustin et al. (1985) noted the improvement in illite ‘crystallinity’ with increasing coal rank. This suggests that illite ‘crystallinity’ may be a useful parameter for ranking the engineering properties of mudrocks. Illite ‘crystallinity’ has received much attention in the field of very low temperature metamorphic studies, particularly for mapping out metamorphic zones within argillaceous terrains (Frey, 1970; Dunoyer de Segonzac, 1970; Foscolus and Kodama, 1974; Gill et al., 1977; Frey, 1978; Kisch, 1980; Merriman and Roberts, 1985; Frey, 1987; Fernandez- Caliani and Galan, 1992; etc.). Due to its popularity in such studies, illite 'crystallinity' controls have been investigated and are well documented, therefore the technique has become standardized, and can be applied with precision and repeatability to mudrock studies.

Since much research has been carried out on the mechanics of mudrock degradation, the topic has gained a high degree of understanding. At present no work has been carried out to investigate the role of the illite 'crystallinity' parameter as a means of determining the engineering classification of mudrocks which is the aim of this study with the intention of setting up a database of engineering characteristics of mudrocks using illite 'crystallinity'.

## 1.2. Outline of research.

This work forms part of on going research into the engineering properties of mudrocks (Al Dabbagh, 1986; Steward, 1984; Campbell, 1993). Particular emphasis has been placed on understanding the controls exerted by composition and geological history. Research being carried out by Dr. R. Merriman of the British Geological Survey into the modelling of illite 'crystallinity' in mudrocks could provide a useful means of assessing the extent of burial diagenesis in mudrocks. In the case of the research being undertaken by Dr. R. Merriman, the results have led to the production of a correlation chart for the hydrocarbon potential of sedimentary basins using illite 'crystallinity' (Merriman and Kemp, 1996). It is intended to investigate the potential use of illite 'crystallinity' values from mudrocks for predictive characterization within the field of engineering geology. Mudrocks are commonly encountered in civil engineering schemes where they are generally considered as problematic material. The most problematic responses of certain mudrocks are swelling and slaking characteristics upon exposure to the atmosphere and moisture. These problems are commonly encountered in tunnelling projects ( Olivier, 1990; and Varley, 1990), road cuttings and engineering slopes (Buist et al., 1979; and Dick and Shakoor, 1995) and foundation construction (

Erol and Dhowain, 1990). The greatest problem with mudrocks is the prediction of their long term behaviour, with this knowledge appropriate action could be taken to minimise the problems commonly encountered in engineering projects. Detailed research at Sheffield University by Campbell (1993), into the durability of Jurassic mudrocks, following on from the work by Al-Dabbagh (1986) has provided much information into the controls of mudrock breakdown and weathering. In his recommendations for future research, Campbell (1993) suggested the need for more extensive research into the weathering behaviour (durability) of mudrocks, extending to a range of material studied to those of widely different ages and geological histories. Slaking experiments should concentrate on natural weathering behaviour, and more detailed mudrock fabric analysis in relation to slaking was suggested as a principal requirement.

Accordingly, a programme of research following these recommendations was instigated. A range of mudrocks with varying diagenetic histories and geological ages ranging from Cambrian to Carboniferous Coal Measures were tested. The samples were selected from outcrops and open cast quarries within mainland UK. They consist of a large range of mudrock lithotypes ranging from argillites to siltstones and claystones. The samples were selected from the older British mudrock formations as they undergo the greatest change in properties such as density, strength, durability, porosity, textural and mineralogical changes with conversion to residual soils during degradation. Many of Britain's major conurbations and industrial centres lie on the outcrop of the Carboniferous Coal Measures. This formation is of great interest in view of the engineering works, including redevelopment of these areas, present mining activities and waste disposal in terms of both the tipping of coal mining and processing waste materials and the construction of present day landfills for the safe disposal of domestic, industrial and other waste. The sampling was therefore concentrated on Carboniferous Coal Measures material due to its economic importance, availability and the wide range of mudrock lithotypes available within this geological unit which would account for most problematic situations encountered within engineering projects.

### 1.2.2. Experimental programme.

An outline of the experimental programme is presented in Figure 1.1 and briefly outlined below.

The work is set out in the context of the classification of mudrocks as this has the potential of allowing wide application of the results. In Chapter 2 a review of mudrocks is presented, with discussions on mineralogies, terminologies, the present published approaches to geological description and engineering classification.

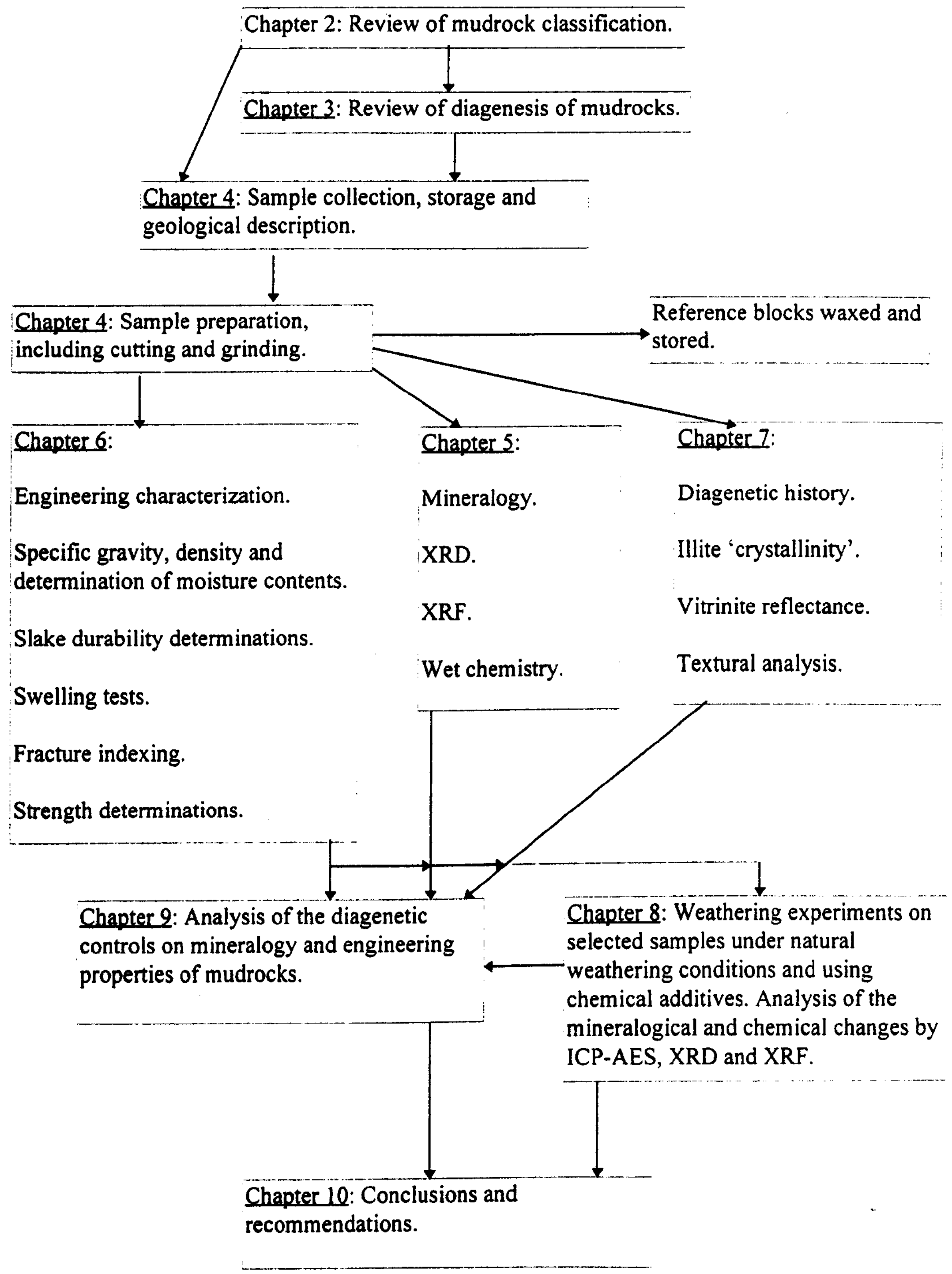


Figure 1.1 Flowchart of the experimental programme.

The rational underlying the description and classification schemes is discussed, and the chapter concludes with a proposed method for mudrock description. This has been adhered to in this study. It provides a means of cross-referencing these findings with other research and may form the basis for an improved classification of mudrocks for engineering purposes.

Further background to the research is provided in Chapter 3 which is concerned with the diagenesis of mudrocks. It presents the mineralogical and physical changes during progressive burial diagenesis and considers factors that control the effects of the processes concerned. This Chapter includes a review on illite 'crystallinity' and vitrinite reflectance, to familiarise the reader with these diagenetic indicators which will be investigated in this study. Sample collection, storage methods, preparation for the various testing procedures, and geological descriptions following the recommendations of Chapter 2, are presented in Chapter 4.

The mineralogical compositions of the samples, quantified by standard techniques are reviewed and presented in Chapter 5. The physical characterization of the mudrocks, including justification for and details of any modifications made to standard index tests are discussed in Chapter 6, along with a brief review of the usefulness of these test results. In Chapter 7 a detailed diagentic investigation of the mudrock samples is presented. This consists of diagenetic characterization (ranking) of the samples using illite 'crystallinity' measurements, and vitrinite reflectance results. Detailed textural data are also presented for each sample, consisting of an initial description of standard petrographic thin sections, and more detailed mineralogical and fabric descriptions obtained using backscattered electron microscope imagery. The textural data are presented in the form of visual observations, along with a textural ranking scheme modified for this study.

Chapter 8 describes a series of natural weathering experiments performed over a 12 month period. Seven representative samples were selected from the available Carboniferous samples which were subjected to normal atmospheric conditions with some samples also receiving regular additions of selected chemical reagents. This was to study the processes of breakdown and formed part of the research into methods of enhancing mudrock breakdown to render the material suitable for the use in mineral linings of landfill sites. These samples were monitored visually for breakdown, and additionally samples of the leachates were collected on a regular basis and analysed using ICP-AES qualitatively to monitor the mineralogical changes affected by natural and assisted weathering. The samples were analysed mineralogically after the 12 month period, sieved to accertain the state of breakdown and the results discussed.

In Chapter 9 the results of the mineralogical, physical and textural investigations are compared to enable a picture of the controls of diagenetic processes upon engineering properties to be established. The findings are presented as a classification chart of engineering properties compared with diagenetic parameters. The conclusions of the work are presented in Chapter 10 together with some criticisms of the experimental programme and recommendations for the direction of future research based on the findings of this study.

# Chapter 2.

# The constituents and classification of mudrocks

## 2.1. Objectives of rock classification.

To geologists rocks are masses of naturally occurring mineral matter of which, due to the vast varieties of inorganic and organic materials in nature, there are many types. Rock classification arises to satisfy scientific and practical needs. From the scientific point of view rocks are usually assigned into one of of three groups, namely igneous, metamorphic and sedimentary on the basis of their genesis. These groups are further subdivided according to various mineralogical and textural features, many of which relate to the particular environment and condition of formation. According to the Geological Society Engineering Group Working Party report on classification of weathered rock (Anon, 1995), the first step in designing a useful classification should be to determine the relevant parameters or characteristics of the rock. Class names are then assigned according to the predetermined grouping of these attributes. Rocks are classified in a number of ways, depending on the purpose for which the classification is required. In geological classifications, the main considerations are the mineral composition of the rock, the physical and chemical interactions of the mineral grains, and the processes which affected the rock during and after formation. In an engineering classification of rock, it is more important to describe those aspects which influence engineering behaviour, such as discontinuities and mineralogy.

## 2.2. Mineral constituents of mudrocks.

Mineralogies of mudrocks tend to be divided into two main groups, these being clay minerals which tend to give mudrocks their unique geological and engineering properties such as fine grain size, plasticity and susceptability to swelling and slaking. Non-clay minerals constitute the other group consisting of mineral species from a detrital origin such as quartz, feldspars and organic carbon and constituents of authogenic origin such as carbonate and sulphur derived mineral species. These two mineral groups shall be covered in further detail and their use and controls in the classification of mudrocks shall be evaluated.

### 2.2.1. Introduction to clay minerals.

This section is a brief review and discussion of clay mineral types and their structures which introduces a consideration for the terminology which shall be commonly used in this study. More detailed general reviews are given by Brindley & Brown (1984), Weaver (1989) and Moore and Reynolds (1989) and by Srodon and Eberl (1984) who deal with illites.

There are various definitions of clay minerals which can be summarised by the following two examples:

1. In a geological context, clay minerals tend to be considered as phyllosilicate minerals with a hydrous aluminosilicate composition (Greensmith, 1989; Tucker, 1994).
2. Clay minerals as defined by the Clay Mineral Society (Guggenheim and Martin, 1995) constitutes phyllosilicate minerals which impart plasticity to clay and which harden upon drying or firing.

It is pointed out by Guggenheim and Martin (1995) that workers should take care with terminologies used, as confusion may arise since the Clay Mineral Society (Guggenheim and Martin, 1995) further define clay as being -

> "Naturally occurring material composed primarily of fine-grained minerals, which are generally plastic at appropriate water contents and will harden when dried or fired. Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fired."

Clay minerals have a sheet like structure composed of one of two basic unit types. The first consists of a layer of silicon-oxygen tetrahedra with the three oxygens in the tetrahedra shared with adjacent tetrahedra, and linked together forming a hexagonal network with the basic unit consisting of $Si_2O_5$ (see Fig. 2.1-a). Within these layers aluminium may replace up to half the silicon atoms. The second layer type consists of aluminium ions located between sheets of oxygen and hydroxide ions formed in an octahedral coordination (see Fig. 2.1-b). In the octahedral unit not all the aluminium sites may be occupied, or they may be substituted by magnesium, iron or other ions.

Clay minerals therefore consist of sheets of tetrahedra and/or octahedra linked together by oxygen atoms common to both. The stacking arrangement of the sheets and replacement of silicon and aluminium ions by other elements determines the clay mineral type.

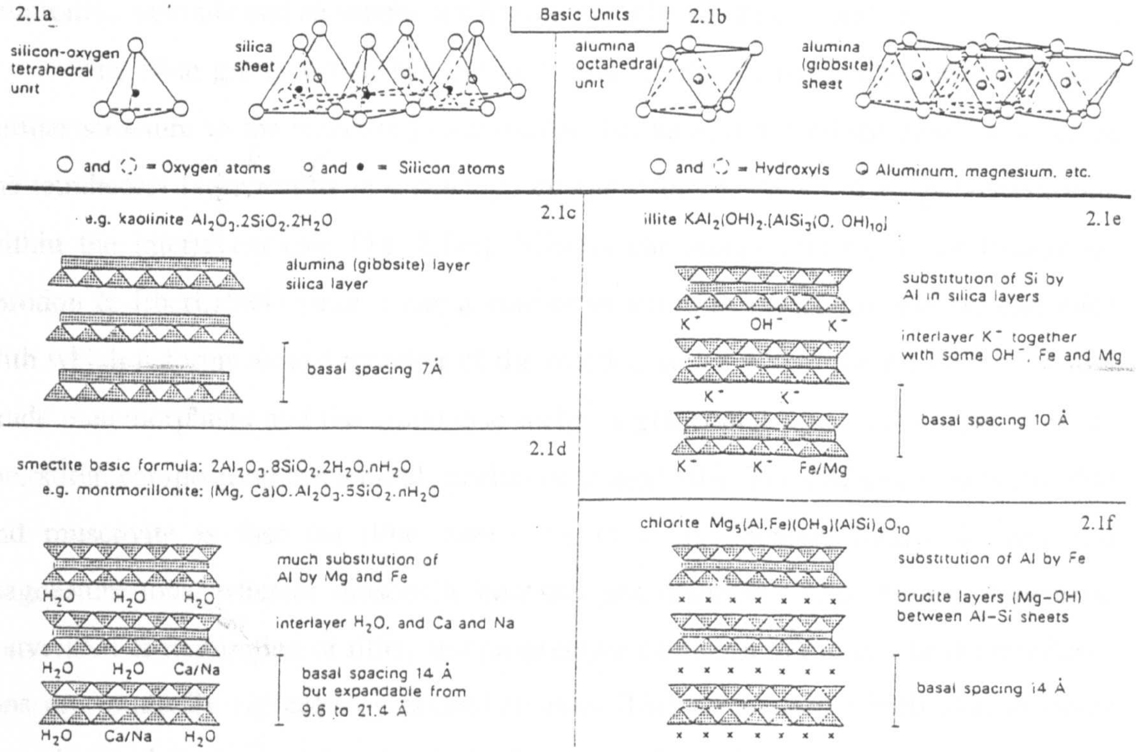


Fig.2.1. Clay mineral structures.

There are basically two major types of clay minerals, namely two-layered structure types or three-layered structure types. The two-layered structure type basically consist of the kandite group, kaolinite being the most commonly encountered member and dickite, nacite and chamosite are less common. The two-layered structure consists of a silica tetrahedral sheet linked to an aluminium octahedral sheet by associated oxide and hydroxide ions (see Fig. 2.1-c). This results in a basic basal spacing of 7Å as detected by X-ray diffraction or transmission electron microscope studies.

The three-layered structure clay mineral types consist of three groups which are the smectite, illite and chlorite groups. The smectite group is composed of an alumina octahedral layer positioned between two silica tetrahedra layers (see Fig. 2.1-d). The aluminium ion may be substituted by iron, magnesium or zinc, which results in a net negative charge which is balanced by other cations especially calcium or sodium within the interlayer position. The structure results in a basic basal spacing of 14Å which may vary between 9.6Å to 21.4Å due to the ability of the smectite group to adsorb water thus giving them their unique swelling property. Montmorillonite and vermiculite are common varieties of the smectite group which possess the ability to swell, and nontronite, saponite and stevensite are less commonly occurring varieties.

The illite group which has the most commonly occurring clay minerals has a similar structure to the smectite group except that aluminium substitution for silica in the tetrahedral layer results in a negative charge which is balanced by potassium ions within the interlayers (see Fig. 2.1-e). Illite is commonly referred to as hydromica (Srodon & Eberl,1984) since it has a similar structure to muscovite and sericite mica with which it forms an end member of the reaction series within the realm of very low grade metamorphism and the group also includes glauconite. Illite, depending upon its interstitial composition has a basal spacing of around 10Å. The difference between illite and muscovite is that the illite interlayers may also contain hydroxyl, iron and magnesium ions, whereas muscovite contains just potassium ions. During diagenetic conversion or maturation of illite, and progressive alteration to muscovite the interlayer ions are gradually replaced by potassium ions. This maturation which also involves crystal growth is the basis upon which illite 'crystallinity' measurements are made, as described in Chapter 3.

The chlorite group has a similar structure to that of the smectite group in that the interlayer units consist of magnesium hydroxide and the substitution of aluminium by iron occurs (see Fig. 2.1-e). This latter feature imparts the characteristic green colour of this mineral. Other less commonly occurring magnesium rich aluminosilicates are sepiolite and palygorskite.

In addition to the four common clay mineral groups are the mixed-layer clays which consist of interleaves of the common clay minerals, the most abundent combination being that of illite-smectite. Due to the confusion that would arise from naming the individual combinations of mixed-layer clays many geologists refer to them by their component end members. During weathering degradation of illite may result due to base exchange with circulating ground water which results in the stripping of interlayer ions and their replacement by $OH^-$ groups. This leads to the progressive conversion of illite to smectite via mixed layer illite-smectite (Hawkins, Lawrence & Pinches,1988). Similarly diagenetic processes cause dehydration of smectite and the replacement of $OH^+$ groups by potassium ions. In this case the crystallinity or regularity of the crystal structure is enhanced with eventual conversion to a stable muscovite structure. The progress of this change can be measured using X-ray diffraction techniques as an illite 'crystallinity' parameter but this topic is covered in more detail in Chapter 3.

The replacement of interlayer cations associated with weathering processes can have an important effect on the properties of clay since different replacement bases change the permeability of clays and the degree of flocculation (Greensmith, 1989; Grim, 1962).Base exchange is a commonly occurring weathering process that commonly occurs especially in smectite and expandable mixed-layer clays. If Ca-smectite is affected by percolating saline waters, Na ions replace the Ca ions within the smectite interlayers and the Ca goes into solution leaving a Na clay behind. Acid rain replaces interstitial ions with hydrogen, and other common exchange species are Mg, $NH_4$ and K. As hydrogen clays are highly dispersed they are relatively impermeable. On the other hand Na clays tend to be moderately flocculated and therefore allow a slow passage of water whereas Ca clays formed under hard water conditions become highly flocculated which imparts relatively high permeability to clay deposits ($\sim 10^{-5}$ to $10^{-3}$ m/s).

### 2.2.2. Non-clay mineralogy of mudrocks.

Quartz tends to be a major constituent in many mudrocks, much of which tends to be of detrital origin. Quartz may also be present in more indurated mudrocks as a cementing phase which forms due to the diagenetic transformation of clay minerals upon deep burial (Shaw, 1981). Quartz occurs mainly as the silt-grade size component in mudrocks, although coarser sand-grade size grains do occur and as do finer clay-grade size grains (Weaver, 1989 and Tucker, 1991).

Feldspar is usually present in small percentages in mudrocks, it is generally of detrital origin and the commonest species being plagioclase feldspar (Shaw and Weaver, 1965).

Carbonates are commonly present in mudrocks occurring as discrete clasts or cements. Calcite and, to a lesser extent, dolomite are commonly present in mudrocks of marine origin, whilst siderite is commonly present as the authigenic phase in mudrocks from a brackish, partly reducing environment (Curtis, 1977 and Shaw, 1981).

Sulphur compounds are commonly present in low concentrations, the most common species being the iron sulphide pyrite, which tends to precipitate in the depositional environment forming cubes, framboids or nodules. Gypsum-anhydrite are the most important sulphate species found in mudrocks, but they are of restricted stratographic occurrence mainly associated with evaporite environments.

Organic matter is an economically important, common constituent of mudrocks being the source of hydrocarbons. Proportions of organic carbon have been shown by Potter et al., (1980) to affect the colour of the mudrocks.

Iron oxides and oxyhydroxides are usually present in mudrocks as grain coatings, haematite being the most common form, but in weathered mudrocks, hydrous forms such as goethite tend to be more common.

Mineralogical analysis of mudrocks have tended to concentrate on the clay mineral fraction with respect to diagenetic studies, although a select number of studies have been carried out which have characterized the average mineralogy of mudrocks. Average mineralogical compositions of mudrocks from studies by Shaw and Weaver

| | Shaw and Weaver (1965) | Pettijohn (1975) | Taylor and Smith (1986) | | Taylor (1988)** |
|---|---|---|---|---|---|
| | | | UK** | USA* | |
| Clay minerals | 61 | 43 | 73 | 60 | 77 |
| Quartz | 31 | 29 | 20 | 32 | 19.5 |
| Feldspar | 4 | 11 | 1 | 3 | 0.5 |
| Iron oxides | 0.5 | 5 | _ | _ | _ |
| Carbonates | 4 | 9 | 4 | 3 | 1 |
| Organic matter | 1 | 0.3 | 1 | 1 | 2.3 |
| Pyrite | _ | _ | 2 | trace | 0.5 |
| Gypsum | _ | _ | _ | _ | trace |
| Other minerals | 2 | 3 | _ | _ | _ |

* = Cretaceous to Tertiary mudrocks.

** = UK Carboniferous mudrocks.

Table 2.1. Average composition of worldwide mudrocks

(1965), Pettijohn (1975), Taylor and Smith (1986) and Taylor (1988) are presented in Table 2.1.

### 2.2.3. Formation and diagenesis of mudrocks.

The main constituents of mudrocks are clay minerals and silt grade quartz, which are largely of detrital origin. Clay minerals have three types of origin which are inheritance, neoformation and transformation (Tucker, 1991). The most common clay minerals are inherited from another area by erosion of soils and rock land masses and deposited as detrital material. Clay minerals formed by transformation are from two sources of origin, primarily they form in weathered rocks and unconsolidated sediment mantles by the alteration and replacement of silicate minerals such as feldspars and existing phyllosilicate minerals. After formation in the provenance environment clay minerals are available for erosion, transportation and deposition. Clay minerals are commonly transported to their point of deposition by water bodies such as rivers. Clay minerals may also form in situ, this is referred to as neoformation and the clay minerals are either precipitated from solution or formed from amorphous silicate materials. Neoformed clay minerals are commonly formed in the accumulated sediment body as a result of the actions of circulating groundwater. With increasing burial the second type of clay mineral transformation may result, this is where inherent clay mineral species are modified by ion exchange or cation rearrangement.

Mudrocks can be deposited in practically any environment but the major depositional sites tend to be continental areas such as river flood plains, lakes and large deltas and more distal areas such as continental shelves, basin slopes and sea floors. These clay mineral assemblages which are deposited in the shallow and deep water environments tend to reflect the climate and geology of the source area. In temporate areas with limited leaching of soils illite tends to be the typical clay mineral formed, during intermediate stages of leaching in temperate acidic soils chlorite tends to be produced. When temperate climate soils have good drainage and neutral pH, then smectites are produced, mixed-layer clays commonly form through the leaching of pre-existing illites, micas and chlorites, and kaolinite is common in highly leached acidic tropical soils (Blatt, 1982 and Tucker, 1991).

In marine clays lateral variations in the clay mineral abundances are common (Shaw, 1981). These lateral variations are thought to be caused by differential settling rates of the individual clay mineral species, with kaolinite particles being up to 5μm in size, illite particles commonly between 0.1 - 0.3μm in size and smectite particles commonly <0.1μm in size (Gibbs, 1977). Whitehouse et al. (1960) proposed a differential flocculation mechanism to explain this lateral variation. They showed that with small increases in salinity there are rapid increases in settling rates of kaolinite and illite, but these have far less affect on smectites. This lateral variation in clay mineral abundance is also evident from fluvial and lacustrine environments.

The greatest changes which unconsolidated sediments undergo are post depositional changes which are referred to as diagenetic changes. During diagenesis and burial clay minerals can be modified and altered due to dehydration of interlayer waters caused by temperature increases and conversion dependent upon the pore water chemistry. These conversions, including recrystallization, converts the buried sediments into lithified mudrocks and the process is covered in detail in Chapter 3.

### 2.2.4. Classification of rocks.

Sedimentary rocks and allochthonous sediments tend to be classified according to the size of the detrital or pyroclastic constituent grains and according to their chemical composition. Due to the different lineages of classification, slight discrepancies in the grain size class boundaries between different countries and scientists of different geological specialism exist, the British Standard classification (BS 5930: 1981) presented in Figure 2.2 is adhered to in this study. These classifications are based on a scale of grain size and the rock name is derived from the dominant grain size constituent which usually comprises more than 50% of the constituent rock mineral grains. The major difficulty which exists in the classification of lithified rocks is that their particle size distribution cannot be easily determined as dissagregation of the mineral grains is difficult if not sometimes impossible. Generally the naked eye is believed to be able to discern particles down to a size of 0.05mm, which approximates to a coarse silt size. So, using just basic tools like a hand lens, particle size charts and a steel probe it is possible to reliably classify sandstones and conglomerates. Unfortunately argillaceous rocks, such as those involved in this study, are very difficult to classify by these methods although three catagories of mudrocks can be fairly accurately distinguished in the field by means of touch and a handlens. The method by which mudstone may be distinguished from siltstone is discussed in Section 2.3.

Conventional detailed rock analyses tend to rely on data from petrographic thin sections. Such sections are analysed with a petrological microscope using transmitted light. Theoretically it is possible, with perfect imaging and monochromatic light, to resolve grains to 0.2μm diameter but in practice the best that can be achieved is a resolution of around 1μm. In addition it is impossible to distinguish such small particles in slides 30μm thick. Clay minerals tend to be less than 2μm in size and Weaver (1989) reports that illite and smectite can be as small as 0.1μm in size. Generally clay minerals in lithified rocks occur as flocs or clusters of particles up to 20μm in size. Unfortunately, with the petrological microscope these aggregates appear as an irresolvable birefringent mass making identification impossible unless the individual grains can be isolated. Although the petrological microscope is of limited use in the identification of clay mineral species it is very useful in studies of small scale structural and textural features such as small scale bedding, bioturbation and mineral orientation.

Mudrock classification presents many difficulties, although there are fewer class names than in other major groups of sedimentary rocks such as sandstones. In the past, for the reasons mentioned by Blatt (1982) and listed below, detailed studies of mudrocks have been avoided:

- Mudrocks largely consist of clay minerals and having low durability they tend to form valleys rather than cliffs, so good mudrock exposures are not very common.
- Mudrocks are fine grained so there is not much to describe at outcrop except colour and presence of fissility.
- In thin section many of the rock constituents cannot be resolved due to their small grain size, intermixing of different clay minerals, mineral grain staining by opaque iron oxide or the presence of organic matter. Those minerals which are resolvable such as quartz and feldspars are usually difficult to distinguish because of the presence of untwinned silt sized feldspar fragments.

| *Grain size (mm)* | *Bedded rocks* | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| > 20<br>20 | Grain size description | | | At least 50% of grains are carbonate | | | At least 50% of volcanic grains | Chemical & carbon |
| 6 | RUDACEOUS | | CONGLOMERATE, rounded clasts<br>BRECCIA, angular clasts | LIMESTONE | | | Volcanic ejecta in fine matrix<br>AGGLOMERTE<br>VOLCANIC BRECCIA | HALITE |
| 2 | ARENACEOUS | Coa | SANDSTONE grains often cement by clay calcite or iron minerals | | | OOLITIC LIMESTONE | Cemented volcanic ash | ANHYDRITE<br>GYPSUM |
| 0.6 | | Med | SEDIMENTARY QUARTZITE quartz grains and silicic cement | MAGNESIUM LIMESTONE | DOLOMITE | | TUFF | |
| 0.2 | | Fine | ARKOSE much feldspar<br>GREYWACKE many rock chips | | | | | |
| 0.06<br>0.002 | ARGILLACEOUS | | MUDSTONE SHALE fissile<br>SILTSTONE- mostly silt<br>CLAYSTONE- mostly clay | | | CHALK | FINE-GRAINED TUFF<br>VERY FINE-GRAINED TUFF | |
| <0.002<br>Amorphous or cryptocrystalline | | | FLINT: occurs as bands of nodules in Chalk<br>CHERT: occurs in limestone and calcareous sandstone | | | | | COAL<br>LIGNITE |

Figure 2.2 Field identification of sedimentary rocks, adapted from BS 5930:1981

- Due to their small size and crystal structure, clay minerals tend to be readily altered by diagenetic processes so that the original clays become recrystallised or changed in chemical composition.
- Due to the difficulty of preserving samples and the preparation of thin sections.

Some of the difficulties with studying mudrocks have been overcome in the past 20-30 years with the availability of X-ray diffraction, electron microscopy and chemical analysis by X ray fluorescence and mass spectrometry. In the present research these techniques and others have been used. Data derived by such methods is reviewed in the forthcoming sections.

## 2.3. Problems associated with mudrock classification.

Mudrocks have been variously classified. A generally accepted definition of mudrocks is that they consist of >50% siliclastic constituents with >50% being less than 63 µm in grain size (Stow,1981). It is estimated by Tucker (1991) that 70% of the rocks at the earth's surface are sedimentary in origin and the major proportion of these consist of mudrocks.The actual proportion depends on the method of determination. Anon (1982) quote figures of 47% and 77% based respectively on stratigraphic sections and geochemical calculations. Most classifications rely on grain size criteria and so mudrocks can be further subdivided according to the proportion of clay size material present. The upper limit for clay size particles is variously set at 2µm by engineering geologists, clay and soil scientists and 4µm by sedimentologists. Similar difficulties exist with defining the upper limit of silt sized particles as being respectively 63µm and 74µm as shown in Figure 2.3. Sedimentologists place the silt-clay size boundary at 4µm which represents the the upper size limit of particles which exhibit cohesion due to colloidal action thus separating material dominated by clay minerals from that of quartz material (Bates and Jackson, 1987 and Hawkins and Pinches, 1992). In this situation a proportion of non-clay minerals will always be present in the clay-size fraction and clay minerals present in the silt-size fraction. Therefore by using the 2µm clay-silt size boundary engineers have knowingly included material which does not have physiochemical properties typical of clay minerals in the clay size fraction and a minimal quantity of clay minerals in the silt-sized fraction (Hawkins and Pinches, 1992). Analytical techniques such as XRD and SEM reveal that clay minerals can be found with particle sizes of upto 20μm (Lee, White and Ingles ,1983) while quartz grains are common down to <1.8μm in size (Blatt and Schultz,1976).

Mudrocks have been classified in a number of ways depending on the purpose for which the classification is intended. In geological classifications the textural, mineralogical, chemical and processes leading to the formation of the mudrock are the main considerations. For engineering purposes a brief detailed geological description is enhanced with an engineering classification based on weathering, discontinuities and engineering properties such as consistency limits and strength. Within the separate classification schemes the use of different terminologies to describe the same rock has led to confusion. Mudrock descriptions fall into two main catagories: geological and engineering. Within these there are four general approaches to classification: genetic, visual, analytical and geotechnical.

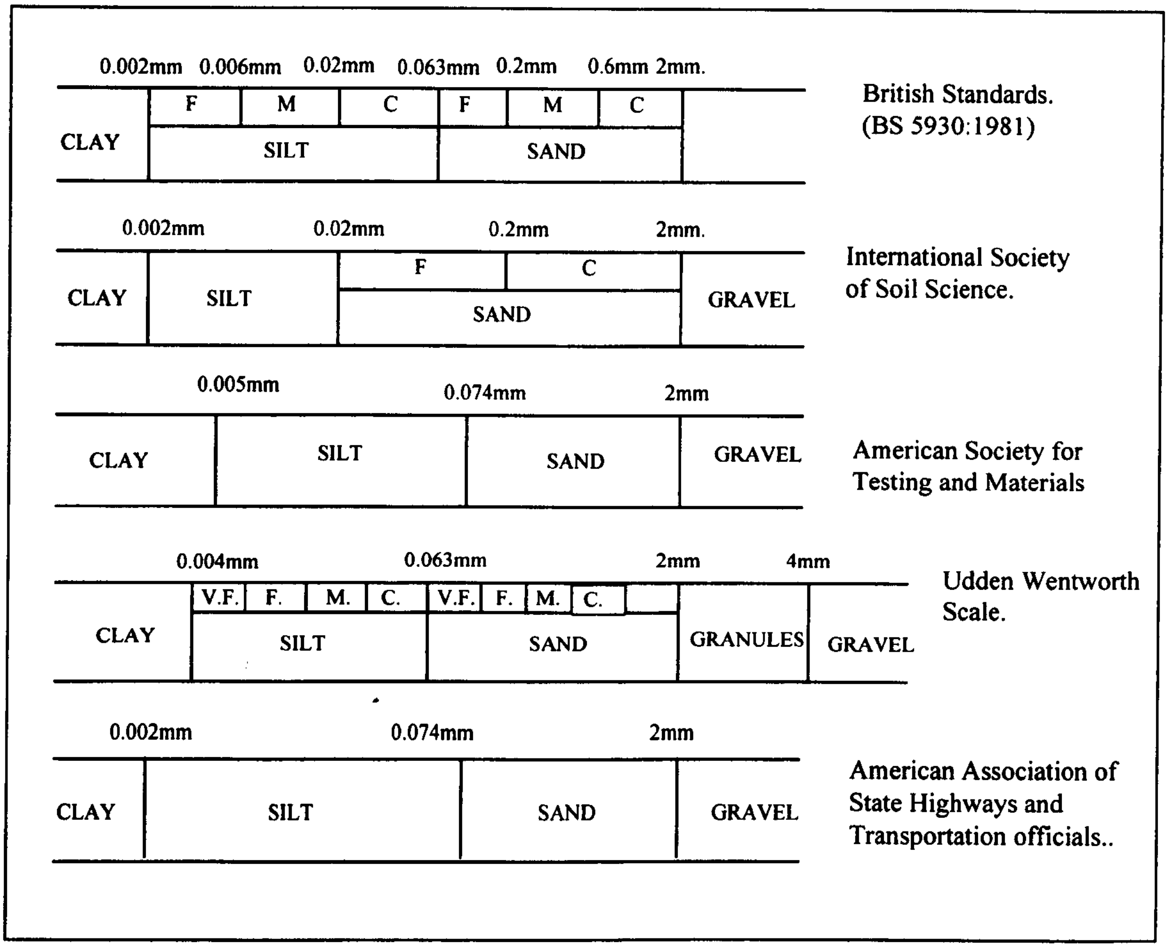


Figure 2.3. Grain size comparisons for different applications.

## 2.3.1. Geological classification of mudrocks.

In mudrocks as for all rock types, the classification is part of a thorough geological description of the sample. Graham (1989) lists the main aspects of sedimentary rocks which should be recorded in the field:

1. Lithology- mineralogy/composition and colour, recommended use of a standard rock colour chart.
2. Texture- grain size, shape, sorting and fabric.
3. Beds- description of bedding, including such things as bed thickness, geometry and nature of inter-bed contacts.
4. Sedimentary structure- internal structure of beds, structure on bedding surfaces etc.
5. Fossil content- type.
6. Palaeocurrent data- orientation of palaeocurrent indicators and essential structural orientation.

In many sedimentary successions there is an abundance of geological information but in mudrocks this is seldom the case. Laboratory techniques are more suited for a detailed evaluation of mineralogy, or texture in mudrocks, but use of these techniques cannot always be warranted, therefore a detailed description of what is seen is vital and this is the reason why useable classifications are so important to mudrocks, especially field applicable ones.

Many geological classifications of mudrocks have been proposed, these tend to fall into one of three catagories which are genetic, textural or analytical.

### *2.3.1.1. Genetic classification.*

This approach classifies the mudrock according to the most important possible source area and environment of deposition (Krumbein,1947). This type of classification has not proved to be very useful, and therefore has found limited application in the field of geology.

### *2.3.1.2. Textural classification.*

These classifications are based upon the dominance of a particular grain size group as a means of naming the rock. A similar approach as is used for sediments and may be carried out using laboratory classification or field classification methods. In the laboratory schemes reliance is based on the disaggregation of the specimen followed by particle size analysis of the resulting grains. Field classifications depend on visual and textural characteristics ascertained by feel and the use of a hand lens which is used to assist the estimation of the dominant grain size.

The general grain size categories that are recognised for sediments were proposed by Wentworth (1922), and for argillaceous materials they are as follows:

- sandy silt (silt > sand >10%; others < 10%)
- silt (silt > 80%)
- clayey silt (silt >clay > 10%; others <10%)
- silty clay (clay > silt > 10%; others <10%)
- clay (clay > 80%)

In general these catagories are still used in geological descriptions, with slight quantitative variations between workers. Mudrocks have been classified using a ternary diagram with clay, silt and sand end members as proposed by Shepard (1954), Folk (1954), and Picard (1971) as seen in Figure.2.4.

Three-fold geological subdivisions classification schemes based on clay and silt and consisting of siltstone, mudstone and claystone categories have been proposed for mudrocks, these tend to have 33% boundaries between group types. As mentioned by Hawkins and Pinches (1992) these schemes have much to recommend them as they are capable of reflecting geomechanical differences between the rock categories. Such schemes have been proposed by Ingram (1953), Pettijohn (1975), Potter et al. (1980), Blatt et al. (1980) and Stow (1981), of which three examples are presented in Table 2.2.

It has been suggested by many researchers (Picard, 1971; Blatt et al., 1980; Spears, 1980; and Weaver, 1989) that the ambiguities associated with mudrock classifications arise from the misapplication of non-indurated sediment terminology to rocks which have undergone induration and diagenetic alteration. Upon being subjected to diagenetic changes the process of recrystallisation of the clay minerals leads to the formation of silt-sized grains in the resultant mudrocks which are mistaken for original sedimentary particles. Picard (1971), Spears (1980) and others have also stated that the particle size analysis on mudrocks is only as good as the method of dissagregation used, and that grain separation in mudrocks tends to leave grains either as aggregates or causes breakage of what are low strength mineral particles. It has been observed by Picard, (1971) that most of the data available from grain size analyses of mudrocks are biased towards the silt-size category, probably due to the difficulty encountered in dissagregating the clay rich rocks. Grain size analysis of mudrocks is therefore not a reliable procedure for classification as the results mainly reflect the method used to

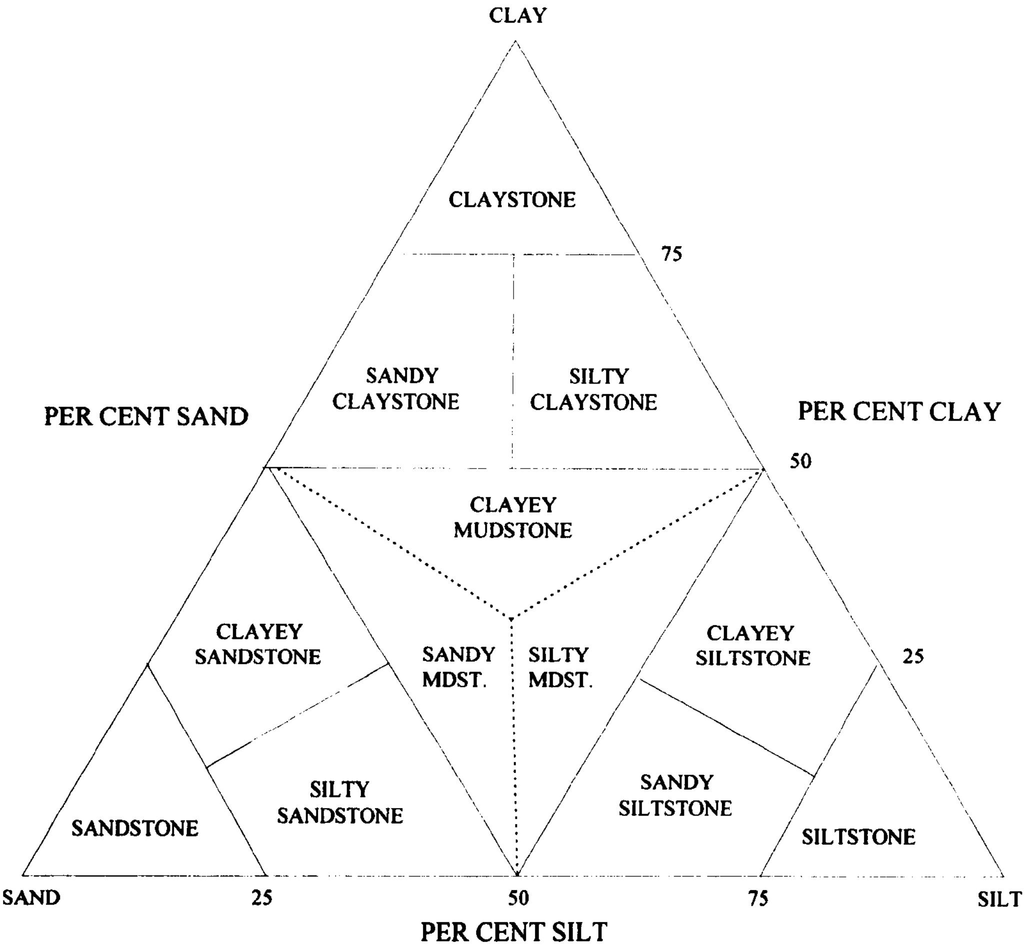


Figure 2.4. Example of a ternary diagram for the classification of fine grained sedimentary rocks after Picard (1971).

break down the rock. Due to the confusion that has arisen with mudrock classifications, Weaver (1989) goes on to suggest the introduction of yet another non-ambiguous new term, "Physil"- which is an abbreviation for phyllosilicate and carries no size connotation. He proposes the classification scheme for mudrocks and sediments based on compositional and textural data as seen in Table 2.3.

Potter et al. (1980)

| | % Clay size particles. | | |
|---|---|---|---|
| | 0-33% | 33-50% | 50-100% |
| Non-laminated. | Siltstone. | Mudstone. | Claystone |
| Laminated. | Siltshale. | Mudshale. | Clayshale |
| Metamorphosed. | Argillite. | Argillite. | Argillite. |

Blatt et al. (1980)

| Ideal size definition. | Field criteria. | Fissile mudrock. | Non-fissile mudrock. |
|---|---|---|---|
| >66% Silt. | Abundant silt visible with hand lens. | silt-shale. | siltstone. |
| >33<66% Silt. | Feels gritty when chewed. | mud-shale. | mudstone. |
| >66% Silt. | Feels smooth when chewed. | clay-shale. | claystone. |

Stow (1981)

Mudrock (>50% Siliclastic, >50% <63µm)

| Basic terms.<br>Unlithified. | Lithified/non-fissile. | Lithified/fissile. | Approx.grain size proportion. |
|---|---|---|---|
| Silt. | Siltstone. | Silt-shale. | >66% silt sized. (4-63µm) |
| Mud. | Mudstone. | Mud-shale. | Silt+clay mixture (<63µm) |
| Clay. | Claystone. | Clay-shale. | >66% clay sized. (<4µm) |
| Metamorphic terms. | | | |
| Argillite. | Slightly metamorphosed/non-fissile. | | silt and clay mix. |
| Slate. | Metamorphosed/fissile. | | silt and clay mix. |

Table 2.2. Examples of three-fold mudrock classifications.

| Texture. | Composition. | | Indurated. | |
|---|---|---|---|---|
| | >50%Physils. | <50%Physils. | >50%Physils. | <50%Physils. |
| >50%Silt(4-63 µm) | Physil silt. | Physilitic silt | Physil siltstone. | Physilitic siltstone. |
| >50%Clay(<4 µm) | Physil clay. | Physilitic clay | Physil claystone. | Physilitic claystone. |

Table 2.3. Classification of mudrocks after Weaver, (1989).

In all studies a detailed as possible description of the mudrock should be made, using such classification schemes as Blatt et al. (1980) or Lundegard and Samuels (1980) who suggest particular field observational characteristics which are useful for distinguishing between mudrock types. These pointers have been expanded on by Hawkins and Pinches (1992) as follows:-

1. Polishability - persistent rubbing of a smooth claystone surface with a finger produces a noticeable sheen or polish.
2. Scratchability - a pocket knife (or steel probe) carves a relatively smooth groove in claystones but forms a shallower less regular cut in siltstones, frequently accompanied by a scratching sound.
3. Cuttability - when claystones are cut (or broken) they form a smooth surface ( often with conchoidal fracture patterns) whereas siltstones are often uncuttable (and when broken have a rough surface); mudstones have a pitted surface as a result of the dislodgement of quartz grains.
4. Abrasivity - When claystones are passed across the teeth little if any quartz is felt. In the case of mudstones or siltstones however the abrasive quartz is encountered, frequently accompanied by a gentle gritty noise.
5. Visibility - the coarser silt grains can be observed with a ×10 hand lens.

#### *2.3.1.3. Analytical classification.*

It has been suggested that it is more meaningful to classify mudrocks according to their mineralogy in terms of the quantity of clay minerals and non-clay mineral constituents (Picard, 1971; Lewans, 1978; Spears, 1980; and Weaver 1989). Elliot and Strauss (1970) suggested the use of quartz content as a means of classification for Carboniferous Coal Measures mudrocks, this scheme was further expanded upon by Spears (1980). He proposed a scheme shown in Table 2.4 based on quartz content which he states is equivalent to the proportion of original silt sized material in the mudrock. In view of the difficulties of using visual methods it seems that the best method of quantification is based on XRD mineralogical analysis. The disadvantage of this is that the analysis is a costly procedure which, since it may be outside the budget for most projects, would limit its wide acceptance.

| Quartz content. | Fissile. | Non-fissile. |
|---|---|---|
| > 40% Quartz. | Flaggy siltstone. | Massive siltstone. |
| 30-40% Quartz. | Very coarse shale. | Very coarse mudstone. |
| 20-30% Quartz. | Coarse shale. | coarse mudstone. |
| 10-20% Quartz. | Fine shale. | Fine mudstone. |
| < 10% Quartz. | Very fine shale. | Very fine mudstone. |

Table 2.4. Mudrock classification based on quartz content after Spears (1980).

Establishing the proportion of silt to clay sized grains using SEM also has potential as a method of classification, but again this technique is expensive and since only a small area of the sample is actually examined it may not be representative of the whole sample.

### 2.3.2. Engineering classification and characterization of mudrocks.

Descriptions of mudrocks in the field of engineering geology and geotechnics are not aimed only at a generic classification as would be appropriate in a geological context. Instead they are geared towards a prediction of the future behaviour of the material within an engineering application. It is useful to include in descriptions index properties such as Atterberg limits, strength and slaking potential. Beavins (1989) suggests that detailed rock descriptions are not as important within the field of geotechnics, but in fact the opposite seems to be the case. There is much to be learned about mudrocks from a knowledge of their geological and environmental history that follows from observable features.

Many mudrock classification and characterization schemes were proposed in the 1970's but most were found to be of limited use and of site specific application only. These characterization schemes consisted of a limited, if any, geological rock description, and a mudrock name such as shale or claystone. Such schemes tended to be based on a number of specific index properties which were found useful in predicting the response of the mudrock within a specific engineering situation. Gamble (1971) analysed a large suite of American mudrocks and discovered shortcomings in the geological classification systems then used. He proposed a classification similar to that of Pettijohn (1975) in which the primary factors are grain size and breaking characteristics. A durability classification based on the second cycle slake durability index, Atterberg limits of the fines and the relative durability were developed for rock description. The scheme improved upon a classification proposed by Franklin (1970) which was based upon the one cycle slake durability index. Olivier (1979) discovered that Gamble's (1971) classification was inappropriate in the tunnelling project in which he was involved so he devised a classification based on uniaxial compressive strength and Duncan free swell test. However Varley (1990) had difficulty applying Olivier's (1979) classification in a British tunnelling project in the Carboniferous Coal Measures. All this demonstrates the difficulty of applying schemes beyond the sites for which they were developed and of arriving at a universally applicable classification.

Morgenstern and Eigenbrod (1974) stated that the boundaries between non-indurated, indurated and weakly metamorphosed mudrocks seemed to be of limited interest to geologists and are therefore not clearly defined. For engineers these boundaries are very important due to the sensitivity of the geotechnical properties related to the nature and degree of induration as a material changes from soil to rock. Accordingly, Morgenstern and Eigenbrod (1974) advocated the use of the terms *compaction shale* which is a mudrock formed by compaction due to burial, and *cementation shale* which is a mudrock bound with either a significant amount of cementing material formed by precipitation of diagenetic minerals such as carbonates, or indurated by recrystallisation of clays and cementation by quartz. These terms were originally introduced by Mead (1936) and due to the ambiguities of the early classification schemes led to the introduction of terms such as "clay-shale". Morgenstern and Eigenbrod (1974) suggested that degradation in water could be used to distinguish between compaction and cementation shales. Their scheme involves monitoring the amount of compression softening due to immersion of a sample in water, and measuring the liquidity index based on immersing an oven dried sample in water for two hours and measuring its moisture content. They state that relative stability when immersed in water provides a means of distinguishing between non- to poorly-indurated clay and indurated mudstone.

Wood and Deo (1975) recognised the need to distinguish between compaction and cementation shales. Their scheme involves key tests including the jar slake test, modified slake durability test (500 revolutions both on dry and saturated samples) and a modified sodium sulphate soundness test. Although this represents a severe testing programme they suggest that it is useful in distinguishing "more" durable shales, suitable as material for use in embankment construction.

Hopkins and Deen (1984) suggested a scheme for distinguishing "rock-like" and "soil-like" shales, and argued that geological classifications are not applicable to engineering use. They advocate the use of the Decay Index which is measured using the slake durability apparatus on samples at saturated moisture content and the jar slake test which is useful for distinguishing low durability from medium to high durability mudrocks.

The schemes covered have found limited application and have proved to be site or project rather than material specific, but the general intention is to distinguish non-durable from durable mudrocks. Grainger (1984) addressed the problem of mudrock classification in an attempt to present a scheme that would be more generally applicable. His classification does not change any ground rules set by previous authors instead it unified a number of established classifications. He suggested that compressive strength and the second cycle slake durability index could be used as the basis of distinguishing between rock types as follows:

- Soil: UCS $\leq 0.6$ MN/m$^2$
- Non-durable mudrock: UCS 0.6 MN/m$^2$ - 3.6 MN/m$^2$ & $Id_2<90\%$
- Durable mudrock: UCS 3.6 MN/m$^2$ -100 MN/m$^2$ & $Id_2>90\%$
- Metamudrocks: UCS > 100 MN/m$^2$

The lower strength limit between soil and rock is based on Morgenstern and Eigenbrod's (1974) value. Grainger (1984) suggests that properties for classification are to establish firm boundaries between different rock types. Granger suggested classifying mudrocks on a visual description basis and, with border-line cases, the use of simple index tests to aid classification. In view of the difficulties with the use of grain size analysis for the classification of mudrocks he advocates generic classification based on the XRD quartz determination of Till and Spears (1969). The class divisions of Spears (1980) are used but with a boundary between mudstone and claystone at 20% quartz content added. Grainger (1984) also advocates the use of the term "shale" based on platyness of the rock fragments. This is expressed as the flakiness ratio in weak mudrocks, while for more durable mudrocks the anisotropy is measured using the point load test.

Taylor (1988) supports the Grainger (1984) classification but suggests that the upper boundary between siltstone and sandstone corresponds with a 60% quartz content. To distinguish between non-durable and durable mudrocks Taylor (1988) suggests a boundary at UCS>3.6 MN/m$^2$ and $Id_3$>60%. This is intended to be adopted as equivalent to the $Id_2$>90% criterion based on the two cycle test as the three cycle test provides more consistant results.

Taylor (1988) argued that mineralogy cannot be used as a basis for distinguishing between lithified and non-lithified materials. Four years previously Grainger (1984) suggested this, although he suggests that illite crystallinity may be a useful means of distinguishing between indurated and metamudrocks he opts for a UCS > 100MN/m$^2$ boundary in his classification scheme.

Franklin and Dusseault (1989) suggest that a thorough geological description of mudrocks and any other material should be made for the purposes of classification. They present a classification system based on the two cycle slake durability index, where $Id_2$ >80%, which is based on the suggested slake durability classification scheme presented by Franklin and Chandra (1972). The mudrock is further classified using the point load test, and when $Id_2$ <80% the material is classified using the plasticity index. The authors caution that the scheme was developed specifically for a particular suite of mudrocks and may not be of universal application.

Dick and Shakoor (1992) suggest that first mudrocks should be classified geologically into claystones, mudstones, siltstones, shales or argillites as no single lithological characteristic can be used to predict durability of all the mudrock types. Dick and Shakoor (1992) advocate the use of the geological classification scheme of Potter et al. (1980) presented in Table 2.2. Once the mudrock has been classified geologically then they suggest the use of specific characteristics for durability classification of each mudrock type ie.

A) Claystones - expandable clay mineral content as determined by XRD.

B) Mudstones - the microfracture index count.

C) Shales - water absorption.

D) Siltstones - water adsorption.

E) Argillites - second cycle slake durability index of >85%.

In the UK, the standard procedure for the description of rocks for engineering works is outlined in BS5930:1981. The method is a combination of a general geological rock description which is augmented by mechanical and weathering descriptions of the material, with the data presented in a set order as follows:

1. Colour.
2. Grain size.
3. Texture and structure.
4. Weathering state and alteration.
5. Minor lithological characteristics.
6. ROCK NAME.
7. Estimated mechanical strength.
8. Discontinuities.
9. Other terms indicating special geological & engineering characteristics.

The colour is generally estimated with the aid of a rock colour chart. The weathering state is described in terms of the volume of weathered to fresh material. Recently Anon (1995) have produced an aide memoir for the description of weathering states in mudrocks. Strength is estimated by use of a standard geological hammer with strength catagories presented in BS5930:1981.The standard also presents recommended catagories for discontinuity and lamination spacing.

The American unified rock classification scheme is similar in operation to BS5930:1981, except it involves measuring four basic elements in the field as follows:

1. The degree of weathering - estimated by eye.
2. The rock strength - estimated using a standard hammer.
3. The planar and linear elements - estimated by observing the rock discontinuities.
4. The unit weight - measured by weighing the rock specimen in air and water using a spring balance and bucket.

Hawkins and Pinches (1992) discussed the application of BS5930:1981 to the classification of mudrocks. They suggest certain amendments in the description of mudrocks of which the most salient points are:

- Fissility is not defined, a bedding spacing of 20mm which is equivalent to the boundary between bedding and sedimentary laminations is given in BS5930:1981.
- A three-fold classification system is proposed as follows:

  Claystone >40% clay fraction.

  Mudstone 25-40% clay fraction.

  Siltstone <25% clay fraction.

  This they suggest is capable of reflecting significant geomechanical differences as supported by the work of numerous authors.
- Presenting soil and rock descriptions in a uniform manner with rock descriptions starting with strength, as is the case with soil descriptions.

It is evident that a thorough rock description is required for engineering purposes. This needs to consist of a geological classification with a geomechanical description and should be capable of being carried out with a bare minimum of equipment under field conditions. Useful aide-memoires are presented in BS5930:1981 and Hawkins & Pinches (1992), which help to standardize rock descriptions making them more widely applicable and therefore should be used. Where possible relevant parameters should be quantified using XRD, slake durability and other equipment to provide further descriptors which qualify the basic engineering description. However in many cases such additional tests are not contemplated due to cost or budget constraints. The description scheme used in this study is presented in Section 2.4.

### 2.3.3. Terminologies and definitions used to describe argillaceous material.

Early attempts at mudrock classification were hindered by the difficulty entailed in deriving a knowledge of their mineralogy using the petrological microscope and wet chemical analysis techniques. This led to the development of a diverse terminology based on field observations and intuition. It has been necessary to redefine certain terms as knowledge has increased with improvements to analytical techniques. As no standard terminologies and definitions exist for the mudrock group with workers using their own favoured terms, confusion can easily arise, therefore a knowledge of the terms and definitions used can be an advantage. Many of the common terms refering to mudrocks and defined by various workers are presented in Table 2.5.

Table 2.5. Commonly used terms and definitions for mudrocks.

| **Term and definition.** | **Reference.** |
|---|---|
| Shale. | |
| • Claystone and siltstone with cleavage parallel to bedding. | Twenhofel, 1950 |
| • Fine grained rock containing 50-100% clay size particles with clay minerals constituting at least 25% of the total rock volume. | Picard, 1953 |
| • More indurated than claystone. | Flawn, 1953 |
| • Fissile claystone, siltstone and mudstone. | Ingram, 1953 |
| • Laminated or fissile mudstone. | Pettijohn, 1975 |
| • Fissile mudrock. | Folk, 1974 |
| • Fissile equivalent of a mudstone. | Tucker, 1991 |
| • Term used for fissile mudrock and more generally for the entire class of fine grained sedimentary rocks containing substantial quantities of clay minerals. | Blatt, Middleton & Murray, 1980 |
| • Fissile mudrock useage varies as some authors use shale as a synonym for mudrock. | Leeder, 1982 |
| • An argillaceous rock possessing laminations or fissility. | Underwood, 1967 |
| • Loose term applied to laminated clayey or argillaceous sedimentary rocks which are sufficiently consolidated and lithified with the ability to maintain its structure when subjected to weathering. Can be divided into 2 broad groups:<br>1-Compaction or "soil-like shales" consolidated primarily by weight of overlying sediments and lacks significant amounts of intergranular cement.<br>2-Cemented or "rock-like shales" consolidated and significantly lithified cement agents may be calcareous, siliceous, ferruginous, gypsiferous etc. If cementing material is lacking the shale may be bonded by recrystallisation of its clay minerals. | Wood & Deo, 1975 |
| • Fissile or laminated, indurated, non-metamorphosed fine grained clastic rock. | Twenhofel, 1937 |
| • The whole group of silty and clayey rocks specifically used for rocks primarily composed of silt and clay with fissility of a tendancy to split along fairly close bedding planes. | Deere & Gamble, 1971 |
| • A product could not be called a shale unless it possesses two properties, when struck with a hammer it should give a clear ring and when immersed in water its volume should remain unchanged. | Terzaghi, 1946 |
| • Consolidated fine sediments usually hardened clay or mud which have a characteristic fracture. Generally dull in appearance shale can be scratched with a fingernail. | Leggett, 1962 |
| • Fissile or laminated fine grained rock, subsequently used as a group name for all fine grained sediments. | Spears, 1980 |
| Mudrocks. | |
| • Massive claystone or siltstone. Contains at least 50% silt | Ingram, 1953 |

| | |
|---|---|
| and clay. | |
| • Terrigenous rocks that contain more than 50% silt or clay. | Folk, 1974<br>Spears, 1980 |
| • Prefered as a general term for the group name for all fine grained sediments. | Hawkins & Pinches,1992 |
| • Term used to describe all non-metamorphosed argillaceous deposits. | Grainger, 1984 |
| • An increasingly accepted term in geology as a group name for fine grained, siliciclastic sedimentary rocks. | Tucker, 1991 |
| • A group name for lithologies which consist mainly of clay and silt size siliciclastic sediments. | Stow, 1981 |
| • Rock with >50% siliclastic content of which >50% is less than 63μm in size. | Dick & Shakoor, 1992 |
| • Very fine grained argillaceous sedimentary rocks. | |
| <u>Claystone</u>. | |
| • Indurated clays. Retain considerable coherance on being wetted after being dried. | Twenhofel, 1950 |
| • Weakly indurated, composed predominantly of "clay sized" particles (<10μm). | Flawn, 1953 |
| • Massive rock in which clay predominates. | Ingram, 1953 |
| • Contains two-thirds clay. | Folk, 1974 |
| • Contains more than 75% clay. | Picard, 1971 |
| • Indurated clay. | Pettijohn, 1975 |
| • Sedimentary rock dominated by clay grade material. | Tucker, 1991 |
| • Lithified, non fissile rock containing >75% clay size material (<4μm). | Stow, 1981 |
| • A mudrock with>50% of grains being less than 2μm. | Grainger, 1984 |
| • Mudrocks containing >40% clay fraction. | Hawkins & Pinches, 1992 |
| <u>Mudstone.</u> | |
| • Major class name for sedimentary rocks containing more than 50% clastic grains smaller than 63μm. | Blatt, Middleton & Murrey, 1980 |
| • Partly indurated argillaceous rock which slakes readily to mud when repeatedly dried and wetted. | Shrock, 1948 |
| • Clays and silts mingled with water form muds and both claystones and siltstones have been termed mudstones. | Twenhofel, 1950 |
| • Fourty sedimentologists recommended the term mud be dropped (why not drop mudstone?) | Shepard, 1954 |
| • Rocks with subequal silt and clay. | Folk, 1974 |
| • Blocky or massive claystones. | Pettijohn, 1975 |
| • Indurated, non-fissile blocky equivalent of mud. | Tucker, 1991 |
| • Intermediate mudrock material containing between 25-40% clay fraction. | Hawkins & Pinches, 1992 |
| • Neither a fissile nor laminated equivalent of shale. | Spears, 1980 |
| • Mixture of silt, clay and sand sized material, of which none of these components exceeds 50%. | Picard, 1971 |
| <u>Siltstone.</u> | |
| • Contains two-thirds silt. | Folk, 1974 |

| | |
|---|---|
| • Contains more than 50%, 4-63μm sized material. | Picard, 1971 |
| • Comprises less than 25% clay fraction. | Hawkins & Pinches, 1992 |
| • Mudrock which contains more silt grade particles than clay grade. | Tucker, 1991 |
| • Indurated silt containing >50%, 4-63μm sized material. | Pettijohn, 1975 |
| • >Two-thirds of the siliciclastic fraction to be silt sized (4-63μm). | Stow, 1981 |
| • Well accepted and unambiguous term for rocks at the coarse end of the mudrock range. | Granger, 1984 |
| • Mudrock with >40% quartz content. | Spears, 1980 |
| Argillite. | |
| • Siltstone or shale with a high degree of induration. | Twenhofel, 1950 |
| • Indurated argillaceous rock without visible partings, cleavage or foliation. Less than half the micaceous and clay minerals have been reconstituted. | Flawn, 1953 |
| • Massive shale. | Grim, 1968 |
| • Metamorphosed mudstone or shale with no cleavage. | Pettijohn, 1975 |
| • Claystone. | Millot, 1970 |
| • More indurated mudstone. | Tucker, 1991 |
| • Slightly metamorphosed non-fissile mudrock. | Stow, 1981 |
| • Mudrocks hardened by incipient metamorphism but showing no slaty cleavage. | Blatt, Middleton & Murrey, 1980 |
| • Argillaceous rocks that are very weakly metamorphosed. | Dunbar & Rodgers, 1957 |
| Slate. | |
| • Low-grade metamorphosed argillaceous rocks with well developed penetrative cleavage but having suffered little recrystallisation so the rocks are still fine grained. | Penguin dictionary of Geology, 1972 |

From the list presented in Table 2.5 which is by no means exhaustive when describing argillaceous deposits, it can be seen that many of the terms are especially vague and ill defined. Geologists must be clear about the definition of a particular rock type, but also must be aware of the other definitions that people may use.

### 2.3.4. Fissility in classification of mudrocks.

The mudrock classification schemes covered so far can be seen to include splitting characteristics in terms of fissility as part of the classification. Fissility is a derived property which is a function of particle orientation, bedding, mineral composition, moisture content and weathering. Therefore it has been suggested by researchers such as Picard (1971), Lundegard and Samuels (1980) and Weaver (1989) that fissility only be used as a descriptive term and not as a means of classification. All argillaceous rocks are massive before unloading but on removal of overburden some mudrocks develop fissility by exfoliation, others require considerable weathering including water penetration before they develop fissility, as Weaver (1989) states, " there are no shales in the subsurface only potential shales", therefore fissility should be used only as a descriptive factor and not a means of classification.Weaver (1989) also states that "sedimentary rock names should not have a structural connotation, structural terms should be used as prefixes ie. fissile-, a two to three word description is not as succinct as a single word but ambiguity is considerably reduced". Fissility where possible should be described based on breaking characteristics (Ingram, 1953) and frequency of natural splitting (McKnee and Weir, 1953) as seen in Table 2.6.

| Breaking characteristics. | Splitting frequency. |
|---|---|
| Massive. - blocky. | < 2mm - papery. |
| Flaky. - wedge and chip shaped fragments. | 2-10mm - platy. |
| Flaggy. - parallel sided fragments. | 10-50mm - flaggy. |
|  | >50mm - slabby (generally for siltstones). |

Table 2.6. Descriptors for fissility after Ingram, (1953) and McKnee & Weir, (1953).

## 2.4. Systematic engineering geological rock description scheme used in the study.

It must be emphasised that mudrock classification in engineering geology needs to be thorough and accurate. Fundamental geological factors and features of engineering relevance need to be outlined which is the aim of the systematic approach presented. In this study the term shale is not used since as mentioned by Weaver (1989) and current BGS thinking (Dr. R. Merriman, 1996 pers.comm.), the term is liable to cause confusion due to many years of misuse. It is therefore intended that fissility descriptions be placed before the mudrock type to make the reader aware of this fundamental property.

The practice recommended and presented in BS5930:1981 and Hawkins and Pinches (1992) has been used, in which the following word order was applied for the rock descriptions:-

1. Estimated mechanical strength.
2. Colour
3. Bedding and lamination thickness.

4. Weathering state.
5. Fissility (where applicable).
6. ROCK NAME.
7. Discontinuity patterns.
8. Alteration state where applicable.
9. Other terms indicating special geological and engineering characteristics.

1. Strength:- The estimated mechanical strength was classified and determined according to the recommendations of BS5930:1981 and modifications to these recommendations presented in Hawkins and Pinches (1992) as shown in Table 2.7.

2. Colour:- Described with the aid of a Munsell rock colour chart, at the natural moisture content of the rock and under natural lighting conditions.

3. Bedding and lamination :- The thickness of the bedding and laminae are described according to the recommendation presented in BS5930:1981 and shown in Table 2.8. The nature of the laminae and beds are also described with reference to features such as the persistence, degree of waviness, grading and cross stratification.

| Strength description | Field description | Unconfined compressive strength MN/m$^2$ |
|---|---|---|
| Extremely strong | Rocks ring on hammer blows. Cannot be scratched with a knife but leaves knife marks | >200 |
| Very strong | Fragments chipped by heavy hammer blows. Cannot be scratched with a knife but often leaves knife marks | 100-200 |
| Strong | Hand held specimen can be broken by heavy hammer blows. Can only be scratched with a knife with difficulty | 50-100 |
| Moderately strong | Hand held specimen can be broken with light hammer blows. Can be grooved and scratched with a knife | 12.5-50 |
| Moderately weak | Thin slabs just broken by heavy hand pressure. Difficult to cut with a knife | 5-12.5 |
| Weak | Can be broken by heavy hand pressure. Cut by knife with some difficulty | 1.25-5 |
| Very weak | Easily broken with applied hand pressure. Cuts easily with a knife | <1.25 |

Table 2.7. Suggested rock strength estimates.

4. Fissility:- Fissility is shown by Spears,(1976) to be caused by a combination of structural boundaries between oriented clay minerals, randomly oriented clay, horizons consisting of different mineral species, organic and non-organic layers and separate

| Bedding | Mean spacing (mm) |
|---|---|
| Very thickly bedded | >2000 |
| Thickly bedded | 600-2000 |
| Medium bedded | 200-600 |
| Thinly bedded | 60-200 |
| Very thinly bedded | 20-60 |
| Thickly laminated | 6-20 |
| Thinly laminated | 2-6 |
| Very thinly laminated | <2 |

Table 2.8. Classification of bedding and laminations.

depositional sequences. Therefore fissility in mudrocks develops during weathering between boundaries separating small scale depositional, compositional and orientation boundaries. As such the scale of fissility is based on the thickness criteria of Potter et al. (1980), and divided into the three classes shown in Table 2.9.

| Thickness | Fissility |
|---|---|
| > 5 mm | Moderately fissile |
| 1 mm - 5 mm | Very fissile |
| < 1 mm | Extremely fissile |

Table 2.9. Degrees of fissility.

5. Rock name:- Mudrocks forming the study material are described according to the scheme of Blatt et al. (1980) using the field criteria of Hawkins and Pinches (1992). Only the terms claystone, mudstone and siltstone are used. Difficulties ascribing certain samples to a class were resolved by recourse to the methods described by Spears (1980) and Taylor (1988), which involves XRD analysis of the quartz content. Their combined scheme is presented in Table 2.10:

6. Discontinuity patterns. This concerns the spacing distribution and orientation of discontinuities in relation to each other including natural and incipient fractures. The classes presented in Table 2.11 follow the recommendations of BS5930:1981. Observational details of the discontinuities are also presented, these include the number

of sets of discontinuities and their orientation such as vertical or inclined, their persistence, degree of openness, planearity, nature of the surface and nature of the infill if present.

| | INDURATED | METAMORPHOSED | |
|---|---|---|---|
| % Quartz. | Rock name. | Low grade(no cleavage) | Low grade(cleaved). |
| >40% | Siltstone. | | |
| 40-10% | Mudstone. | → Argillite. → | Slate. |
| <10% | Claystone. | | |

Table 2.10. Mudrock classification after Spears (1980) and Taylor (1988).

| Discontinuity spacing term. | Mean spacing (mm). |
|---|---|
| Very widely spaced. | >2000 |
| Widely spaced. | 2000-600 |
| Moderately widely spaced. | 600-200 |
| Closely spaced. | 200-60 |
| Very closely spaced. | 60-20 |
| Extremely closely spaced. | <20 |

Table 2.11. Scale of discontinuity spacing.

7. Weathering and alteration state. The degree of weathering and alteration is described according to the recommendations of the Engineering Group of the Geological Society Working Party (Anon ,1995). The recommendations which are applicable to mudrocks follow Spinks and Norbury (1993) and are summarized in Table 2.12. The descriptive scheme is based on colour changes in the mudrock, changes in fracture state, reduction in strength and the presence of weathering products. Changes in strength are often difficult to evaluate for samples as fresh unweathered material is commonly unavailable as a reference point. This difficulty may also arise with fracture state, which can only be observed if a rock profile including fresh material such as in borehole core is available. Therefore, fractures in this study are evaluated as a geomechanical property of the mudrock controlled more by cementation, diagenetic recrystallization and stress relief. Colour changes and extent of weathering product are the most obviously visible and easily determinable manifestations of weathering in mudrocks. These effects are

commonly seen on the surfaces of discontinuities and penetrating into the sample from discontinuities. As such they are the mainstay of weathering descriptions in this study.

8. Other terms indicating special geological or engineering characteristics - The geological situation, for instance if the material is from near a fault zone or tectonically altered, is described. Engineering data including point load, slake durability, anisotropic index test results were recorded. The latter parameter can be indicative as to whether fissility is liable to develop during weathering of the material.

## 2.5. Comments.

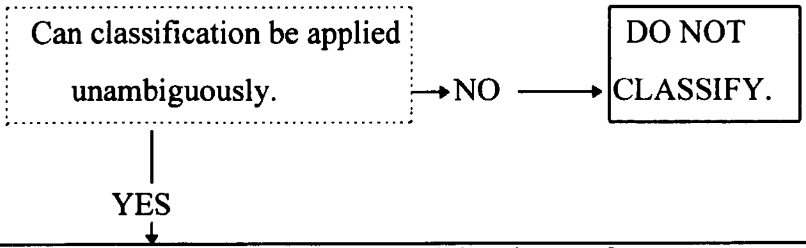
Mudrocks are difficult to study due to their fine grain size which requires specialist equipment for a detailed analysis. This unfortunately tends to be beyond the budget of most commercial contracts and studies. Whilst some of the classification schemes do offer field techniques for distinguishing between mudrock classes , these interpretations can become very subjective. Conflicts exist between specialists in the two main areas of mudrock classification this leads to difficulties with defining boundaries between grain size classes and which textural features are considered important for classification. Resolution of the discrepancies, classification confusion and conflicts which have arisen in the main over terminologies used in mudrock classification depends on standardization of terminology and practice, for example the confusion over what is meant by the term shale. What is apparent when describing mudrock samples is that as detailed a description as is possible should be made regardless of the word order used. Then specialists from other fields can extract information which is of interest to them without actually seeing the specimen, but an agreement over terminologies is needed for this to work. It is apparent from the different classification styles that engineering geological descriptions are the most systematic and detailed commonly used, with many available check lists and aide-memoirs to assist in logging of the material. It may be useful for scientists from other specialities such as sedimentologists and clay scientists to take on board these schemes and adapt them to their own needs. It becomes evident that to avoid confusion the term fissility should be applied with caution. It is a descriptive term as opposed to a generic rock name. The descriptive scheme applied in this study proved easy to follow and logical to apply but none the less it remains subjective and as always depends on regular, careful, attention to detail when describing the material.

### Factual description of weathering.

Standard descriptions should always include comments on the degree, extent and nature of any weathering effects at material (or mass) scale. This may allow subsequent classification and provide information for separating rock into zones of like character. Typical indications of weathering include:

- ◆Changes in colour
- ◆Changes in fracture state.
- ◆Reduction in strength
- ◆Presence,character & extent of weathering products

These features should be described using standard terminology, quantified as appropriate together with non-standard 'English' descriptors as necessary to describe the results of weathering. At the mass scale, the distribution and proportions of the various weathered materials (eg. corestones versus matrix) should be recorded.



| Classification incorperating material and mass features. | | |
|---|---|---|
| Class | Classifier | Typical Characteristics |
| A | Unweathered | Original strength, colour, fracture spacing. |
| B | Pertially weathered. | Slightly reduced strength,slightly closer fracture spacing,weathering penetrating in from fractures brown oxidation. |
| C | Distinctly weathered | Further weakened, much closer fracture spacing, grey colour reduction. |
| D | Destructured | Greatly weakened, mottled, ordered lithorelicts in matrix becoming weakened and disordered bedding disturbed. |
| E | Residual or reworked | Matrix with occasional altered random or "apparent" lithorelics, bedding destroyed. Classed as reworked when foreign inclusions are present as a result of transportation. |

Table 2.12. Mudrock weathering scheme after (Anon, 1995).

# Chapter 3.

# Diagenesis of mudrocks: a review.

## 3.1 Introduction

Diagenesis of mudrocks is a large topic on which many books have been written (Weaver, 1989; Frey, 1987; Larsen & Chilingar, 1979 etc.). This is a brief review of the subject intended to cover the changes that muddy sediments undergo in their transformation into lithified mudrocks, and the further changes into the realm of low temperature metamorphism with particular reference to the consequences to engineering behaviour. Diagenesis has different meanings to workers in different fields. Sedimentary geochemists tend to be more interested in the initial stages of sediment deposition in the water column. Clay mineralogists are more concerned with the mid- to late- stages of diagenesis where decarboxylation of organic matter occurs with the resultant production of petroleum and natural gas. Metamorphic petrologists tend to be interested in late diagenesis into early metamorphism and the resultant mineralogical changes. To engineering geologists, who do not really concern themselves with diagenetic studies, interest should be throughout the whole process as this will aid the understanding of the rock being dealt with and its expected response to environmental changes entailed by engineering projects. This Chapter intends to clarify the terminology in use, and cover the fundamental changes taking place during the diagenetic to early metamorphic progression with an attempt to explain the final effects on the engineering behaviour of mudrocks.

## 3.2. Terminology and different stages of diagenesis.

Diagenesis is the term given to the chemical and physical processes which act upon a sediment from the moment of deposition through the lithification stage up to the point of low temperature metamorphism, which is agreed to be ~150 ±50°C (Bucher & Frey, 1994). It excludes the intervention of tectonic activity for instance the formation of slaty cleavage. These changes are many and complex and as pointed out by Bucher & Frey (1994), the largest problem is that diagenetic and metamorphic are purely arbitrary terms. Weaver (1989) draws attention to the varying use of these terms by geologists from different backgrounds as will be seen.

From the point of sedimentologists and geochemists the scheme proposed by Curtis (1977) has proved to be a useful summary, especially for the changes in the early stages of diagenesis as is seen in Figure 3.1.

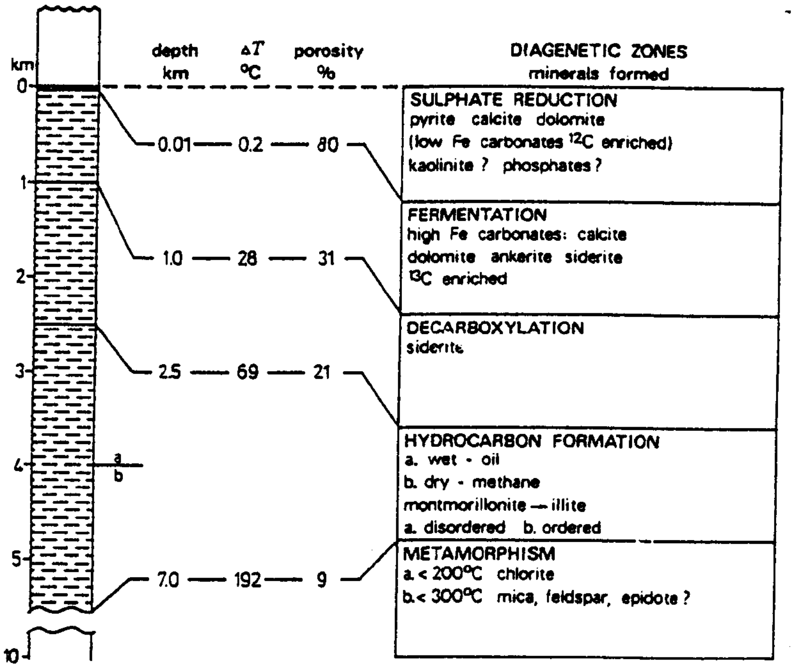


Figure 3.1. Zones of diagenesis from the water interface. (Curtis, 1977)

The scheme is divided into five reaction zones as follows:-

Zone 1 - This shallowest zone may be only up to 10cm thick and is at the water-sediment interface. Sulphate reducing bacteria convert sulphate to dissolved sulphide species, formation of which also utilises the ferric iron of soil sesquioxide material. Carbon dioxide formed by bacterial action on organic material causes precipitation of calcite or dolomite and possibly phosphates.

Zone 2 - Below a sediment depth of 10m the sulphate is usually spent, and fermentation of organic matter takes over and methane and carbon dioxide are produced. Possible further reduction of iron, may produce a suite of carbonate material.

Zone 3 - This zone tends to be below a depth of 1000m, where bacterial processes give way to inorganic reactions, with the remaining organic complexes breaking down causing precipitation of iron-rich carbonates.

Zone 4 - This zone is in excess of 2500m, here diagenetic changes are apparent with formation of middle-range hydrocarbons, with further depth generation of methane occurs. Clay transformations occur, the most prolific being the conversion of smectite to illite (which is covered in more detail in section 3.3).

Zone 5 - Depths of about 7000m see the start of mass recrystallisation, such as conversion of kaolinite to chlorite, and illite to muscovite. As such these are very low temperature metamorphic reactions.

This scheme is very simplistic and the values of porosities, depths and temperatures are only tentative suggestions of what they could be in specific situations. The scheme is useful at the early stages, particularly zones 1-3 where the formation of non clay and quartz cements occur, but unfortunately the scheme offers no mineral categories to predict to which diagenetic rank a particular specimen may belong to. Such a problem has led to the use of a specific mineral species common to most mudrocks with an observable reaction series. Thus the conversion of smectite to illite, and progressive increase in 'crystallinity' of illite has been correlated with diagenetic rank by a number of workers ( G.Dunoyer De Segonzac, 1970; Weaver, 1989) whose work is reviewed below.

Schemes proposed by Dunoyer de Segonzac (1970) and Weaver et al., (1984) that are based upon the stability of clay minerals, divided the diagenetic process into the three stages seen in Table 3.1(a) and Table 3.1(b).

Beyond diagenesis the rock enters the realm of very low grade metamorphism, which is a buffer zone between diagenesis and true metamorphism. This zone has recently gained in interest due to the evaluation of sedimentary basin maturity for assessing hydrocarbon potential (Merriman and Kemp, 1996) . Transformations occur over an approximate temperature range of 150-200 to 350-400°C. There are no unique mineral assemblages as would define a metamorphic facies, and as such the zone is divided into the Anchizone and Epizone. As mentioned by Frey and Kisch (1987) these zones are recognised only on the basis of illite "crystallinity" data which is the method used for indication of grade for very low-grade metaclastics.

Early Diagenesis:- The zone consists of the shallow burial extending from the depositional environment. Inherent clays are stable with mainly biochemical changes. Some interstitial water loss with burial.

Middle Diagenesis:- Sediment compacted but still porous therefore not excessive depths of burial with circulating groundwater. Clay minerals not dehydrated therefore kaolinite and montmorillonite still stable.

Late Diagenesis:- Intense compaction, expulsion of water, increase in temperature and pressure and recrystallisation of feldspar and quartz. Ions become concentrated. Aggregation of clay minerals. Montmorillonite absent and kaolinite becomes unstable to form dickite in an acidic environment but is destroyed in a basic environment.

Table 3.1(a). Classification of Diagenesis - G Dunoyer De Segonzac (1970)

Early Diagenesis:- Zone from the sediment-water contact, to the stage of Regularly spaced Mixed Layer Clays (~60% I ~ 90-140°C)

Middle Diagenesis:- Zone from first appearance of Regularly spaced Mixed Layer Clays (~14-13Å glycolated peak) to the disappearance of the discrete glycolated Mixed Layer Clay peak (90% illite ~ 200°C).

Late Diagenesis:- Where the glycolated Mixed Layer peak appears as an integral part of the 10Å peak (<10% smectite) to the anchizone (Kubler Index = 0.42 °2θ : Weaver Index = 2.3 ~ 250-280°C)

Table 3.1(b). Diagenesis Classification - Based on the illite/smectite ratio from work on the Appalachian Mountains.( Weaver and Associates, 1984 and Weaver, 1989)

Measurement of vitrinite reflectance values has also been used as a means of assigning diagenetic and metamorphic grade to mudrocks. As such the terminologies again differ from those mentioned previously. Teichmuller (1987) uses the following terminologies which are used by organic geochemists to designate the main stages of hydrocarbon maturity, and as such should not be used for classification of diagenetic to very low grade metamorphic zones in mudrocks.

| Term | Maturity | Vitrinite Reflectance |
|---|---|---|
| Diagenesis | Immature | <0.5 - 0.6% |
| Catagenesis | Mature | 0.5 - 0.6% to 2.0 -2.3% |
| Metagenesis | Overmature | >2.0 - 2.3% |

Diagenesis and very low grade metamorphic rocks can be thus assigned into one of 5 zones of development. These zones are generally based on illite "crystallinity" measurements, the percentage of illite in mixed-layer clays and on vitrinite reflectance data. Correlations of these parameters have been made by many researchers in the field, including Foscolos and Kodama (1974), Kisch (1980), Hillier and Clayton (1989), Pierce, Clayton and Kemp (1991), Miki, Nakamuta and Aizawa (1991), Velde and Lanson (1993), Hillier et al (1995) and others. They have come up with acceptable correlations between parameters as seen in Fig 3.2.

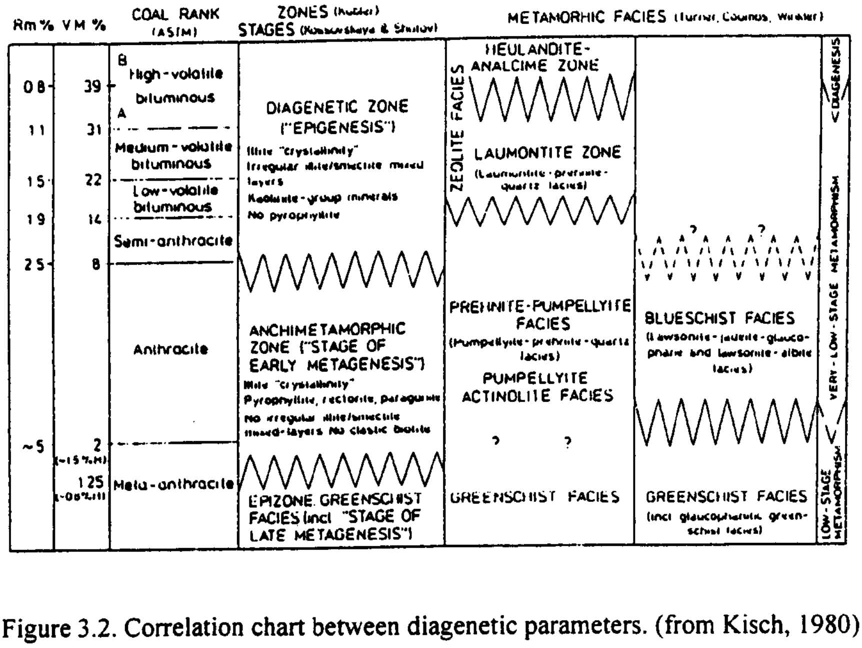


Figure 3.2. Correlation chart between diagenetic parameters. (from Kisch, 1980)

Teichmuller (1987) cautions that although good correlations are apparent, in certain cases where strong short bursts of heating have occurred, coalification may proceed in advance of mineral transformation.

As a general summary, Merriman and Kemp (1996) produced a chart of the various rank indicators and their relationship to hydrocarbon maturity in basins (see Figure 3.3), as such it is intended in this study to further this chart to include engineering parameters of mudrocks, and their change with increasing rank.

Further explanation of the changes that mixed-layer clays, illite and vitrinite undergo during diagenesis and the relationships these mineralogical changes bear to physical changes in mudrocks with respect to engineering geology will be given in the following sections.

## 3.3. The effects of diagenesis on illite/smectite.

With progressive burial and action of diagenetic processes such as water expulsion and dehydration of clays due to compression, there is a massive through flow of water through compacting muds. This water could be accompanied by the transfer of distilled hydrocarbons from the mud source to the more porous sandstone reservoirs. The latter process may be accompanied by the precipitation of clay minerals within sandstone pores from the additional material carried by the interstitial waters. With increasing costs of exploration and exploitation for hydrocarbons, oil companies invested heavily in the investigation of the processes of clay mineral neoformation, and the effects that this has on the hydrocarbon reservoirs and their exploitation. These studies were greatly enhanced by the use of X-ray diffraction and scanning electron microscope analysis of the formation rocks. In early and subsequent research on Gulf Coast well material (Burst, 1959 and Weaver, 1959) it was found that the most impressive diagenetic reaction was the conversion of smectite to illite.

### 3.3.1. The diagenetic conversion of smectite to illite.

In spite of the amount attention devoted to this topic, it is still not fully understood. This section briefly presents the general reactions, more detail is provided by Weaver (1989).

Numerous studies of sedimentary basins from around the world have shown similar reactions in the conversion of smectite via mixed layer illite/smectite to illite (Dunuyer de Segonzac, 1970., Foscolos and Kodama, 1974., Heling, 1974., Pearson et

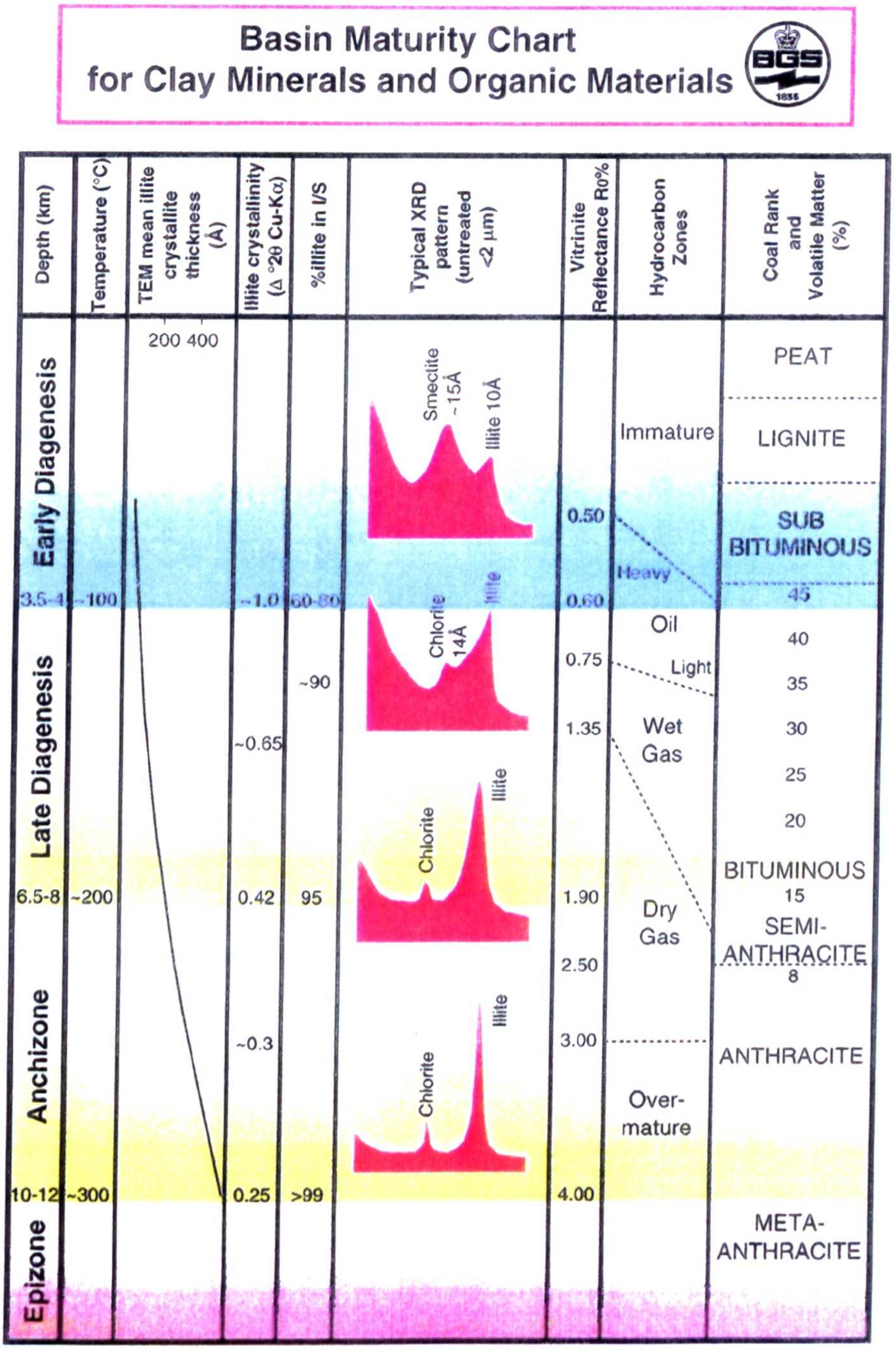


Figure 3.3. British Geological Survey basin maturity chart. (Merriman and Kemp, 1996)

al, 1982., Srodon, 1984, etc.). The reaction is thought to be controlled by several variables including temperature, reaction times and, most importantly, chemical components, so it is shown that smectite will persist to higher temperatures if the system lacks adequate K. The conversion of smectite to illite involves the removal of interstitial $OH^-$ ions from the smectite lattice to be replaced by Al and K, thus gradually converting smectite via mixed layer illite/smectite to illite as the end member. The reaction has been shown to follow one of three routes:

a) Solid State Conversion: In this model the basic 2:1 layers remain intact. Initially Weaver and Beck (1971) proposed that the solid state reaction involves Al and K derived from K-feldspar and/or kaolinite breakdown entering the tetrahedral sheet replacing Si:

   smectite ($Fe^{3+}$) + K - feldspar ± kaolinite $\Rightarrow$ I/S/Ch ($Fe^{2+}$) + $Si^{+4}$.

   Subsequent theories (Hower et al., 1975) that assumed this reaction series, proposed that most of the K was derived from K-feldspar and mica:

   smectite $+Al^{3+} + K^+ \Rightarrow$ illite + $Si^{+4}$

b) Dissolution - precipitation: This reaction model was postulated by Boles and Franks (1979), who suggested that there is no external source of Al, but that it is obtained by partial dissolution within the smectite layers, and the main dissolved product is Si :

   smectite $+K^+ \Rightarrow$ illite + chlorite + quartz + $H^+$

c) Ahn and Peacor (1986) who based their model on TEM investigations suggest that a combination of a) and b) takes place. They propose that illite layers lie parallel or sub-parallel to the smectite layers as discrete particles. With depth of burial illite packets thicken, consuming smectite therefore resulting in a conversion with no volume change, just crystallite growth or 'Ostwald ripening'.

The reaction range has been shown to start at 55 -100°C (Weaver, 1989) with the first appearance of authigenic illite, but this varies from basin to basin. Smectite persists through intermediate stages up to temperatures of 350°C (Weaver and Associates, 1984). Srodon and Eberl (1984) concluded that reaction time plays an important role as does rock and fluid composition in the formation of illite/smectite profiles, and they suggest that illite/smectite should not be used for geothermometric purposes.

Electron microscopy studies have shown that the fundamental errors have arisen in the study of the illite/smectite reaction due to flaws in preparation of samples and analysis of X-ray traces. Srodon (1980) suggests that interpretative errors of X-ray traces may be anything from ±15 to 20% of the actual illite/smectite composition. With TEM analysis Ahn and Peacor (1986) showed that, contrary to XRD studies, illite occurs as pockets within smectite matrix pockets. During sample preparation for XRD analysis these interlayers are broken down, highly dispersed and resedimented on slides. They would then be recorded as a mixed-layer form (Nadeau et al., 1984). Shaw and Primmer (1991), noted from their studies of two well sequences from the North Sea that the variations in illite/smectite between the two wells was not due to diagenetic conversions, but was more likely to be due to the effects of detrital input. Most deep well studies are based on the assumption that the precursor mineral is a pure smectite, neglecting to consider the possibility that detrital input may consist of already established mixed-layer clays.

By comparing evidence from different techniques Jeans (1989) found that the illite/smectite transformation hypothesis is largely an artefact of over-reliance on a single technique such as XRD. He concludes that the smectite - illite change observed in burial diagenesis of mudrocks results from the dissolution of smectite particles and the neoformation of illite crystals if the pore-fluid composition is suitable. Since Gulf Coast well and other studies have shown that the temperature and reaction rate for the smectite-illite transformation varies over a vast range, this reaction is not a reliable temperature indicator. He suggests that greater consideration should be given to vitrinite reflectance, spore colour and illite 'crystallinity'.

As can be seen from the brief discussion there are many uncertainties concerning the conversion of smectite to illite. As new techniques become available further insight will be provided. For example Gharrabi, Velde and Sagon (1996) discovered with the aid of an advanced computer software deconvolution package that many of the reactions may involve two expandable mixed-layer minerals that evolve at different rates, leading to difficulties during interpretation.

For petroleum geologists the main impetus for studying mixed-layer clays is to accertain burial conditions. Temperature and pressure affect the type of hydrocarbons produced, and as such effect the conversion of smectite to illite. Perry and Gillot (1992) found that studying the overall clay mineralogy of mudrocks, temperatures in the range of 350-700°C could be estimated with an accuracy of ± 50°C. To engineering geologists the temperature is of no lesser significance but the associated changes to the mineral assemblage and textural changes are of primary importance. These will be covered in section 3.6.

## 3.4. Illite "crystallinity".

The term 'crystallinity' is a useful term commonly applied for illite determinations by XRD. Strictly speaking the term signifies the amount of crystalline material within a substance but it has other connotations when applied to diagenetic changes to smectite. For instance Kubler (1967) defined it "as the degree of ordering in a crystalline lattice" but without specifying the meaning of ordering. Subsequently Kubler (1984) suggested changing the terminology for two main reasons:

a) From a strictly crystallographic standpoint, illite does not exist except as the end member muscovite.

b) The degree of crystallinity is only implied in XRD studies.

Weaver (1989) states that the term 'crystallinity' is a poor choice of term since it tends to be a measure of illite and the proportion of interstratified smectite layers which occur with it. However the term is so well established in the literature that it would cause problems in applying a new term, and as such Frey (1987) and others advocate retaining it but presenting it within quotation marks i.e. illite 'crystallinity'.

### 3.4.1. Illite 'crystallinity' indices.

In his study of the Ouachita Mountain range of Texas, Weaver (1960) observed a relationship between the shape of the illite 10Å X-ray diffraction peak and metamorphic grade of the mudrocks. He proposed a measure of the illite peak which he referred to as the "Sharpness Ratio" which is an intensity ratio between the middle of the 10 Å illite peak, and the flank at 10.5 Å (see Figure 3.4(a)).

In studies of metamorphic terrains in the European Alps, Kubler (1964) observed similar changes but to overcome the difficulties of measuring the Weaver Index on very narrow, high crystallinity peaks he introduced the Kubler 'crystallinity' Index. This is the width of the 10 Å illite peak at half height above background, as seen in Figure 3.4(b). Initially the Kubler Index was expressed in (mm), but the standard is now to express the value in ($\Delta^{o}$ 2θ). Since the measurement of the Kubler index is dependent on experimental conditions the method is standardised (see Chapter 7). Initially, in order to standardise the method, Weber (1972) related the Kubler Index or illite peak width at half height ($H_b$(001)Illite) to the peak width at half height of the quartz 100 peak ($H_b$(100) quartz), therefore defining the peak width as:-

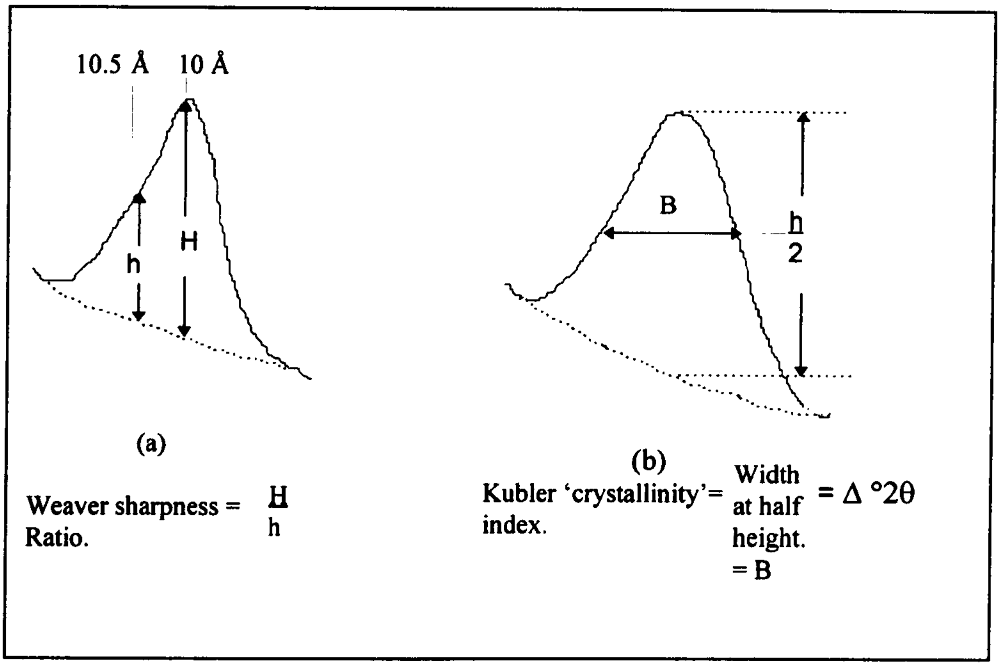


Figure 3.4. Illite 'crystallinity' measurements.

$$\text{Weber Index} = H_{brel} = \frac{H_b(001)\text{Illite}}{H_b(100)\text{ quartz}} \quad \times 100$$

The intention was to standardise results from different types of XRD equipment, but this is only true if $H_b$(100) quartz is standardised.

Correlations between the values from the Kubler and Weaver Indices derived by Weaver and Broekstra (1984) are given in Table 3.2. Of the three standards covered, the Kubler Index has gained the widest usage (Frey, 1970., Foscolos and Kodama, 1974., Merriman and Roberts, 1985., Spötl et al., 1993., Torre et al, 1996 etc.), especially in Europe, with occasional joint usage with the Weaver Index (Foscolos and Kodama, 1974., Gill et al, 1977).

| Zone | Weavers Sharpness Ratio | Kublers 'Crystallinity' Index ($\Delta^{\circ}2\theta$) |
|---|---|---|
| Diagenesis | | |
| | 2.3 | 0.42 |
| Anchizone | | |
| | 12.1 | 0.25 |
| Epizone | | |

Table 3.2. Correlation between Kubler and Weavers illite 'crystallinity' indices.

Frey (1987) points out that the Weaver Index works in unmetamorphosed sediments, but is less suited to the anchizone due to the increased error in determining the Sharpness Ratio on a sharp, narrow peak. The Kubler Index posed problems in variations in results from similar materials, therefore standardised testing conditions were applied, but did not solve the problem. Since the 1980's crystallinity standards have become available for inter-laboratory correlations. With this the use of the Weber Index has declined such that it is confined to German authors (Weber, 1972., Teichmuller, et al, 1979). Errors in the determination of the two indices work in opposite directions, in that unlike the Weaver Index, the accuracy with which the Kubler Index can be determined increases with improved 'crystallinity' (Kubler, 1968).

### 3.4.2. Controls on illite 'crystallinity'.

As mentioned previously, the the determinations of illite indices are not strictly speaking a crystallinity measure. Weaver (1989) points out that the measurement of the 10Å illite peak width is usually affected by the proportion of 12Å-14Å mixed-layer clay interstratified with illite. Once beyond the diagenetic zone and into the facies of very low grade metamorphism, the index is more a measure of the X-ray scattering domain size (Eberl and Velde, 1989) that is size of the diffracting crystallites.

The illite 'crystallinity' is dependent on several environmental factors. Here experimental conditions are excluded as these can be controlled. If present interfering basal reflectors, such as pyrophyllite, paragonite, margarite and biotite may be encountered at the epizone prevent the determinations of illite 'crystallinity' values. The factors controlling illite crystallinity are not clearly understood. Temperature is believed to be the most important physical factor controlling crystallinity (Kubler, 1967), a view supported by studies based on contact metamorphic aureoles (Frey, 1987). The role of stress is not yet clear although it is a possible controlling factor, in that Roberts and Merriman (1985) and Caliani and Galan (1992) found enhanced crystallinity values within the hinge zones of anticlines, therefore showing a direct relationship between illite 'crystallinity' and regional strain. Lithology also plays an important part in illite 'crystallinity' values. Coarse grained clastic sediments have better crystallised illites than fine grained sediments, presumably because while coarser sediments contain more detrial illite and muscovite with higher crystallinity values, they usually are more porous, allowing better circulation of interstitial solutions leading to aggregation of illite (Dunoyer de Segonzac, 1970). The different ways in which pelitic and psammitic sediments react to applied stress may also affect the process. Sediments containing a high proportion of organic matter tend to contain illites with retarded crystallinity values (Kubler, 1968). This is caused by a mantle of hydrophobic organic material isolating illite grains from circulating ionic solutions. It has been shown by Weaver and Beck (1971) that where increasing K contact due to degradation of K-feldspar and micas has occurred this leads to better illite 'crystallinity' values. Fluid pressure is considered to be of negligable importance although Frey (1987) states that there is no direct evidence to prove or disprove this statement. It is assumed that the attainment of illite 'crystallinity' is time dependant, typical of a metastable material tending towards equilibrium, such that the longer period of time illite remains at a constant temperature, the better crystallized it would be. Frey (1987) states that no evidence exists to support this time rate hypothesis. Bearing in mind all the factors mentioned, care should be taken with the application of illite 'crystallinity'. Frey (1987) states that the parameter should not be used for geothermometric purposes with the present state of knowledge, although it remains one of the most suitable and generally applicable monitors in very low grade metamorphic studies of clastic sediments.

## 3.5. Effects of diagenesis on organic material.

Organic matter is commonly found in most mudrocks. According to Tucker (1994) the average content is ~2%. It consists primarily of carbon, with hydrogen, oxygen and nitrogen and is derived either from land plants, as in the case of coal products which are referred to as macerals, or from algae or algal spores from which kerogen is derived. Collectively organic inclusions in rocks are referred to as phytoclasts (Bostick, 1974). Phytoclasts found in mudrocks are modified by diagenetic processes, the most important of which are controlled by temperature and reaction time acting upon deposited organic matter.

### 3.5.1. Formation of kerogen - bituminization.

Living organisms consisting of carbohydrates, lignin, proteins and lipids, upon death and if deposited in a reducing environment, are decomposed by anaerobic bacteria through the process of fermentation producing residual organic compounds, $CH_4$ and $CO_2$. These residual organic compounds recombine by polycondensation and polymerisation to form insoluble compounds such as humic acid. At this stage diagenetic factors take over, on burial the organic acids are converted to humin, and on further burial the O/C and N/C ratios decrease leading to the formation of kerogen (North, 1985). In polished sections of kerogen the change from shallow burial to deep burial and evolution of kerogen is accompanied by a colour change of the organic matter from yellow-amber through brown to black (Tucker, 1994). Petroleum geologists tend to study strew mounts of acid concentrated kerogen by means of transmitted light microscopy to determine the rank of potential reservoirs. The maturation parameters are extremely important in delineating oil and gas windows and their boundaries.

### 3.5.2. Formation of coal - coalification.

Carbonized plant debris or coal is commonly found in mudrocks as disseminated phytoclasts, lenses or seams of coal. Coalification involves the development of organic matter derived from land plants, through stages of peat→ lignite → bituminous coal → anthracite formation. This process involves an increase in carbon content and a decrease of volatile matter in the resulting phytoclasts. It is dependent on temperature and heating duration, and the aspect that makes this process of interest to diagenetic studies is the fact that the process is irreversible (Mukhopadhyay, 1992).

Land plants or macerals are divided into three main groups as seen in Table 3.3.

| **Maceral Group** | **Maceral** | **Source and Process of formation** |
|---|---|---|
| Huminite/Vitrinite | Telinite<br>Collinite<br>Corpocollinite<br>Vitrodentrinite | Woody tissues, Bark leaves, cell fillings etc. - formed by mummification. |
| Liptinite | Resinite<br>Sporinite<br>Cutinite<br>Alginite<br>Subernite<br>Bitumite<br>Chlorophyllite<br>Liptodetrinite<br>Exudatinite<br>Flourinite | Resins oils and waxes, spore exines cuticles and algae, cork and chlorophyll - formed as resistant material |
| Internite | Micrinite<br>Fusinite<br>Semifusinite<br>Sclerotinite<br>Macrinite<br>Inertodetrinite | Cell walls, fungal debris, wood tissues etc. - formed as degradation products due to charring or fungal attack before and during the peat stage. |

Table 3.3. Maceral catagories. (After Teichmüller 1987, and Bustin et al, 1985)

The study of coal material was initially carried out by identification of the organic constituents using thin sections under the microscope, this is possible on low rank material, but as rank increases the thickness of the coal thin section has to be reduced until at ~5μm the technique becomes impractical (Teichmüller, 1987).

Chemical and physical changes during coalification are not uniform and vary at rank stages and due to this factor it was decided to study vitrinite rather than use bulk coal analysis for these comparative studies (Teichmüller, 1949). Vitrinite consists of at least 95% of the maceral group vitrinite, it is also the dominant maceral in coals and sediments, and its change is relatively uniform during diagenesis and into low temperature metamorphism. For these reasons vitrinite change is the most widely used parameter for measuring organic diagenesis and metamorphism.

### 3.5.3. Vitrinite reflectance as a maturation index.

Vitrinite reflectance measurements are carried out on acid separates of phytoclasts from mudrocks or crushed coal. These are made into pellets with epoxy resin, once set they are ground and polished, measurements are made on these pellets with the use of a reflectance microscope and an oil immersion lens (details of the procedures are given in Chapter 7). Values of mean reflectance of vitrinite ($R_o$%) change with the mineral composition of the phytoclasts. With an increase in diagenetic rank, the vitrinite phytoclasts tend to be richer in carbon as the volatile constituents are driven off. This increase in carbon content also increases the quantity of light reflected by the sample. As there may be slight variation in the results due to anisotropy of the phytoclasts, these measurements are usually performed on at least 100 grains (Mukhopadhyay, 1992), so as to calculate a mean value and standard deviation of the results. A larger data set allows a statistically acceptable mean value to be obtained. Values of vitrinite reflectance tend to be assigned to coal stages as is seen in Table 3.4. These values are based on American and German classifications, values given by Tucker (1994) based on UK samples are presented in Table 3.5.

It is generally well established that vitrinite reflectance values increase with the rank of the mudrock. Soft lignites tend to be associated with consolidated clays, bituminous coals with lithified mudrocks and anthracites with very durable well lithified mudrocks. So the reflectance values of vitrinite run parallel to the diagenesis of associated mudrocks (Heling and Teichmüller, 1974) and therefore it is a useful rank parameter when used in conjunction with illite 'crystallinity' values. If the organic matter is virgin and not reworked material, then it can prove to be more sensitive as a rank indicator than clay minerals. In clay mineral studies, especially conversion of smectite to illite it is generally assumed that the reaction commences from a 100% smectite, which is rarely the case. Whereas in clay profiles changes in illite 'crystallinity' can be seen and related to diagenetic changes. However in single samples the original 'crystallinity' is not known so the percentage of illite in smectite is not indicative of grade. On the other hand vitrinite provides a measure of grade which explains its increasing popularity with researchers.

Table 3.4. Coalification stages according to German and North American classifications. (Teichmuller, 1987)

Table 3.5. Rank stages for UK coals. (Tucker, 1994)

## 3.6. The effects of diagenesis on engineering properties of mudrocks.

As can be seen in the brief discussion of diagenetic processes due to the many variables encountered, there is no standard sequence of evolution of a mineral suite with increasing diagenesis. Within an engineering geology framework the actual limits of mineral conversion are not as important as either the mineral suite present, or the diagenetic history of the rock. It is this mineralogy and diagenetic sequence of events which control the eventual outcome of the mudrock in an engineering context. As such diagenetic changes are two-fold when considering mudrocks, primarily there is the mineralogical maturation, and secondly the physical maturation.

### 3.6.1. Mineralogy controls on engineering mudrocks.

A fundamental property of mudrocks is their capacity to swell and slake in respect to changes in moisture content. The major control on their mass strength is the presence of discontinuities of which the most important are micro-fractures (Dick and Shakoor, 1992). Swelling and slaking in mudrocks is primarily controlled by the mineralogy and porosity. Expansive clays such as smectite, mixed-layer illite/smectite and vermiculite expand and shrink with successive cycles of wetting and drying, and this has led to many problems in construction and engineering works (Taylor and Smith, 1986., Olivier, 1990., Varley, 1990., Shakoor, 1995., etc.). As noted by Taylor and

Smith (1986) geotechnically more inert clay mineral assemblages are found in geologically older rock (Figure 3.5). Interparticle swelling due to expansive clays like smectite and mixed-layer clays is reduced with geological age. Post-burial modifications of temperature, heat flow rate, time and pore water chemistry alter the mineralogy. A number of associated processes such as progressive illitization of smectite below ~500m depth by removal of expandable layers from clay structures and decomposition of kaolinite with depth and its replacement by neoformed chlorite increase the mechanical stability of mudrocks due to loss of porosity and healing of microfractures. Reactions involving the conversion of less stable to more stable clays are accompanied by the release of $Si^{4+}$ and $Ca^{2+}$ (as seen in section 3.3.1), which

Figure 3.5. Average clay mineral composition of UK argillaceous deposits through geological time.(Shaw, 1981)

results in the precipitation of quartz and carbonate cements. The conversion to a new mineral suite is also accompanied by growth of the new minerals, commonly referred to as Ostwald ripening (Eberl et al, 1990), which contributes to the loss of porosity and increase in cementation.

It is difficult to follow the extent of conversion in clay mineral suites in mudrocks during deep burial as starting mineralogies are generally not known. Illite 'crystallinity' is a useful indicator of relative diagenetic rank and therefore the maturity of the clay mineral suite as seen in Figure 3.6.

In diagenetic studies it is only prograde sequences of events that are considered, in engineering geology weathering of mudrocks is an important parameter to consider in understanding the rocks behaviour. Coulthard and Bell (1993) noted a change in mineralogy within a weathered sequence of Lower Lias Clay, which is accompanied by

Figure 3.6. Diagram showing the general changes in clay minerals with increasing depth of burial. (Tucker, 1994)

parameter when used in conjunction with illite 'crystallinity' values. If the organic matter is virgin and not reworked material, then it can prove to be more sensitive as a rank indicator than clay minerals. In clay mineral studies, especially conversion of smectite to illite it is generally assumed that the reaction commences from a 100% smectite, which is rarely the case. Whereas in clay profiles changes in illite 'crystallinity' can be seen and related to diagenetic changes. However in single samples the original 'crystallinity' is not known so the percentage of illite in smectite is not indicative of grade. On the other hand vitrinite provides a measure of grade which explains its increasing popularity with researchers.

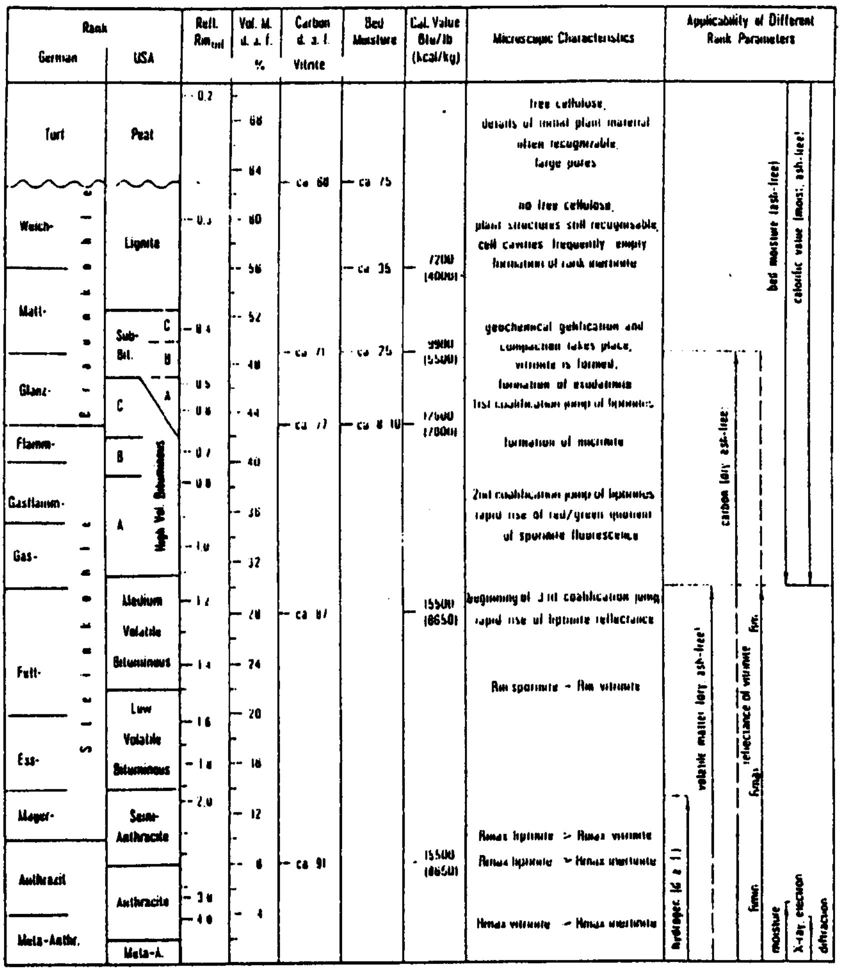


Table 3.4. Coalification stages according to German and North American classifications. (Teichmuller, 1987)

| Rank stages | Carbon content % dry ash free | Volatile content % | Calorific value (kJ $g^{-1}$) | Vitrinite reflectance in oil |
|---|---|---|---|---|
| Peat | <50 | >50 | | |
| Lignite | 60 | 50 | 15–26 | 0.3 |
| Sub-bituminous coal | 75 | 45 | 25–30 | 0.5 |
| Bituminous coal | 85 | 35 | 31–35 | 1.0 |
| Semi-anthracite | 87 | 25 | 30–34 | 1.5 |
| Anthracite | 90 | 10 | 30–33 | 2.5 |
| Graphite | >95 | < 5 | | |

Table 3.5. Rank stages for UK coals. (Tucker, 1994)

## 3.6. The effects of diagenesis on engineering properties of mudrocks.

As can be seen in the brief discussion of diagenetic processes due to the many variables encountered, there is no standard sequence of evolution of a mineral suite with increasing diagenesis. Within an engineering geology framework the actual limits of mineral conversion are not as important as either the mineral suite present, or the diagenetic history of the rock. It is this mineralogy and diagenetic sequence of events which control the eventual outcome of the mudrock in an engineering context. As such diagenetic changes are two-fold when considering mudrocks, primarily there is the mineralogical maturation, and secondly the physical maturation.

### 3.6.1. Mineralogy controls on engineering mudrocks.

A fundamental property of mudrocks is their capacity to swell and slake in respect to changes in moisture content. The major control on their mass strength is the presence of discontinuities of which the most important are micro-fractures (Dick and Shakoor, 1992). Swelling and slaking in mudrocks is primarily controlled by the mineralogy and porosity. Expansive clays such as smectite, mixed-layer illite/smectite and vermiculite expand and shrink with successive cycles of wetting and drying, and this has led to many problems in construction and engineering works (Taylor and Smith, 1986., Olivier, 1990., Varley, 1990., Shakoor, 1995., etc.). As noted by Taylor and

Smith (1986) geotechnically more inert clay mineral assemblages are found in geologically older rock (Figure 3.5). Interparticle swelling due to expansive clays like smectite and mixed-layer clays is reduced with geological age. Post-burial modifications of temperature, heat flow rate, time and pore water chemistry alter the mineralogy. A number of associated processes such as progressive illitization of smectite below ~500m depth by removal of expandable layers from clay structures and decomposition of kaolinite with depth and its replacement by neoformed chlorite increase the mechanical stability of mudrocks due to loss of porosity and healing of microfractures. Reactions involving the conversion of less stable to more stable clays are accompanied by the release of $Si^{4+}$ and $Ca^{2+}$ (as seen in section 3.3.1), which

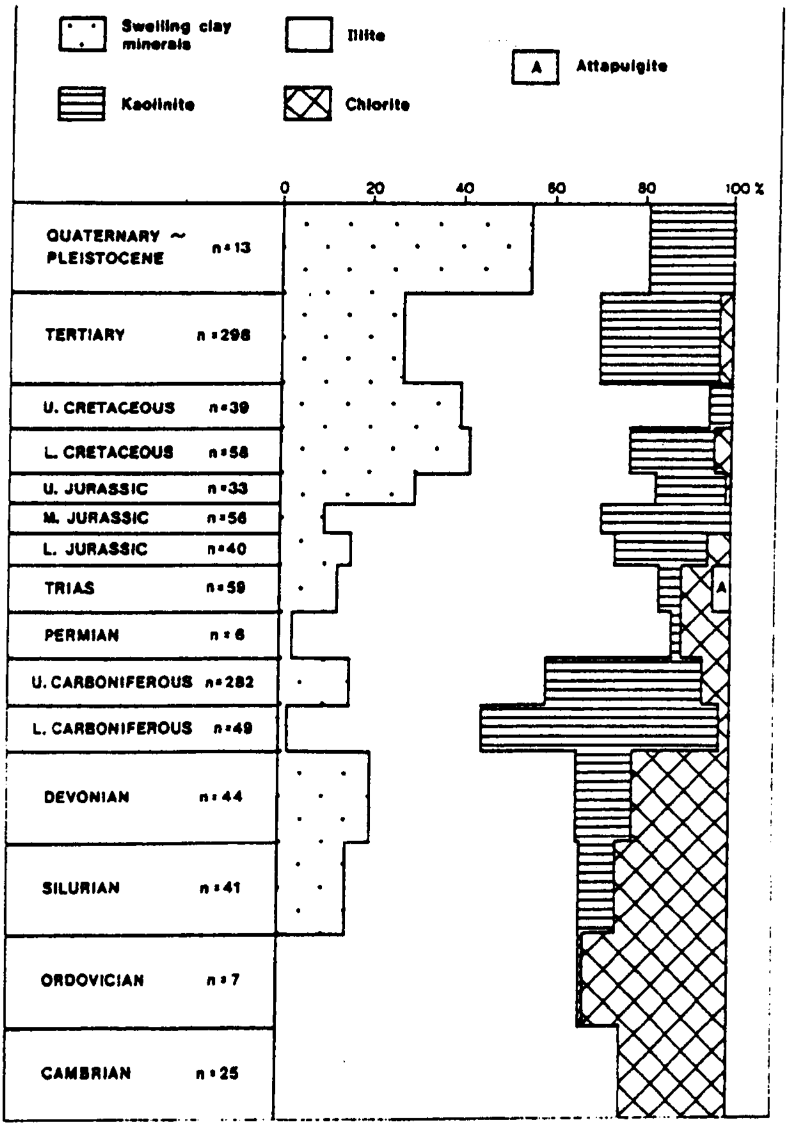


Figure 3.5. Average clay mineral composition of UK argillaceous deposits through geological time.(Shaw, 1981)

results in the precipitation of quartz and carbonate cements. The conversion to a new mineral suite is also accompanied by growth of the new minerals, commonly referred to as Ostwald ripening (Eberl et al, 1990), which contributes to the loss of porosity and increase in cementation.

It is difficult to follow the extent of conversion in clay mineral suites in mudrocks during deep burial as starting mineralogies are generally not known. Illite 'crystallinity' is a useful indicator of relative diagenetic rank and therefore the maturity of the clay mineral suite as seen in Figure 3.6.

In diagenetic studies it is only prograde sequences of events that are considered, in engineering geology weathering of mudrocks is an important parameter to consider in understanding the rocks behaviour. Coulthard and Bell (1993) noted a change in mineralogy within a weathered sequence of Lower Lias Clay, which is accompanied by

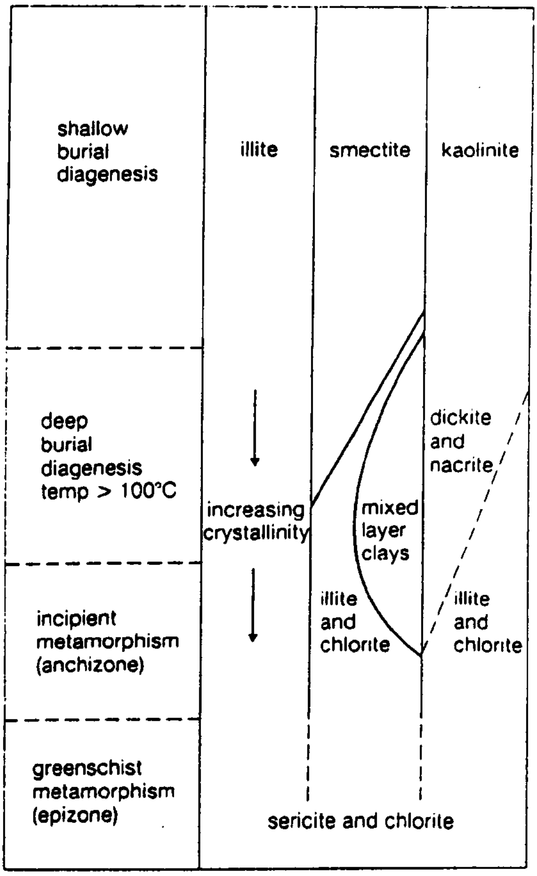


Figure 3.6. Diagram showing the general changes in clay minerals with increasing depth of burial. (Tucker, 1994)

a degradation in engineering properties. It can be seen from their XRD traces that the illite 'crystallinity' changes through the profile which is a useful indicator to the state of weathering of the material. This degradation of clays especially illite with weathering was also noted by Hawkins, Lawrence and Pinches (1988) as can be seen in Figure 3.7. This degradation in illite would be detectable with XRD clay analysis, and also this degradation means that the sequence as a whole would be more prone to swelling and slaking behaviour.

### 3.6.2. Physical changes in mudrocks during diagenesis.

Compaction of sediments is thoroughly reviewed in a book by Rieke and Chilingarian (1974) which should be referred to for further information. As sediments settle out at the bottom of the water body they tend to have a porosity in the region of 70-90%. The accumulating sediments exert overburden pressure which causes compaction by particle rearrangement and deformation. It is generally accepted that

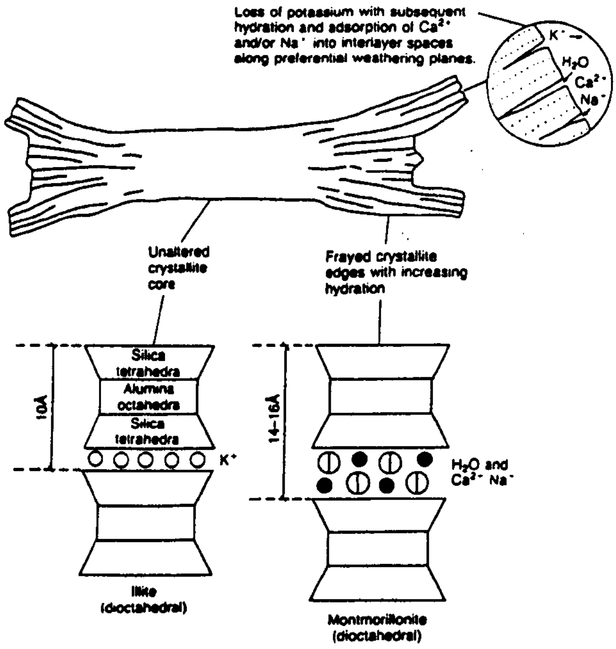


Figure 3.7. Degradation of illite to montmorillonite. (Hawkins, Lawrence and Pinches, 1988)

under fresh water conditions, clay particles are not flocculated and therefore tend to settle in a well oriented face to face condition, whereas under marine conditions, dissolved salts tend to flocculate clay particles into aggregates consisting of a more open cardhouse or honeycomb structure, therefore initial porosities do vary under different environmental conditions (Moon and Hurst, 1984). Porosity of deposited argillaceous material decreases rapidly for the first 300-500m (1000-1500ft) of burial as is seen in Figure 3.8 from Baldwin (1971). This change is governed by a number of factors which include composition, rate of deposition, pore structure and permeability, availability of permeable zones to allow the removal of pore water, decomposition of organic matter, chemical diagenetic processes and the state of the interstitial fluids (Chilingarian, 1983).

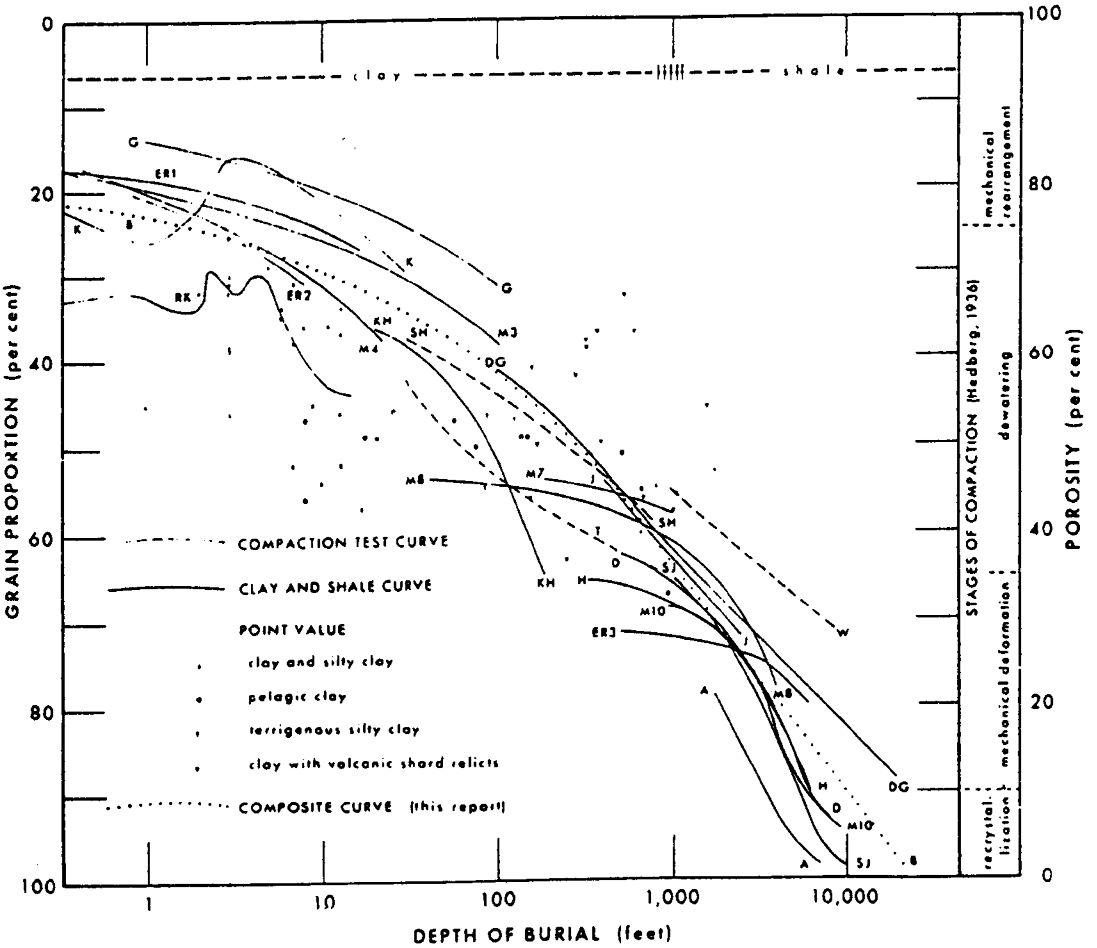


Figure 3.8. Changes in clay and mudrock porosity with depth of burial. (Baldwin, 1971)

The process of burial compaction converts argillaceous sediments into rock by means of lithification, and as such the physical properties of the resultant material change. During progressive burial, the porosity of the sediments is reduced, and the constituent grains are brought into closer contact as water is expelled from pore spaces. If the non-clay constituents are brought into contact a framework of pores is provided and clay minerals tend to be squeezed and reorientated to fill these voids. Once in close contact the clay minerals develop strong diagenetic bonds binding them together. These strong bonds have the ability to release strain energy on a time-dependent basis once the rocks undergo prograde processes such as uplift and weathering. Stress relief tends to result in a release of elastic strain energy which leads to progressive failure over time due to fracture development especially in less indurated mudrocks (Cripps and Taylor, 1981). Whereas with more indurated mudrocks, which have been affected by clay mineral regrowth, this stored stress is gradually eliminated with increasing diagenetic rank. Dick and Shakoor (1992) noted that one of the fundamental lithological physical characteristics of mudrocks is their degree of microfracturing, produced as a result of released strain energy. In more indurated mudrocks, diagenetic cementation may bind bent crystals which retain their elastic strain, with uplift and the progressive removal of the cement, this stored strain energy is released resulting in slaking.

As porosity decreases there is also a marked decrease in measured void ratio, and an increase in bulk density of the associated mudrocks, the density of a rock is one of its most fundamental properties, being influenced by mineral composition, and void space. These parameters are useable indicators for increasing diagenetic rank, since mudrocks have broadly similar compositions and specific gravity of the constituents. It has also been shown that as porosity decreases, and bulk density increases so the mechanical strength of the rock improves (Jeager and Cook, 1979). Beall (1970) also found that as burial diagenesis increases, porosities in mudrocks decrease, and as minerals are forced closer together with recrystallisation pore throat diameters are reduced. On exposure, this decrease in pore size means that mudrocks will be more durable, as water is not as able to enter into the rock and engage in mineralogical swelling and slaking behaviour.

It can be seen that with increasing diagenesis, mudrocks become physically more durable due to recrystallisation and a decrease in void ratio, which also leads to an increase in compressive and tensile strength. With an increase in lithification and recrystallisation microfractures are also eliminated which also improves the mass strength of the mudrocks, so diagenesis plays a key role in improving the physical response of mudrocks in an engineering environment.

# Chapter 4.

## Sample collection and initial preparation.

### 4.1. Sample collection.

A total of 41 mudrock samples were collected from 26 localities within the mainland UK, excluding N. Ireland. The sample localities and ages were selected to provide a range of mudrocks with similar mineralogies but varying diagenetic histories. Samples were selected specifically to investigate the significance of the presence of mixed-layer clays. The variations in illite 'crystallinity' with engineering properties was an important facet of the study. The samples ranged from Cambrian to Carboniferous Coal Measures in age. The sample localities which were chosen to be near to major conurbations or industrial areas mainly consisted of opencast quarries.It was considered that such sites could have a potential use as landfill sites and that a practical evaluation of the mudrocks would provide information relevant to their potential use as landfill construction material.

In most cases the material collected was excavated by quarrying plant on the day of collection and care was taken to ensure that the samples were relatively fresh and not noticeably affected by excavation. Where samples were collected from quarries which had not recently been worked, the exposures were cleared back using hand tools to exclude any surface weathered material. Sample C.4.1. was obtained as a stick of 102mm diameter rotary core material from a site investigation in the Firth of Forth at Queensferry, Scotland. The sample localities, ages, and quarry details are given in Table 4.1, and the geographical localities are shown in Figure 4.1 the geological data presented in Table 4.1 is taken from Duff and Smith (1992) and Trueman (1954).

The samples were collected as block samples, generally 300 x 300 x 300 mm in size and as fragments ranging from 20 - 100g in weight which were broken up on site from blocks adjacent to the main block sample. The fragments were collected for initial moisture content determinations and slake durability testing. The fragments were stored in one litre capacity air tight PVC sample tubs and in addition adjacent pockets of

Figure 4.1. Geographical map of the sample localities.

Table 4.1. Sample details.

| SAMPLE | AGE | LOCALITY | SITE DETAILS |
|---|---|---|---|
| Ca11/Ca12/Ca13 | Cambrian | Bethesda. North Wales<br>SH 617643 | Penrhyn Quarry - McAlpine Slate |
| 011/012 | Ordovician | Caernarvon, North Wales<br>SH 490615 | Seiont Quarry - Brick Pit. Butterley Bricks Ltd. |
| 021 | Ordovician | Fishguard, West Wales<br>SM 948336 | Pant-y-Phillip Quarry - Lawrence J.E. (Transport) Ltd. |
| 031 | Ordovician | Crymmych: West Wales<br>SM 220328 | Glogue Quarry - Brickpit Mansel Davies and Son Ltd. |
| S11 | Silurian | Middletown,Welsh Borders<br>SJ 265100 | Buttington Brickworks Quarry - Middleton Aggregates Ltd. |
| S31/S32 | Silurian | New Quay. West Wales<br>SN 407590 | Gilfachrheda Quarry - D.E. Lewis |
| D11/D12 | Devonian | Brixton South Devon<br>SX 544503 | Steer Point Brickworks Quarry - Tarmac |
| D21 | Devonian | Plymstock, South Devon<br>SX 518546 | Plymstock Quarry - Blue Circle Ltd. |
| C1B1/C1B2/C1B4/C1B5 | Carboniferous Westphalian A (L.C.M.) | Glynneath, South Wales<br>SS 900060 | Derlwyn. OCC - British Coal Opencast |
| C21 | Carboniferous Westphalian C/B | Rother Valley, South Yorkshire<br>SK 383446 | Pithouse West. OCC - Budge Mining |
| C31 | Carboniferous Westphalian B | Nant Gwranon, South Wales<br>SS 204292 | Ffyndaff South OCC - British Coal Opencast |
| C41<br>(Core sample) | Carboniferous Upper Oil Shale | Queensferry, Southern Scotland<br>NT 114807 | Site Investigation, Forth Road Bridge - Soil Mechanics Ltd. |
| C51/C52 | Carboniferous Westphalian C | Barnsley, South Yorkshire<br>SK 405443 | Kingston Works OCC - nr. Little Houghton Med contracting. |
| C61 | Carboniferous Accrington Mudstone L.C.M. | Accrington, Lancashire<br>SD 757305 | Accrington Brick Pit - Marshall Clay Products |
| C71 | Carboniferous Namurian | Claughton, Lancashire<br>SD 577648 | Claughton Moor Quarry - Butterley Bricks Ltd. |
| C82/C83 | Carboniferous | Arkwright Town, Derbyshire | Arkwright Opencast - |

| | | | |
|---|---|---|---|
| | Westphalian B | SK 370442 | Budge Mining |
| C92 | Carboniferous<br>Westphalian B | Barnsley, South Yorkshire<br>SK 010358 | Rockingham OCC.<br>Budge Mining |
| C101 | Carboniferous<br>Westphalian B | Bowburn Co. Durham,<br>Northumberland<br>NZ 318393 | Whitwell OCC.<br>Budge Mining |
| C111/C112 | Carboniferous<br>Westphalian B/C | Houghton-le-Spring, Co. Durham<br>NZ 324483 | Priors Close North OCC.<br>Budge Mining |
| C121/C122 | Carboniferous<br>Westphalian B | Dearham, Cumbria<br>NY 063337 | Broughton Lodge OCC.<br>- Budge Mining |
| C131/C132/ C133 | Carboniferous<br>Westphalian<br>Carboniferous<br>Limestone Group | Rosewell Mains Midlothian, Scotland<br>NT 269599 | Rosslynlea OCC<br>- Budge Mining |
| C141 | Carboniferous<br>Westphalian B | Wednesbury, Midlands<br>SP 982943 | Leabrook Road OCC.<br>Wardell Armstrong |
| C151 | Carboniferous<br>Westphalian B | Almondsbury, Avon<br>ST 593835 | Cattybrook Brickworks - Ibstock Brick Company |
| C161 | Carboniferous<br>Westphalian B | Catleford, Yorkshire<br>SE 378225 | Robin Hood OCC.<br>Wakefield Waste Management |
| C171/C172 | Carboniferous<br>Westphalian B | Westhouhgton, Greater Manchester<br>SD 606045 | Rackwood OCC. |
| C181 | Carboniferous<br>Westphalian B | Swillington, nr. Leeds, Yorkshire<br>SE 385315 | Swillington Brickpit - Marshalls Clay Products Ltd. |

LCM = Lower Coal Measures. OCC = Open cast coal site.

organic debris or coal seams, especially from the Carboniferous deposits were sampled to provide material for vitrinite reflectance determinations. The block samples were brushed clean of any loose debris, wrapped in PVC film, then in aluminium foil, labelled and then stored in a cushioned plastic container on site awaiting transportation back to the laboratory. The samples were generally delivered to the laboratory within one to two days of being collected. On arrival at the laboratory the samples were immediately described, then they were labelled, wrapped in PVC film and aluminium foil, labelled again and then coated with "coreseal" which has a low moisture and gas permeability thus preventing the sample from drying out over the short-term storage period. The "coreseal" which was obtained from the USA by Core Laboratories, Aberdeen, comes in blocks, which were generally melted at around 90-100°C and then applied onto the sample blocks using a brush, a second coating was applied to each sample to minimize changes in moisture content.

### 4.2. Sample descriptions.

The samples were described according to BS:5930:1981 and modification suggested by Hawkins and Pinches (1992) as discussed in Chapter 2. To help in the description a x30 binocular microscope, rock colour chart, a steel probe and 10% HCL were used.

| **Sample** | **Description and sampling depth** (b.g.l = below ground level) |
|---|---|
| Ca.1.1 - | Extremely strong, grey, medium bedded, fresh, fine grained SLATE. Cleavage parallel to 7$^{0}$ from bedding. Locally with light green reduction spots, <20mm diameter.<br>- Sample taken from ~130m b.g.l. |
| Ca.1.2 - | Extremely strong, blue grey, medium bedded with occasional thin silty laminations, fresh, fine grained SLATE. Cleavage parallel or sub-parallel (0 to 7°) from bedding.<br>- Sample taken from ~135m b.g.l.. |
| Ca.1.3 | Extremely strong, purple, medium bedded locally thinly interlaminated with grey silty horizons, fresh, fine grained SLATE. Cleavage parallel to bedding.<br>- Sample taken from ~140m b.g.l. |
| 0.1.1 | Moderately weak to moderately strong, grey to dark grey, very thinly to thinly bedded,fresh, CLAYSTONE. Very closely to closely fractured, randomly orientated, incipient to <0.5mm open, smooth, polished with occasional slickensides.<br>- Sample taken from ~10m b.l.g. |
| 0.1.2 | Moderately weak, olive grey and dark grey thickly interlaminated to thinly interbedded fresh to slightly weathered CLAYSTONE AND |

MUDSTONE, locally becoming silty MUDSTONE. Locally with closely spaced, randomly orientated, incipient fractures, planar to undulose, slight staining on surfaces, non penetrating.
- Sample taken from ~22m b.g.l.

0.2.1 Strong to very strong, dark grey to locally blue grey, medium bedded, locally thickly laminated fresh to locally slightly weathered, micaceous MUDSTONE [ARGILLITE].
- Sample taken from ~12m b.g.l.

0.3.1 Strong to very strong, grey, medium bedded, fresh, locally micaceous MUDSTONE [ARGILLITE]. Locally with evident cleavage parallel to bedding. Rare graptolite fragments.
- Sample taken from ~35m b.g.l.

S.1.1 Moderately strong to strong, grey and olive grey, thinly to medium bedded, thickly interlaminated, slightly weathered MUDSTONE. Occasional grey ellipsoidal calcareous claystone nodules, <180mm in diameter.
- Sample taken from ~30m b.g.l.

S.3.1 Moderately strong, grey, thinly bedded, locally thinly to thickly interlaminated, slightly weathered, fissile MUDSTONE. Locally with rare silty partings.
- Sample taken from ~16m b.g.l.

S.3.2 Strong to very strong, grey to brown grey, thinly bedded, slightly to locally moderately weathered, very silty MUDSTONE/SILTSTONE. Locally weathering penetrating <6mm. Locally with bifurcating burrows on bedding planes.
- Sample taken from ~20m b.g.l.

D.1.1 Moderately strong to strong, grey, light grey and blue grey, thickly interlaminated to thickly interbedded, fresh MUDSTONE [ARGILLITE]. Locally with cleavage parallel to bedding. Moderately wide to wide open <2mm bedding joints. With occasional iron stained carbonate and quartz veins <2mm wide, generally perpendicular to bedding.
- Sample taken from ~18m b.g.l.

D.1.2 Moderately weak to moderately strong, red brown very thinly to medium bedded, slightly to locally moderately weathered, clayey MUDSTONE [ARGILLITE]. Locally evident cleavage parallel to bedding. With occasional incipient fractures perpendicular to bedding, planar, smooth with <1mm carbonate infill.
- Sample taken from ~6m b.g.l.

D.2.1 Strong to very strong, purple grey, locally olive grey, very closely to closely bedded, locally thinly laminated slightly weathered, locally

| | |
|---|---|
| | moderately weathered to a green colour, clayey MUDSTONE [ARGILLITE], with MUDSTONE laminae. Locally cleavage evident parallel to bedding. Locally with closely spaced randomly orientated fractures, slightly open <0.5mm undulose, polished.<br>- Sample taken from ~10m b.g.l. |
| C.1.B1 | Moderately strong, dark grey, thinly to medium bedded, fresh, organic, moderately fissile, CLAYSTONE. Locally with incipient bedding fractures, occasionally open <0.5mm, planar to undulose<br>- Sample taken from ~47m b.g.l. |
| C.1.B2 | Strong, grey, thickly interlaminated, fresh MUDSTONE AND very silty MUDSTONE. With very closely to closely spaced, randomly oriented, incipient fractures, planar, irregular.<br>- Sample taken from ~45m b.g.l. |
| C.1.B4 | Moderately strong to strong, grey, very thinly to thickly interlaminated, fresh MUDSTONE AND SILTSTONE. Occasional fragments of dark grey carbonaceous plant debris (<10mm).<br>- Sample taken from ~42m b.g.l. |
| C.1.B5 | Moderately strong, grey, massive, fresh, micaceous, silty MUDSTONE. With much carbonaceous plant debris (<30mm) including stigmaria fragments.<br>[Seatearth]<br>- Sample taken from ~40m b.g.l. |
| C.2.1 | Moderately strong, dark grey, fresh, slightly fissile, clayey MUDSTONE. Rare bedding fractures with conchoidal surfaces. Much disseminated carbonaceous plant debris and occasional pyrite nodules <5-8mm in diameter.<br>- Sample taken from ~53m b.g.l. |
| C.3.1 | Strong to very strong, grey and dark grey, medium bedded, thickly laminated, fresh, micaceous, calcareous MUDSTONE AND SILTSTONE. With closely spaced slickensided bedded fractures, polished crenulated.<br>- Sample taken from ~40m b.g.l. |
| C.4.1 | Moderately strong to moderately weak, brown grey, thinly laminated, fresh, calcareous CLAYSTONE. Much disseminated pyrite and occasional fragments of organic debris <0.5mm in size.<br>- Sample taken from ~51m b.g.l. below mud level. |
| C.5.1 | Moderately weak, light olive grey, thin bedded, fresh to slightly weathered, blocky MUDSTONE locally with pale yellow brown gleying. Many disseminated red brown pisoliths and rare rootlets.<br>- Sample taken from ~7m b.g.l. |

| | |
|---|---|
| C.5.2 | Moderately strong, light grey to locally brown grey, thinly bedded, thinly interlaminated, fresh, micaceous, clayey SILTSTONE. Locally with very thin light brown siltstone laminae parallel to bedding.<br>- Sample taken from ~9m b.g.l. |
| C.6.1 | Moderately strong, grey, medium bedded, fresh to locally slightly weathered, blocky MUDSTONE. Very closely to closely spaced, parallel to bedding incipient to <0.5mm open fractures.<br>- Sample taken from ~70m b.g.l. |
| C.7.1 | Moderately strong to strong, light grey to grey, medium bedded, micaceous MUDSTONE. Very closely spaced, randomly orientated incipient fractures.<br>- Sample taken from ~7m b.g.l. |
| C.8.2 | Moderately strong, grey and light grey, very thinly to thinly interlaminated, fresh, fissile CLAYSTONE. Closely spaced, randomly orientated incipient fractures, locally evident cross laminae.<br>- Sample taken from ~40m b.g.l. |
| C.8.3 | Strong to very strong, light grey and grey, thickly bedded, very thinly interlaminated, fresh, silty MUDSTONE. Closely spaced, randomly orientated, incipient fractures. Occasional ironstone nodules <10mm in diameter and pockets of organic debris. Locally cross bedded.<br>- Sample taken from ~70m b.g.l. |
| C.9.2 | Moderately strong, black, thickly interlaminated, fresh organic CLAYSTONE. Locally very closely to closely, randomly orientated fractures, generally open <2mm with pyrite in fill. Occasional laminae of dark grey silty mudstone [Canneloid Mudrock].<br>- Sample taken from ~40m b.g.l. |
| C.10.1 | Moderately strong, light grey, massive, fresh, silty MUDSTONE. With much organic debris.<br>- Sample taken from ~28m b.g.l. |
| C.11.1 | Moderately weak to moderately strong, grey, fresh, moderately fissile, CLAYSTONE. With extremely closely spaced bedding fractures, incipient to <0.5mm open. With much carbonaceous debris.<br>- Sample taken from ~12m b.g.l. |
| C.11.2 | Strong to very strong, light grey, fresh, very silty MUDSTONE. With occasional pockets of carbonaceous debris.<br>- Sample taken from ~35m b.g.l. |

| | |
|---|---|
| C.12.1 | Moderately strong, grey to light grey, fresh, blocky, CLAYSTONE. With very closely spaced, crossed fractures, incipient, irregular. Locally with fragments of carbonaceous debris.<br>- Sample taken from ~59m b.g.l. |
| C.12.2 | Moderately strong, grey to dark grey, fresh to locally slightly weathered, organic, fissile, clayey MUDSTONE. With occasional closely spaced, randomly orientated fractures, open <0.5mm. Locally with micaceous partings. Occasional orange red staining along fractures. Rare stigmaria fragments.<br>- Sample taken from ~61m b.g.l. |
| C.13.1 | Moderately weak to moderately strong, thickly laminated, fresh, very fissile, CLAYSTONE. With extremely closely spaced fractures, generally parallel to bedding, open <0.5mm.<br>- Sample taken from ~20m b.g.l. |
| C.13.2 | Strong to very strong, thinly interlaminated, fresh SILTSTONE and very silty MUDSTONE. Occasional micaceous partings and fragments of carbonaceous debris.<br>- Sample taken from ~53m b.g.l. |
| C.13.3 | Moderately weak, brown grey, fresh, blocky, clayey MUDSTONE. Locally with very closely spaced, randomly orientated slickensides, polished. Occasional stigmaria fragments [seatearth].<br>- Sample taken from ~57m b.g.l. |
| C.14.1 | Moderately weak to moderately strong, light grey and grey, thinly to thickly interlaminated, fresh MUDSTONE. With very closely spaced fractures, generally parallel to bedding, open <0.5mm. Locally with micaceous partings and occasional fragments of carbonaceous matter.<br>- Sample taken from ~22m b.g.l. |
| C.15.1 | Moderately strong, grey to light grey, very thinly to thinly bedded, slightly weathered blocky MUDSTONE. Many very closely spaced, randomly orientated fractures, generally closed, many as polished slickensides. Occasional red brown surface staining along slickensides. Occasional stigmaria fragments [Seatearth].<br>- Sample taken from ~15m b.g.l. |
| C.16.1 | Moderately weak to moderately strong dark grey, thinly to thickly laminated, slightly to locally moderately weathered, micaceous, calcareous, very fissile CLAYSTONE. Locally with very thin brown grey, calcareous mudstone laminae. Occasional pockets of carbonaceous debris.<br>- Sample taken from ~20m b.g.l. |

| | |
|---|---|
| C.17.1 | Strong, light grey to grey, thinly interlaminated, fresh, locally fissile silty MUDSTONE AND SILTSTONE. With closely spaced bedding fractures, closed. Occasional pockets of carbonaceous matter.<br>- Sample taken from ~11m b.g.l. |
| C.17.2 | Strong to very strong, light grey to grey, massive, fresh, silty MUDSTONE. Locally micaceous, with occasional light grey silty partings.<br>- Sample taken from ~17m b.g.l. |
| C.18.1 | Moderately strong, light grey, medium bedded, fresh, locally slightly fissile MUDSTONE. Locally with very closely spaced, randomly orientated fractures, closed to slightly opened <0.5mm. Occasional micaceous horizons, and light grey silty partings.<br>- Sample taken from ~40m b.g.l. |

( Ca = Cambrian, O = Ordovician, S = Silurian, D = Devonian, C = Carboniferous.)

## 4.3. Initial sample preparation for testing.

To avoid any degradation due to stress relief samples were prepared for testing within a month of collection. Sampling was conducted over 5 field excursions over a period of 2 years, to avoid any sample backlog awaiting testing. The sample preparation was of two types:-

a. Cutting into regular shapes for physical characterisation and textural analysis.

b. Crushing and grinding for geochemical and mineralogical analysis.

Since mudrocks are prone to slake when in contact with water, the samples had to be cut dry, which proves to be difficult and very dusty. The mudrock blocks were cut using a bench mounted dry saw, using an 18" silicon carbide impregnated masonry disc. Dust was a major problem so an enclosure was constructed with an attached extraction system, the whole unit was mobile so that the cutting could be performed out of doors. The sample blocks were quartered, and then cut into regular 40-50mm cubes and prisms for strength and swell characterization. Thin slabs were also cut parallel and perpendicular to the bedding for fracture testing. Thin slices were obtained for petrographic thin section preparation and the rest of the sample reduced to smaller fragments of regular shape for density, porosity, jar slake, water absorption and adsorption tests. After dry cutting the sample test blocks and fragments were generally dried in an oven set at 60°C for 72 hours, after which they were stored in glass dessicators, to avoid any sample deterioration, and tested as soon as possible.

Approximately 1 kilogram of relatively fresh offcuts were retained from the centre of the blocks for crushing and powdering. These fragments were reduced down to a centimetric size using a fly press, and the material from each sample was thoroughly mixed on a steel tray. After homogenisation the samples were manually coned and quartered and portions amounting to 150 grams were retained for grinding. The crushed material was dried at 105°C for 24 hours, and then ground in a tungsten carbide disc mill (TEMA mill) for a period of only 15 seconds. This period was chosen to minimise the potential effects on the clay mineralogies due to heating, reduction in size of quartz grains, and oxidation of pyrite. The powdered samples were passed through a <100 µm sieve and stored in an air tight glass jar awaiting geochemical and mineralogical characterisation.

Coal samples which were crushed in an agate pestle and mortar until the material was less than 1mm in size.The powder was then stored in 25cc plastic vials awaiting preparation of epoxy resin mounts. Where no organic material was collected the powdered rock material was used for HCL/HF digestion work to isolate the organic constituents.

# Chapter 5.

# Mineralogy - Experimental techniques and results.

## 5.1. Introduction.

In terms of bulk chemistry there can be little difference between well indurated and strong mudrocks and their completely weathered or unlithified equivalents. In terms of the interpretation of the engineering behaviour of mudrocks, the mineralogy has been found to exert more significant controls than the chemical composition of the material geochemistry. Due to the very fine grain size of the constituent mineral particles, standard petrographic techniques are of limited use in the study of the mineralogical features. Such techniques are however very useful in the examination of the microstructure of mudrocks, and also provide a means of the qualitative determination of the silt size fraction, which consists typically of quartz, feldspars and micas. To carry out a thorough analysis of mudrock mineralogies the use of X-ray diffraction and wet geochemical techniques are essential. X-ray diffraction of the whole rock fraction enables the identification of the minerals present, and when the clay fraction (<2μm) is isolated a semi-quantitative estimate of the clay mineral species present can be made. Wet chemical techniques, sometimes in combination with X-ray diffraction and atomic emission spectroscopy, tend to be employed to determine the proportion of the non-clay components, such as quartz, feldspar, pyrite, carbonates and organic carbon. Some techniques provide a final normalised calculation of the bulk mineralogy, from the results of analysis of individual mineral species (Campbell, 1993). This system is based on many assumptions, and errors from individual techniques are carried into the final quantitative results. The techniques described in Chapter 5 were used to measure the non-clay components of the mudrocks, this approach is considered better as it avoids assumptions used in normalisation methods and also avoids errors incured in certain mineral determination techniques being passed onto other mineral recalculations. Quantitative mineral determinations were carried out by wet chemical techniques on mineral phases detected on whole rock X-ray diffraction scans. Clay mineralogy was determined semi-quantitatively by X-ray diffraction, and was assumed to account for the remainder of the total mineralogy of the samples after the estimation of the non-clay mineral components. This method may give rise to errors of a few percent as it ignores the determination of any amorphous phases which may be present such as iron oxides and sesquioxides, but it is considered that it is more accurate than calculations based on the bulk geochemistry.

## 5.2. X-ray Diffraction: Mineral identification and estimate of mineral abundances.

### 5.2.1. X-Ray Diffraction Theory.

Minerals are made up of regular, three-dimensional arrays of atoms organised into planes within the crystalline structure. W.L. Bragg (Moore and Reynolds, 1989) applied the technique of X-ray diffraction to investigate crystal structures. X-rays having wavelengths of the same order of magnitude as the distance between planes or layers of atoms forming a crystal structure, behave as if they were reflected by this plane (see Figure 5.1).

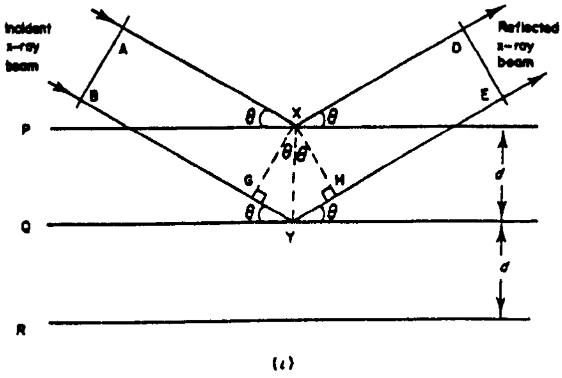


Figure 5.1 - Reflection of X-rays from crystal planes.

Incident X-rays pass into the crystal structure and are reflected by the regular layers of atoms, at the same angle as the angle of incidence, see Figure 5.1. If rays are out of phase by anything other than a whole number of wavelengths then the interference between them cancels them out to a varying degree. If the different reflected rays are in phase then the conditions for X-ray diffraction are satisfied and reinforcement of the reflected ray occurs. This is the basis for X-ray diffraction as expressed by Bragg's Law.

Bragg's Law: $n \lambda = 2d\sin\theta$

where $n$ = integer defining the order of the reflection

$\lambda$ = wavelength of the incident x-rays in Å

$d$ = lattice spacing in Å

$\theta$ = angle of incidence of the X-ray beam in degrees

Using this technique facilitates the identification of mineral species with regular crystalline structure and as such is applicable to the identification and quantification of clay mineral species and other minerals that occur in mudrocks.

Practical XRD (X-ray diffraction) involves rotating a sample in the form of either a mounted crystal or a powder in the path of a focused X-ray beam and measuring the diffracted radiation using a scintillation counter mounted on a goniometer. The diffracted radiation tends to be measured in counts per second and is either stored digitally, or recorded on a chart recorder. During rotation of the sample through the focused X-ray beam, there is an increase in the intensity of the X-radiation detected as diffracted beams from particular lattice planes are encountered. The X-ray counter is rotated at twice the speed of the sample to maintain the geometry of the recording system, so when the specimen turns through an angle ($\theta$) the goniometer rotates through twice this angle, so the angle at which radiation is detected is measured in degrees $2\theta$.

For individual mineral species a combination of peaks of varying intensity, which are unique to that mineral species are seen at various angles of $2\theta$ corresponding to the major and some minor lattice planes within the crystal structure. Tables have been prepared to facilitate the identification of mineral species from this combination of peaks (Chao, 1969; Tucker, 1991), which were used in the present study for mineral identification. Natural samples are mixtures of minerals, so when examined by XRD they present a range of diffraction peaks. Generally the most intense three to five reflections on the diffractometer trace for each component mineral are detected, and by examining their position (lattice spacing) and relative intensities, the identification and relative proportions of the minerals present in the mixture can be determined.

### 5.2.2. Preparation of whole rock for X-ray diffraction analysis.

The purpose of the whole rock analysis was to identify which minerals were present in the samples. These whole rock scans would also be used for determining the percentage of feldspars present in the samples, and to calculate the carbonate ratios. In order to provide useable data great care needed to be taken over the preparation of samples. Gibbs (1965) suggested three methods of sample preparation which provide the required precision and reproducibility :

(1) Smear-on-glass slide
(2) Suction-on-ceramic tile
(3) Power mount

The first two methods produce more oriented mounts in which the plate shaped clay minerals lie parallel to the plane of the slide, whereas the powder mount produces a randomly oriented sample. Difficulties arise in analysing whole rock fractions in mudrocks, as they consist of two different crystallographic mineral types. The clay minerals tend to be platy and so their crystallographic (z) axis is the major reflector, whilst the non-clay minerals tend to be crystallographically three-dimensional, so in combination the intensities of the non-clay minerals tend to be much greater than for clay minerals, as they have more reflection planes exposed to the X-ray beam. This problem tends to be lessened in randomly oriented mounts, and as such this method was applied.

The methods by which the rock samples were obtained, stored and ground for analysis is described in Chapter 4. The X-ray analysis sample mounts were prepared by grinding a small quantity of dried rock powder with acetone in an agate pestle and mortar. This paste was spread over half a glass slide and left to dry. This method of preparation using acetone has been shown by Paterson et al., (1986) to produce randomly oriented mounts. Once the mixture had dried, the slide was trimmed down to fit the diffractometer holder. The slides were scanned between 4 - 44 $^{o}2\theta$ at a rate of $2^{o}$ min. The diffractometer operating conditions are given below.

### Diffractometer operating conditions

Diffractometer Type: Phillips PW 1130/90 - Generator
Phillips PW 1050/70 - Vertical Goniometer

X-ray Tube: Phillips PW 2253/20 Cu broadfocus. Ni filtered
kV = 35
mA = 60

Diffractometer slits: Divergence - 1°
Receiving - 0.1mm
Scatter - 1°
Operating system: Sietronics: SIE112 Autosoftware
Version 1 - operating system
Version 2 - data processing system

Tucker (1991) suggests that in view of the high possibility of affecting the clay mineralogy present, chemical treatments are best avoided. Accordingly, chemical pre-treatment was applied to only two samples (C.9.2 and C.16.1) for the removal of organic matter, excess carbonates and iron oxide. Details of these methods are presented in Appendix A1. When iron oxide, or organic material is present in excess, a high background is seen on the X-ray trace making analysis difficult, on removal of these components the background was greatly reduced, and the traces analysed. The presence of excess carbonates which generally acts as a cementing medium clustering clay minerals together, causes scattering but on removal the traces are greately improved so that the peaks are sharp and distinctive.

The whole rock traces for each sample are presented in Appendix A.2. The following non-clay mineral phases were identified in the mudrock samples using the tables of Chao (1969) & Tucker (1991), based on the principal peak positions presented in Table 5.1.

Clay mineral species present were identified using the flow chart of Starkey et al (1985) presented in Figure 5.2. This provided only a rough estimate as to what species were to be expected, more detailed analysis of the clay mineral species present was performed on the <2μm separated fraction. The list of non-clay mineral species identified in the samples is presented in Table 5.2.

| **Mineral** | **Peak details** | | | | | |
|---|---|---|---|---|---|---|
| | **1** | | | **2** | | |
| | °2 θ | Lattice spacing (Å) | Relative intensity (I) | °2 θ | Lattice spacing (Å) | Relative intensity (I) |
| Quartz | 26.67 | 3.34 | 100 | 20.85 | 4.26 | 35 |
| Orthoclase feldspar | 26.94 | 3.31 | 100 | 23.60 | 3.77 | 80 |
| Plagioclase feldspar | 27.92 | 3.196 | 100 | 23.60 | 3.78 | 25 |
| Calcite | 29.43 | 3.03 | 100 | 39.43 | 2.28 | 18 |
| Dolomite | 30.99 | 2.886 | 100 | 41.18 | 2.19 | 30 |
| Siderite | 32.08 | 2.79 | 100 | 24.80 | 3.59 | 60 |
| Pyrite | 33.07 | 2.709 | 85 | 37.10 | 2.42 | 65 |
| Haematite | 33.31 | 2.69 | 100 | 35.77 | 2.51 | 50 |
| Geothite | 21.25 | 4.18 | 100 | 33.31 | 2.69 | 30 |

Table 5.1 Principal non-clay mineral X-ray peak positions.

### 5.2.3. Analysis of the clay size (<2μm) fraction.

The most efficient method of analysing clay minerals in mudrocks is by means of XRD. Clay minerals can be identified from whole rock diffractograms, but the most satisfactory method is to analyse clay size (<2μm) separations. This is important when the clay minerals are poorly crystalline as they are unlikely to give recognisable diffraction patterns in a whole rock scan. There is no unique method by which to prepare clay materials for XRD analysis and, as McManus (1991) mentions, the greatest problems arising from XRD analysis data is that the workers neglect to mention their sample preparation and analysis methodologies, which may cause variations in their results when compared to those of other workers.

| Sample | Quartz. | Plag.F. | Orth.F. | Pyrite. | Calcite. | Siderite | Dol. | Haem. |
|---|---|---|---|---|---|---|---|---|
| Ca11 | *** | *** | * | | | | | * |
| Ca12 | *** | *** | | * | | | | * |
| Ca13 | *** | *** | * | * | | | | * |
| O11 | * | | | * | * | | | |
| O12 | * | * | | * | * | | | |
| O21 | *** | * | * | * | * | | | |
| O31 | *** | * | * | | * | * | | |
| S11 | *** | ** | | * | * | | | |
| S31 | *** | * | * | | | * | | |
| S32 | *** | *** | | | * | | | |
| D11 | *** | * | | | ** | | * | |
| D12 | ** | * | | * | * | *** | | * |
| D21 | ** | * | | | | | | * |
| C1B1 | * | * | | | ** | | | |
| C1B2 | ** | * | | | * | | | |
| C1B4 | *** | * | | * | * | | | |
| C1B5 | *** | * | | | | | | |
| C21 | *** | * | | | * | * | | |
| C31 | *** | * | | | | *** | | |
| C41 | * | | | * | | | *** | |
| C51 | *** | * | * | | * | | * | |
| C52 | *** | * | * | | * | * | | |
| C61 | ** | * | | * | * | * | | |
| C71 | ** | * | | * | * | * | | |
| C82 | * | | | | | *** | | |
| C83 | *** | *** | | | * | * | | |
| C92 | * | * | | * | | *** | | |
| C101 | *** | * | | * | | | | |
| C111 | * | * | | | * | * | | |
| C112 | *** | * | | | | ** | | |
| C121 | * | * | | | * | * | | |
| C122 | * | * | * | * | * | * | | |
| C131 | * | * | | | | * | | |
| C132 | *** | * | | | | * | | |
| C133 | ** | * | | | | | | |
| C141 | ** | * | * | * | * | * | | |
| C151 | *** | * | * | | * | * | | |
| C161 | * | * | | * | | *** | | |
| C171 | *** | *** | | | * | * | | |
| C172 | *** | * | | * | * | * | | |
| C181 | *** | * | * | * | * | * | | |

Plag.F. = Plagioclase Feldspar. Orth.F. =Orthoclase Feldspar. Dol. =Dolomite.
Haem. =Haematite. * = trace, ** = some to moderate quantity, *** =much present.

Table. 5.2. Non-clay minerals identified on the XRD traces.

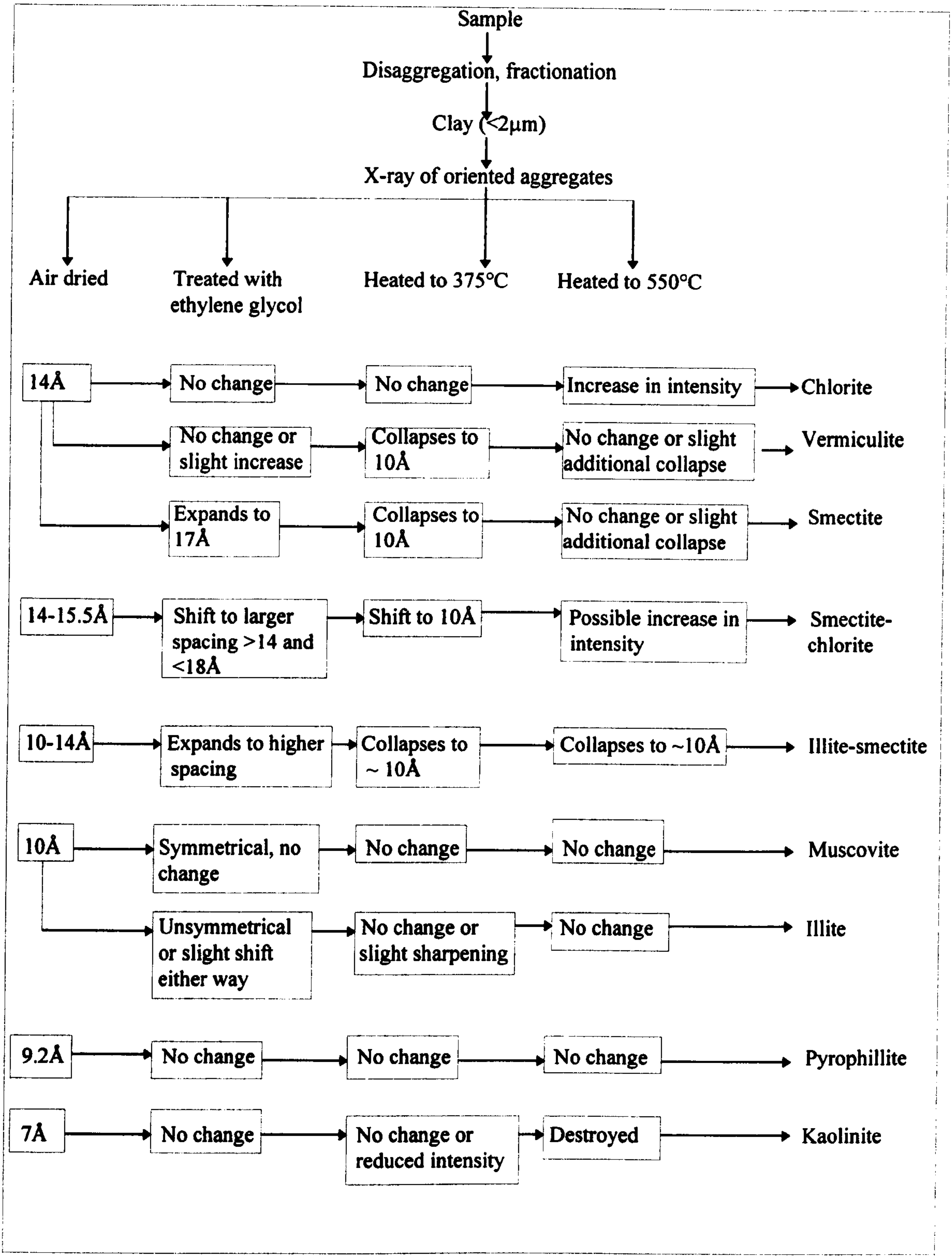


Figure 5.2 Flow sheet for the identification of selected clay minerals (from Starkey et al.,1984)

### *5.2.3.1. Dissagregation of the mudrocks and separation of the <2μm fraction.*

A minimum of preparation is recommended by Moore and Reynolds (1989) for the disaggregation of mudrocks for XRD analysis, as overgrinding may reduce coarser non-clay mineral components to the clay size range. The samples from this study consist of indurated mudrocks, so simple grinding in an iron pestle and mortar, and disaggregation using a blender would prove futile.

The samples were initially oven dried and crushed in a tungsten carbide disc mill (TEMA mill) for 15 seconds, which was adequate to reduce the size fraction to a fine powder. About 10 grams of the crushed sample was placed in a plastic beaker and covered with distilled water to which a 'pinch' of Calgon (sodium hexametaphosphate) had been added to act as a dispersing agent. The sample was then sonified in an ultrasonic bath for 20 minutes. After sonification the sample and water were transferred into centrifuge tubes, and the <2μm clay size fraction was separated. Centrifuge times were calculated according to Jackson (1969) and are presented in Appendix A1. Once the sample was centrifuged for the required time, the supernatant liquid, which contained the <2μm fraction was decanted off into a container and the residue re-suspended in distilled water and recentrifuged to collect any residual clay size minerals. Once the centrifugation was completed the clay size fraction was in suspension and would have taken a long time to settle out. Concentration of the clay minerals from the suspension involved flocculation and collection by gravity settling. For the flocculation $CaCl_2$ was used making the suspension to 0.1M. Since $CaCl_2$ is a divalent salt, this involved adding 11.1g. of $CaCl_2$ to 1 litre of solution to produce a 0.1 M concentrate. The advantage of using a calcium salt is that it also saturates the ion exchange positions in smectites producing a solvated clay species that gives an unambiguous diffraction trace (Eberl and Velde, 1989; Moore and Reynolds, 1989). Once the solution was made up to 0.1M it was left to stand overnight over which time the suspension had settled out.

### *5.2.3.2. Preparation of the oriented clay mineral aggregates.*

X-ray diffraction samples of clays must be smooth, flat, long enough, thick enough and they should be homogenous through their depth. To this end a multitude of techniques have been presented for the preparation of XRD oriented clay slides. Gibbs (1965) reviewed the methods available at that time and found that with some of the techniques as much as 250% variations in the quantitative determinations were obtained for clays of known proportions when compared to the other techniques. He concluded that the cause was different settling rates of the clays during the preparation. Gibbs (1965) concluded that of the seven techniques available, three fulfilled the requirements of precision and accuracy, namely the powder press, smear mount and suction techniques. Moore and Reynolds (1989) suggest that the porous plate method, the filter transfer method and the glass smear slide method give good results.

The porous plate (ceramic tile) method can either be performed in a centrifuge using a prepared sample holder, or by the vaccum suction method (Shaw, 1972). The problem with this technique is that although the preparations have a high degree of orientation, they also suffer from particle size segregation therefore making them useless for quantitative analysis.

The glass slide method, which is probably the most commonly used routine analysis technique involves placing a suspension of the clay sample onto a glass slide and allowing it to dry. Again the problem with this method is that particle segregation occurs making the technique of no use for quantitative analysis.

The filter transfer method (Drever, 1973) was shown by Moore and Reynolds (1989) to be the best technique for quantitative analysis as no sample segregation occurs, and it is also a convenient way to wash any excess cations involved in cation saturation from the sample. This method was employed in this study. In it a millipore vacuum filter apparatus was used, consisting of a side-necked vacuum flask and a funnel reservoir clamped onto a flat porous glass base. Whatmans 0.45μm pore size, 47 mm diameter cellulose nitrate filters were used to collect the sample. Once the device was assembled the flocculated clay suspension was added to the funnel and a filtration period of up to 3 minutes was employed to collect the clay onto the filter paper. This short time period prevents any sample segregation from occurring. Once the clay substrate was collected, distilled water was passed through the sample 3 times to wash away any excess cation used in the floccation and cation exchange process. Once the sample was washed free of excess cations, the filter assembly was disconnected and the filter paper containing the clay was placed clay side down onto a glass slide and placed in an oven set at 50°C for 6-7 minutes. Once the clay had sufficiently dried, the filter paper was removed, leaving the clay on the glass slide. The clay was trimmed down to a size suitable for the XRD goniometer sample holder, and placed in a desiccator awaiting XRD analysis.

#### *5.2.3.3. Chemical pre-treatment of the clay samples.*

It was found that only three samples required pre-treatment to produce useable traces for analysis, these were:-

- Sample C.12.1 - removal of organic carbon using sodium hypochlorate treatment.
- Sample C.9.2 - removal of organic carbon and iron oxide using sodium hypochlorate and citrate-bicarbonate-dithionite treatment.
- Sample C.16.1 - removal of carbonate and iron oxide using sodium acetate-acetic acid and citrate-bicarbonate-dithionite treatment.

The chemical pretreatments employed were the same as for the whole rock analysis and are presented in Appendix A1.

#### *5.2.3.4. XRD analysis of the <2μm preparations.*

Once the clay size fraction glass slide preparations were ready, they were scanned under the same instrument operating conditions as mentioned in section 5.2.2 for 4-44 °2θ at a scan rate of 2 °2θ/minute. The samples were run in the air-dried, glycolated and heated states (375°C), a few of the samples were also initially scanned after heating to 550°C, but it was found that heating to 550°C commonly caused the clay substrate to wharp off the glass slide, therefore rendering them useless for analysis.

Glycolation is performed by introducing the oriented slide preparations into a desiccator, containing 0.25 litres of ethylene glycol and placed in an oven set at 60°C for 12 hours. The method is employed to distinguish smectite minerals by expanding their basal spacing to ~17 Å, and in mixed-layer clays causing a shift of the peak by an amount depending on the quantity of smectite present.

Heating to 375°C for one hour collapses smectite and illite-smectite to 10 Å leaving the other clay minerals unaffected. Whilst heating to 550°C for one hour destroys kaolinite it also affects certain chlorites, so it is not a satisfactory measure for distinguishing between these two clay types.

Once the scans had been run, the clay minerals were identified using the flow chart of Starkey et al., (1984) as shown in Figure 5.2. In the samples examined, a simple clay mineral suite was found which consisted of illite/muscovite; mixed-layer illite/smectite; kaolinite and chlorite, the scans are presented in Appendix A3, and the results are presented in Table 5.4. along with the semiquantitative determinations.

### *5.2.3.5. Calculation of relative clay mineral abundances.*

Many problems exist with quantitative analysis of clay minerals as the X-ray response for a particular clay mineral is dependent on many factors, including instrument conditions, grain size, crystallinity, structure and chemical composition. For quantitative work, relative proportions of minerals can be measured by comparing the area of a particular diffraction peak with that of a peak produced by a known percentage of an added internal standard like boehmite. The method requires calibration of a number of mixtures of the internal standard and reference minerals. This kind of approach is impractical for naturally occurring clay minerals as they tend to be chemically heterogeneous and exhibit variable composition and crystallinity. Gibbs (1967) proposed a method for extracting clay mineral standards from the rocks under study, but this technique is only useable if a large number of samples from a homogenous deposit are to be analysed.

A range of alternative semi-quantitative techniques have been proposed for clay analysis by Schultz (1964), Biscaye (1965) and Weir, Ormerod and El-Mansey (1975) and others. These methods involve measuring the intensities of individual clay minerals after various treatments, including the air dried state, glycolated state and after heating to 375°C and 550°C. This isolates the clay individual components and the sum is normalised to 100%. These techniques are useful for comparative purposes, but as noted by Pierce and Siegel (1969) there can be much variation in the results when comparing these techniques for the same sample. Another problem is that the mineral intensities may vary for the same sample after undergoing the various treatments, especially after heating which may cause the samples to wharp.

Moore and Reynolds (1989) proposed a method of semi-quantitative clay analysis based on the glycolated trace, and their method is used in this study, as it has been shown to have a high degree of reproducibility and is moderately accurate when applied to the range of clay mineralogies found in the samples studied. This method is based on the multiplication of the peak areas of the relevant clay minerals with calculated Mineral Intensity Factors (MIF). This system of using calculated MIF has been shown to be in excellent agreement with actual measured MIF (Reynolds, 1989).

Initially the Mineral Reference Intensities are calculated and converted to MIF by dividing each by a selected standard such as the calculated integrated intensity for the illite 003 reflection which is used for quantitative standardisation. In the present study a specific peak found in all the samples which suffered from minimal neighbour interference was selected for each clay mineral type. The peaks and MIF for the clay minerals are given in Table 5.3.

| Clay Mineral | Reflection | MIF |
|---|---|---|
| Montmonllonite | 003 | 0.79 |
| Illite/Muscovite | 003 | 1 |
| Illite combined with I/S | 003/005 | 1 |
| Chlorite | 003 | 1.12 |
| Kaolite | 003 | 0.21 |

Table 5.3 Semiquantitative clay mineralogy parameters

The illite and illite/smectite 003/003-005 peaks suffer from interference if quartz is present in the sample. This is corrected by measuring the area of the quartz 101 peak at the 20.86°2θ, multiplying by 4.3 and subtracting the value from the combined 002 peak.

This peak is used as it is the one most independent of composition and ordering type for illite and illite/smectite.

| Sample. | Paragonite. | Illite/Muscovite. | Chlorite. | Kaolinite. | ML- I/S. | Smectite. |
|---|---|---|---|---|---|---|
| **Ca11** | 38.2% | 56.6% | 5.2% | ---- | ---- | ---- |
| **Ca12** | 34.9% | 59.9% | 5.2% | ---- | ---- | ---- |
| **Ca13** | 32.4% | 56.8% | 10.8% | ---- | ---- | ---- |
| **O11** | ---- | 41.1% | 22.3% | ---- | 36.6% | ---- |
| **O12** | ---- | 44.4% | 19.7% | ---- | 35.9% | ---- |
| **O21** | 23.7% | 68.3% | 8.0% | ---- | ---- | ---- |
| **O31** | ---- | 90.4% | 9.6% | ---- | ---- | ---- |
| **S11** | ---- | 63.9% | 6.3% | ---- | 29.8% | ---- |
| **S31** | ---- | 89.7% | 10.3% | ---- | ---- | ---- |
| **S32** | ---- | 85.4% | 14.6% | ---- | ---- | ---- |
| **D11** | ---- | 86.1% | ---- | 12.9% | ---- | 1% |
| **D12** | ---- | 89.2% | 2.2% | ---- | ---- | 8.6% |
| **D21** | ---- | 82.5% | 17.5% | ---- | ---- | ---- |
| **C1B1** | ---- | 62.4% | 5.4% | 19.8% | 12.4% | ---- |
| **C1B2** | ---- | 73.9% | 3.2% | 9.6% | 13.3% | ---- |
| **C1B4** | ---- | 65.8% | 3.4% | 15.7% | 15.1% | ---- |
| **C1B5** | ---- | 58.3% | 0.6% | 20.5% | 20.6% | ---- |
| **C21** | ---- | 43.2% | 4.1% | 26.0% | 26.7% | ---- |
| **C31** | ---- | 50.4% | Trace. | 25.9% | 23.7% | ---- |
| **C41** | ---- | 49.4% | 1.7% | 14.2% | 34.7% | ---- |
| **C51** | ---- | 24.7% | 2.9% | 18.5% | 53.9% | ---- |
| **C52** | ---- | 50.7% | 3.6% | 25.8% | 19.9% | ---- |
| **C61** | ---- | 60.2% | 3.6% | 9.6% | 26.6% | ---- |
| **C71** | ---- | 29.3% | 9.8% | 31.2% | 29.7% | ---- |
| **C82** | ---- | 36.1% | 7.1% | 15.2% | 41.6% | ---- |
| **C83** | ---- | 60.3% | 7.3% | 17.6% | 14.8% | ---- |
| **C92** | ---- | 45.4% | 2.7% | 17.1% | 34.8% | ---- |
| **C101** | ---- | 60.9% | 3.3% | 9.1% | 26.7% | ---- |
| **C111** | ---- | 29.7% | 9.5% | 22.3% | 38.5% | ---- |
| **C112** | ---- | 45.2% | 3.6% | 20.0% | 31.2% | ---- |
| **C121** | ---- | 55.6% | 6.7% | 18.1% | 19.6% | ---- |
| **C122** | ---- | 12.5% | 2.2% | 80.8% | 4.5% | ---- |
| **C131** | ---- | 8.6% | ---- | 84.2% | 7.2% | ---- |
| **C132** | ---- | 15.8% | Trace. | 72.9% | 11.3% | ---- |
| **C133** | ---- | 11.9% | ---- | 72.0% | 16.1% | ---- |
| **C141** | ---- | 52.4% | 5.1% | 16.0% | 26.5% | ---- |
| **C151** | ---- | 13.9% | 5.8% | 56.4% | 23.9% | ---- |
| **C161** | ---- | 8.3% | ---- | 81.2% | 10.5% | ---- |
| **C171** | ---- | 55.7% | 6.1% | 21.9% | 16.3% | ---- |
| **C172** | ---- | 49.6% | 4.5% | 20.7% | 25.2% | ---- |
| **C181** | ---- | 21.9% | 7.9% | 57.6% | 12.6% | ---- |

Table 5.4. Semiquantitative clay mineralogy.

As the combined percentage of illite and mixed-layer illite/smectite was calculated the proportion of mixed layer illite/smectite within this total was ascertained using Schultz's, (1960) method. This determination was not possible using the method of Moore and Reynolds (1989) since it is impossible to resolve requisite reflections between illite and near end-member mixed-layer illite-smectite by ordinary XRD methods to determine their areas. For this the proportion of mixed-layer clays was calculated by subtracting the area of the 375°C heated 10Å peak (consisting of illite and collapsed mixed layer illite/smectite) from the area of the 375°C glycolated 10Å peak containing expanded mixed layer illite/smectite.

The results of the semiquantative clay determinations are given in Table 5.4, and the relevant calculations are presented in Appendix A4. The peak areas were measured following the recommendations of Moore and Reynolds (1989). They suggest, and also show, that one of the most accurate methods of calculating peak areas is to multiply the peak height by the width at half height, or for peaks that suffer from neighbouring peak interferance, multiplying the peak height by double the half width at half height on the non effected side. They say that this method eliminates any errors caused by jagged peak shapes, and is only surpassed in accuracy by sophisticated computer modelling techniques. These measurements were performed on the diffractometer scans using an engineering ruler.

## 5.3. Quartz Determinations.

### 5.3.1. Pyrosulphate Fusion.

The determination of quartz (free silica) is possible by chemical means. Trostel and Wynne (1940) proposed a method which involved the fusion of a known weight of sample with potassium pyrosulphate in a silica crucible at a temperature of <1000°C. Once the mixture has been heated past the volatile stage a crust forms, the mixture is then left to cool and then dissolved in hot distilled water in which the silica is precipitated from solution by the addition of sodium hydroxide pellets. Once the digestion is complete the suspension is filtered, washed with hot distilled water 10 times then with hot hydrochloric acid about 5-10 times, which removes iron and any non-dissolved compounds from the quartz. The filter paper is again washed 5 times with hot distilled water. The filter paper is then placed in a tared platinum crucible and ignited. The remaining residue is taken as free quartz. This method is quoted by Trostel and Wynne (1940) to have a coefficient of variation of ~1%. Unfortunately it does not eliminate feldspars and heavy minerals present, which add to the estimated quartz value. However the main difficulty with using this technique is the level of analytical care required and the length of the operation as each analysis may take up to 8 hours to carry out. Campbell (1993) noted the poor results obtained with this method, he obtained a coefficient of variation of 23.7% for his results, which was therefore unacceptable. Problems noted by Steward (1984) were attributed to insufficient washing. This was acted upon by Campbell (1993) but as this made no difference he concluded that possible incomplete fusion may have occurred during the determination and that sodium chloride crystals may have been produced due to the reaction of hydrochloric acid with sodium hydroxide.

The method of pyrosulphate fusion was improved upon by Chapman, Syers and Jackson (1968). Their method involves fusion of the sample with sodium pyrosulphate (sodium bisulphate) in a silica crucible. On completion of the fusion the residue is dissolved in hydrochloric acid, and centrifuged. The residue is then boiled in a sodium hydroxide solution to remove any amorphous material. At this stage the original method of Kiely and Jackson (1965) states that only quartz and feldspar remains in the residue, so total Na and K analysis could be performed to determine the types of feldspars and amounts of feldspar and quartz present. This method, which involves different operations, results in an indirect determination of quartz and feldspar, and these quantities are based on correlation factors derived by Chapman, Syers and Jackson (1968) for different size fractions. The latter authors improved this method by treating the residue after the sodium hydroxide stage with a solution of hydrofluosilicic acid for a total of 3 days. This dissolves feldspars leaving quartz grains relatively unaffected, so the total quartz is then gravimetrically determined. The full methodology is given in Appendix A.5.

Pyrosulphate fusion and hydrofluosilicic acid digestion was performed on 27 of the samples and the results are given in Table 5.5. This method is accurate when performed with care, but due to the many stages of sample transferral, centrifugation and final gravimetric determination there is much scope for the introduction of errors, especially sample loss due to operator error. The hydroflouosilicic acid stage takes a minimum of three days to complete, and when much feldspar is present then 2 to 3 successive acid treatments may be necessary. It was generally found that although the method gave good repeatability, it was very time consuming, with many stages where errors could be introduced, therefore a more reliable, rapid and reproducible means of determining free quartz in the samples was sought.

### 5.3.2. Quartz determination using XRD and boehmite internal standard.

Griffin (1954) used an X-ray diffraction method for determining quartz in mudrock samples which involved the addition of a known quantity of boehmite as an internal standard. This procedure has problems due both to peak inference from other minerals present in a polymineralic system, and the matrix effect due to clays. Till and Spears (1969) improved upon this method by first eliminating the clay minerals by ignition which increases the relative proportion of quartz and enhances the peak due to elimination of clay mineral interference and matrix effects. Boehmite is used as an internal standard as its mass absorption coefficient for CuKα X-radiation is similar to that of quartz found in mudrocks. The technique has been shown to have a coefficient of variation of 1.9% which is not too dissimilar to that of pyrosulphate fusion, except that the XRD method is more rapid and, since it has fewer operational stages, it is less prone to operator error.

In the procedure a quantity of oven dried, TEMA milled sample was placed in a furnace set at 950°C for a minimum of 4 hours. Following ignition, the crucible and contents were weighed and the loss on ignition determined. The ignited sample was further ground to a talc like consistency in an agate pestle and mortar. Then 0.9 grams of the sample was combined with 0.1 gram of boehmite, placed in a plastic tube and homogenised in a automated mixer for about 1 minute. The sample was then packed into an aluminium holder using the backfilling technique recommended by Gibbs (1965), using a frosted glass slide as a front template to ensure a random orientation on the exposed face. The sample was then X-rayed, with scanning performed from 15-21°θ at a speed of 0.5°2θ/min. Each sample was scanned twice.

A series of samples consisting of mixtures of quartz and boehmite from 95% quartz - 5% boehmite to 5% quartz - 95% boehmite were also prepared in a similar fashion to use in calibrating the method. Once the calibration samples were run a calibration curve using quartz-boehmite peak height ratio as ordinate, and ratio of percent quartz in the mixture to percent boehmite as abscissa was plotted as seen in Figure 5.3. A linear regression line was fitted through the data points from which the following quadratic expression was derived:-

$$\% \text{ Ratio} = 2.246 \times \text{Height ratio} - 1.12 \times 10^{-1}.$$

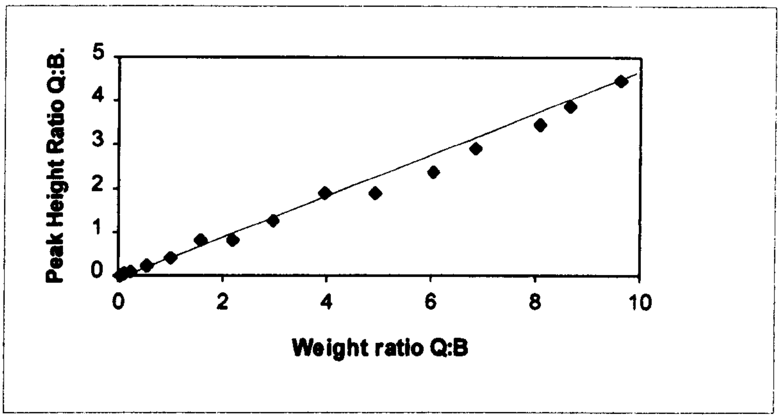


Figure 5.3 Quartz-boehmite calibration graph.

The percentage of quartz for each sample was then calculated using the derived quadratic equation. This result represents the amount of quartz in an ignited sample rather than a whole rock value, so to rectify this the results were multiplied by (100-Loss on Ignition) % giving a whole rock percentage. The raw data are presented in Appendix A6, and the final quartz results are given in Table 5.5.

## 5.4 Feldspar Determination

Although the distribution of feldspars in mudrocks has not been studied in any great detail, they tend to average about 5±2% (Blatt, 1982). As such they do constitute a minor component and so it was decided to determine their distribution in the samples studied.

In thin sections of mudrocks without the use of staining techniques it is difficult to differentiate feldspars from quartz, since during transportation they tend to break along their twin planes and, if present, appear as single extinction grains similar in appearance to quartz. Few definitive methods exist for determining feldspars in mudrocks. Fellows and Spears (1978) suggested a method similar to the ignition method of Till and Spears (1969). This involves pre-ignition of the sample at 950°C and the use of X-ray diffraction with boehmite as an internal standard. Their method applied to research on Coal Measures mudrocks for which they advocated this procedure. With ignition the reaction of albite with K released from clay minerals creates K-feldspars, but this reaction is only partially completed under experimental conditions, and therefore can lead to confusion with interpretation. Blatt et al (1982) suggested the sodium bisulphate fusion technique, which concentrates quartz and feldspars, and the spectrophotometric determination of Na, K and Ca after the fusion and washings. This method is based on work by Kiely and Jackson (1965) who showed that although dissolution of feldspars was reduced in this fusion method, some dissolution occurs depending on the mineralogy and grain size of the feldspars. To account for these errors Kiely and Jackson (1965) presented a series of correction factors based on standard feldspars. Since the correction factor varies with the composition and grain size of the feldspars, difficulties arise in applying an appropriate correction factor to unknown mudrocks (Fellows and Spears, 1978).

A rapid and reproducible means of calculating the quantity of feldspar present in mudrocks (most commonly K-Feldspar) was devised by Hooton and Giorgetta (1977). This involves the use of an internal standard present in the samples, and as such quartz is ideal for mudrocks as it is a common constituent. Reference intensities of the minerals based on their densities and instrument conditions are used. Standard mixtures of the minerals can be scanned and ratios of the relevant peaks to their weight percentage in the mixture calculated. These intensities can be found either in published papers for example (Baylis, 1986) or measured directly from standard minerals, as was done in this study. It was decided to use the weaker 100 peak for quartz as an internal standard as the primary 101 peak suffers from illite interference. This was calculated against the primary plagioclase (albite) 002 peak, and orthoclase 220 peak as follows:

Quartz 100 - reference intensity = 1
Plagioclase 002 - reference intensity = 1.8
Orthoclase 220 - reference intensity = 2.4

| Sample | Quartz.%-Pyr. | Quartz.%-XRD | Plagioclase.% | Orthoclase.% |
|---|---|---|---|---|
| Ca11 | 15.5 | 15.7 | 21.1 | 4.5 |
| Ca12 | 19.2 | 19.3 | 35 | -------- |
| Ca13 | 20.0 | 20.2 | 38 | 3.4 |
| O11 | 10.5 | 9.4 | -------- | -------- |
| O12 | 12.9 | 7.4 | 3.8 | -------- |
| O21 | 22.4 | 22.8 | 8.6 | 7.3 |
| O31 | 18.6 | 18.1 | 11.7 | 3.9 |
| S11 | 19.3 | 18.9 | 12.5 | -------- |
| S31 | 20.0 | 18.8 | 7.9 | 4.7 |
| S32 | 25.3 | 25.8 | 17.8 | -------- |
| D11 | 18.7 | 17.5 | 4.2 | -------- |
| D12 | 11.1 | 11.0 | 3.7 | -------- |
| D21 | 13.2 | 10.0 | 6.2 | -------- |
| C1B1 | 4.5 | 3.1 | 1.2 | -------- |
| C1B2 | 14.6 | 12.5 | 6 | -------- |
| C1B4 | 26.7 | 19.8 | 8.7 | -------- |
| C1B5 | 24.7 | 24.3 | 4.2 | -------- |
| C21 | 19.9 | 17.5 | 4.2 | -------- |
| C31 | 33.5 | 34.7 | 7.7 | -------- |
| C41 | 5.7 | 5.3 | -------- | -------- |
| C51 | 17.6 | 16.3 | 3.4 | 3.0 |
| C52 | 29.1 | 30.4 | 9.8 | 6.6 |
| C61 | 13.5 | 11.1 | 8.2 | -------- |
| C71 | 20.9 | 14.9 | 9.0 | -------- |
| C82 | 6.7 | 7.3 | -------- | -------- |
| C83 | 20.5 | 24.1 | 15.8 | -------- |
| C92 | 5.3 | 2.7 | 1.2 | -------- |
| C101 | N/D | 20.7 | 5.5 | -------- |
| C111 | N/D | 5.4 | 2.4 | -------- |
| C112 | N/D | 23.4 | 6.5 | -------- |
| C121 | N/D | 6.8 | 2.1 | -------- |
| C122 | N/D | 8.1 | 1.4 | 1.2 |
| C131 | N/D | 3.9 | 0.8 | ------- |
| C132 | N/D | 21.8 | 3.6 | -------- |
| C133 | N/D | 10.2 | 0.7 | -------- |
| C141 | N/D | 14.8 | 3.0 | 2.8 |
| C151 | N/D | 17.4 | 1.6 | 1.8 |
| C161 | N/D | 5.4 | 3.0 | -------- |
| C171 | N/D | 33.9 | 23.7 | -------- |
| C172 | N/D | 26.7 | 8.1 | -------- |
| C181 | N/D | 16.6 | 5.7 | 2.8 |

N/D = No determination performed. -------- = None identified. Pyr. = Pyrosulphate fusion.

Table 5.5. Quartz and feldspar contents of the mudrock samples.

The values of intensities of the relevant minerals were then measured off the whole rock scan peaks. Since the weight percentage of quartz is known, the relative weights percent of feldspars were calculated using the following equation taken from Hooton and Giorgetta (1977):-

$$\frac{\text{weight mineral}}{\text{weight quartz}} = \frac{\text{RIR mineral}}{\text{RIR quartz}} \times \frac{\text{I mineral}}{\text{I quartz}}$$

where RIR = Reference intensity ratio

I = Intensity of mineral peak

Results for the feldspars are presented in Table 5.5.

## 5.5. Pyrite Determination

### 5.5.1. XRD and wet geochemical methods.

Pyrite is a common accessory mineral present in most mudrocks, and due to its atmospheric instability is an important factor in mudrock breakdown. Pyrite can be identified in a sample by XRD, but unfortunately quantitative analysis by this technique is not very accurate. Pyrite occurs as a minor constituent in mudrocks, therefore dilution occurs when analysis is performed by XRD due to the other minerals present. Also due to the high specific gravity of pyrite, it tends to settle out first and become covered with other minerals when preparing smear or powder mounts and is therefore quantitatively underestimated.

Pyrite is normally determined using wet geochemical techniques of which there are two general approaches:-

a) Determination of total iron and acid soluble iron with the difference being assigned to pyrite.

b) The determination of sulphide-sulphur.

Determination of total iron is normally carried out by XRF (as $Fe_2O_3$), and since pyrite is insoluble in acid spectrophotometric determination of sulphuric acid/hydrofluoric acid treated samples determines the quantity of pyritic iron. The difference gives the percentage of pyrite present in a sample. With this approach any residual ferrous or ferric iron will also be counted as sulphide iron, therefore overestimates are common (Maxwell, 1981). Alternative techniques such as that of Lord (1982) involve the quantitative release of iron. The method involves pre-treatment with citrate-bicarbonate-dithionite solution followed by hydrofloric acid treatment to remove any iron compounds other than pyrite. Pyrite is then quantitatively dissolved in quartz distilled nitric acid and the liberated iron is determined by AAS. This method yields high selectivity compared with most other methods, but it is very time consuming and involves many stages which may introduce errors.

Determination of sulphur (Maxwell, 1981) normally involves the total determination of sulphur by means of reaction with aqua regia ($HNO_3$/HCI mix) and then precipitation of the released sulphate as barium sulphate using barium chloride. The total residue is measured gravimetrically. If sulphates such as gypsum or organic sulphur are present they will also be included in the quantitative measurement so pretreatments may be necessary. This method is found to be insensitive to small quantities of sulphides due to analytical error in the many stages involved and it is also time consuming.

A method proposed for analysis of sulphur, compounds was proposed by Zhabina and Volkov (1978) involving chromium reduction which proves very promising, and was used in this study.

### 5.5.2. Determination of Pyrite by Chromium Reduction.

A technique for the determination of various sulphur compounds in marine sediments and rocks was proposed by Zhabina and Volkov (1978) involving chromium reduction in a reducing atmosphere. The method was rigorously evaluated by Cranfield et al. (1986) who found that the method gave good precision and accuracy as well as being relatively simple and rapid to carry out. If monosulphides and elemental sulphur are present in the sample then they need to be removed prior to testing as they will also be included in the quantitative measure. As these compounds were not detected on any of the XRD traces, and tend to be relatively uncommon in most mudrocks they were presumed not to be present. Cranfield et al. (1986) also found that if sulphates such as barite or gypsum were present or organo-sulphur compounds, then they were untouched by this method, so the method appears to be specific to sulphides in this case pyrite and marcasite.

The method involves digestion of the sample in an acidified reduced chromic (II) solution within an all glass reaction vessel, which is maintained in a reducing atmosphere by passing nitrogen or argon through the system. The reaction breaks down pyrite and liberates the sulphur component as $H_2S$ which is collected by the carrier gas stream and bubbled into a zinc acetate and ammonium hydroxide solution contained within a trapping vessel. The determination of zinc precipitate is performed by tritation. Cranfield et al. (1986) found that a reaction time of 20-30 minutes is required for sediments whilst lithified mudrocks required a reaction time in the order of 2 hours, it was therefore decided in this study to conduct the experiment for a minimum reaction time of 2.5 hours. Applying this method, Raiswell et al. (1988) used copper sulphate as the trapping medium and titration was performed using EDTA. It was decided to modify further the method for the present work. Accordingly a 2 molar copper sulphate solution was used as the trapping medium, once the reaction was complete the trapping medium was filtered to remove the CuS precipitate created by $H_2S$ reacting with $CuSO_4$, and the solutions were analysed for copper using ICP-AES. The results were compared with a series of blank stock copper sulphate solutions. The complete methodology is presented in Appendix A7, which includes the calculation for determining pyrite. Four standards, two of a prepared mixtures containing a known quantity of pyrite and another two of a pre-analysed coal standards donated by Dr. P. Cavender (P.C) were analysed, and the results proved accurate and are as follows:-

1. P.C donated sample - RHGAWELL. quoted value = 4.48%: Detected value = 4.37%.
2. P.C donated sample - RHGF. quoted value = 0.23%: Detected value = 0.21%.
3. Standard 1 - Contains 10.27% added pyrite: Detected value = 10.1%.
4. Standard 2 - Contains 4.79% added pyrite: Detected value = 4.15%.

The results from the pyrite determinations are presented in Table 5.6. No problems were encountered with this method and two samples were generally analysed at a time, with a total of 8 analysis a day being performed.

| Sample. | Determination 1.% | Determination 2.% | Average Content % |
|---|---|---|---|
| **Ca11** | 0.48 | 0.47 | 0.5 |
| **Ca12** | 1.78 | 2.91 | 2.3 |
| **Ca13** | 1.45 | 1.13 | 1.3 |
| **O11** | 6.98 | 6.27 | 6.6 |
| **O12** | 2.55 | 4.55 | 7.1 |
| **O21** | 3.31 | 3.0 | 3.1 |
| **O31** | 0.69 | 0.1 | 0.4 |
| **S11** | 3.60 | 4.62 | 4.1 |
| **S31** | 2.43 | 4.14 | 3.3 |
| **S32** | 3.79 | 3.14 | 3.5 |
| **D11** | 3.74 | 4.15 | 3.9 |
| **D12** | 4.48 | 4.15 | 4.3 |
| **D21** | 3.30 | 3.67 | 3.5 |
| **C1B1** | 2.44 | 1.83 | 2.1 |
| **C1B2** | 2.81 | 1.31 | 2.1 |
| **C1B4** | 7.70 | 8.76 | 8.2 |
| **C1B5** | 4.72 | 2.06 | 3.4 |
| **C21** | 3.71 | 4.12 | 3.9 |
| **C31** | 2.27 | 2.42 | 2.3 |
| **C41** | 7.86 | 5.89 | 6.9 |
| **C51** | 3.78 | 2.84 | 3.3 |
| **C52** | 2.21 | 1.61 | 1.9 |
| **C61** | 6.90 | 3.79 | 5.3 |
| **C71** | 4.31 | 3.87 | 4.1 |
| **C82** | 0.08 | 0.14 | 0.1 |
| **C83** | 1.80 | 1.94 | 1.9 |
| **C92** | 5.22 | 5.95 | 5.6 |
| **C101** | 4.56 | 6.62 | 5.6 |
| **C111** | 3.75 | 4.54 | 4.1 |
| **C112** | 1.70 | 0.77 | 1.2 |
| **C121** | 2.90 | 2.77 | 2.8 |
| **C122** | 4.33 | 5.10 | 4.7 |
| **C131** | 2.40 | 1.35 | 1.9 |
| **C132** | 2.25 | 1.94 | 2.1 |
| **C133** | 3.45 | 2.95 | 3.2 |
| **C141** | 7.48 | 6.32 | 6.9 |
| **C151** | 1.10 | 0.80 | 0.9 |
| **C161** | 5.05 | 5.57 | 5.3 |
| **C171** | 0.77 | 1.11 | 0.9 |
| **C172** | 4.54 | 5.13 | 4.8 |
| **C181** | 3.68 | 4.55 | 4.1 |

Table 5.6. Results of the pyrite content determinations.

## 5.6. Determination of Carbonates.

The quantity of carbonate minerals present in the mudrock sample can be determined by measuring the quantity of carbon dioxide which is released when the sample is treated with acid, such as orthophosphoric acid. The determination is carried out in a $CO_2$ and water free atmosphere with the quantity of carbon dioxide being measured by non-aqueous titration.

The sample is reacted with orthophosphoric acid and the evolved $CO_2$ collected in a $CO_2$ free carrier gas stream, bubbled through a chromic acid/sulphuric acid water trap and absorbed into a 3.3% solution of ethanolamine in dimethyl formamide containing thymolphthalein indicator. The quantity of carbon dioxide absorbed is determined by titrating with 0.1N tetra-n-butyl ammonium hydroxide in toluene/methanol. The method is presented in detail in Appendix A8.

The volume of titrant used is related to the percentage of $CO_2$ evolved by the following expression:-

$$\%\ \text{soluble}\ CO_2 = \frac{\text{vol. of titrant (ml)} \times 4.4}{\text{wt. of sample (g)} \times 10}$$

Blanks containing a known quantity of $CO_2$ were run prior to the determinations to make sure that the equipment had no leaks. The reproducibility of the method was such that only two determinations per sample were necessary, the results are presented in Appendix A9.

The carbon dioxide can be attributed to calcite, dolomite or siderite in the samples analysed. It was generally found that samples contained calcite and or dolomite, or siderite. If the carbonate present was calcite then the percentage can be calculated by multiplying the carbon dioxide percentage by 2.27 (molecular weight of carbon dioxide). Where siderite was present then the $CO_2$ percentage was multiplied by 2.64 (molecular weight of siderite/molecular weight carbon dioxide). If both calcite and dolomite were

| **Sample.** | **Calcite %** | **Dolomite %** | **Siderite %** | **Organic Carbon %** |
|---|---|---|---|---|
| **Ca11** | ---- | 0.3% | ---- | 0.2% |
| **Ca12** | ---- | 0.8% | ---- | 0.1% |
| **Ca13** | ---- | Trace. | ---- | 0.1% |
| **O11** | 2.7% | ---- | ---- | 0.2% |
| **O12** | 2.2% | ---- | ---- | 0.3% |
| **O21** | 0.1% | ---- | ---- | 0.5% |
| **O31** | 0.2% | ---- | 0.3% | 0.4% |
| **S11** | 1.3% | ---- | ---- | 0.3% |
| **S31** | ---- | ---- | 2.2% | 0.6% |
| **S32** | 1.1% | ---- | ---- | 0.7% |
| **D11** | 10% | 2.2% | ---- | 0.5% |
| **D12** | 4.2% | ---- | 15.3% | 0.2% |
| **D21** | ---- | ---- | ---- | 0.2% |
| **C1B1** | 11.4% | ---- | ---- | 15.0% |
| **C1B2** | 4.3% | ---- | ---- | 0.7% |
| **C1B4** | 4.2% | ---- | ---- | 0.7% |
| **C1B5** | ---- | ---- | ---- | 0.8% |
| **C21** | 1.5% | ---- | 1.8% | 7.5% |
| **C31** | ---- | ---- | 24.7% | 1.2% |
| **C41** | ---- | 32.2% | ---- | 2.7% |
| **C51** | 5.1% | 1.4% | ---- | 0.4% |
| **C52** | 0.2% | ---- | 0.1% | 0.3% |
| **C61** | 1.1% | ---- | 1.3% | 0.9% |
| **C71** | 1.0% | ---- | 2.2% | 3.0% |
| **C82** | ---- | ---- | 15.2% | 1.2% |
| **C83** | 1.5% | ---- | 3.5% | 2.2% |
| **C92** | ---- | ---- | 17.6% | 41.5% |
| **C101** | ---- | ---- | ---- | 0.6% |
| **C111** | 1.1% | ---- | 1.1% | 6.0% |
| **C112** | ---- | ---- | 10.2% | 0.8% |
| **C121** | 2.4% | ---- | 8.2% | 1.4% |
| **C122** | 1.6% | ---- | 1.9% | 6.1% |
| **C131** | ---- | ---- | 4.6% | 9.8% |
| **C132** | ---- | ---- | 6.0% | 1.1% |
| **C133** | ---- | ---- | ---- | 2.0% |
| **C141** | 0.8% | ---- | 2.7% | 2.1% |
| **C151** | 1% | ---- | 3.3% | 0.9% |
| **C161** | ---- | ---- | 37.5% | 6.4% |
| **C171** | 2.5% | ---- | 6.5% | 1.0% |
| **C172** | 2.6% | ---- | 3.3% | 0.8% |
| **C181** | 1.6% | ---- | 1.9% | 1.2% |

Table 5.7. Quantification of carbonates and organic carbon.

present or even traces of siderite in the sample, then the $CO_2$ can be apportioned between the minerals by the comparison of the intensities of the relevant whole rock XRD peaks, and then calculating the ratios of each. The intensities of these peaks is almost linearly related to the amount of acid soluble carbonates present (Schultz, 1964; Bayliss, 1986) and the total carbonate (calculated as calcite or siderite whichever is dominant) can simply be divided between the relevant minerals in proportions equal to the ratios between the peaks. The resultant percentages of the carbonate species are presented in Table 5.7.

## 5.7. Determination of Organic Carbon.

The organic carbon content of the samples were determined using the same method as for carbonate carbon. Once the carbonate $CO_2\%$ was determined, a quantity of chromic acid was added into the reaction vessel and heated for a further 30 minutes. The organic carbon was evolved as $CO_2$ and was collected in the trapping vessel. Determination of the quantity of $CO_2$ was again carried out by titration with 0.1N tetra-n-butyl ammonium hydroxide. The method is presented in Appendix A8. The percentage of organic carbon was calculated using the following expression:-

$$\%C_{ORGANIC} = \frac{\text{vol. of titrate used (ml)} \times 1.2}{\text{wt of sample (g)} \times 10}$$

The results for the organic carbon determination are presented in Table 5.7. It has been stated that for rocks of Cretaceous and older ages, organic carbon should be multiplied by a factor of 1.22 to convert it to total organic matter (Foscolos and Stott, 1975). In the case of this study the experimentally determined organic carbon values are presented.

## 5.8. Bulk Rock composition by X-Ray Fluorescence.

### 5.8.1. XRF Theory.

The bulk geochemistry of the samples is easily and accurately measured by the X-Ray Fluorescence (XRF) techniques (Norrish and Hutton, 1969). The results of the XRF analysis were primarily intended to check the geochemical trends of the samples, to calculate the apatite and rutile content and to be used as a check on the effects of the natural weathering experiments of the samples.

The principle of X-Ray fluorescence, is that when a sample is bombarded with primary high energy X-rays, secondary radiation is emitted with the wavelengths and intensities dependent on the elements present. The abundance of the minerals present in the sample can be determined from this spectrum by reference to mineral standards with known elemental concentrations. Corrections are made for spectral line interference adsorption, and matrix effects. Experimental error is kept to a minimum by careful sample preparation and control of the operating conditions of the X-ray spectrometer. Glass discs and pressed pellets can be analysed, but it is considered that glass discs are superior for major elements (Tucker, 1991).

### 5.8.2. Preparation of fusion discs.

The ground mudrock samples were initially pre-ignited at 950°C for 6 hours in an electric furnace to destroy any volatile materials such as organic matter, carbonates and pyrite, and the loss on ignition was determined. The volatile components would cause problems during preparation of the fusion discs as the pyrite would attack the platinum-gold alloy crucibles used in the preparation if not removed. Once the samples had been pre-ignited they were reground to a fine powder in an agate pestle and mortar. The fusions were prepared by mixing exactly 0.75g of the pre-ignited sample with 7.5g of lithium tetraborate flux (Johnson Matthey Spectroflux 100) in a platinum-gold alloy crucible. The mixture was fused by heating to 1100°C for 21 minutes in an electric muffle furnace stirring the fusion three times at seven minute intervals during this period. The molten sample was then poured into a pre-heated platinum-gold alloy mould and left to cool before analysis. The XRF analysis was carried out using a Phillips PW140 X-ray spectrometer with a DEC PDP 11/23 computer running X14D Phillips analytical software. The raw data are given in Appendix A9, and results corrected for loss on ignition are presented in Table 5.8.

| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | Tot. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cal1 | 58.60 | 0.99 | 20.10 | 8.58 | 0.24 | 2.36 | 0.71 | 1.89 | 3.05 | 0.10 | 0.06 | 96.68 |
| Cal2 | 62.40 | 0.92 | 17.54 | 7.15 | 0.14 | 2.03 | 2.14 | 2.13 | 2.56 | 0.10 | 0.06 | 97.15 |
| Cal3 | 61.83 | 0.80 | 18.71 | 7.52 | 0.17 | 2.09 | 0.61 | 2.18 | 3.07 | 0.10 | 0.07 | 97.13 |
| O11 | 51.54 | 0.84 | 23.32 | 9.45 | 0.49 | 2.03 | 0.87 | 0.94 | 2.88 | 0.49 | 0.10 | 92.95 |
| O12 | 49.77 | 0.92 | 24.02 | 10.40 | 0.54 | 2.01 | 0.43 | 0.70 | 3.05 | 0.18 | 0.06 | 92.08 |
| O21 | 59.70 | 1.05 | 20.83 | 7.39 | 0.37 | 1.58 | 0.02 | 0.96 | 3.16 | 0.14 | 0.05 | 95.26 |
| O31 | 56.65 | 1.04 | 22.17 | 8.60 | 0.19 | 2.27 | 0.18 | 0.64 | 3.72 | 0.08 | 0.03 | 95.56 |
| S11 | 61.65 | 1.02 | 18.54 | 7.93 | 0.05 | 1.87 | 0.29 | 1.26 | 3.23 | 0.07 | 0.07 | 95.99 |
| S31 | 57.24 | 0.97 | 19.10 | 11.52 | 0.08 | 2.34 | 0.39 | 1.09 | 2.81 | 0.21 | 0.03 | 95.78 |
| S32 | 64.15 | 0.79 | 15.39 | 9.74 | 0.05 | 2.07 | 0.27 | 1.73 | 1.89 | 0.16 | 0.05 | 96.29 |
| D11 | 57.94 | 0.96 | 18.43 | 6.57 | 0.09 | 2.04 | 0.82 | 0.38 | 3.92 | 0.14 | 0.23 | 91.54 |
| D12 | 49.19 | 0.81 | 16.58 | 8.58 | 0.18 | 3.60 | 5.53 | 0.53 | 3.94 | 0.10 | 0.13 | 89.16 |
| D21 | 57.08 | 0.85 | 20.64 | 8.75 | 0.24 | 2.55 | 0.18 | 0.67 | 4.71 | 0.11 | 0.04 | 95.82 |
| C1B1 | 37.70 | 0.50 | 18.05 | 11.29 | 0.53 | 1.46 | 0.31 | 0.33 | 3.06 | 0.13 | 0.01 | 73.36 |
| C1B2 | 58.27 | 1.00 | 22.45 | 6.20 | 0.21 | 1.65 | 0.10 | 0.45 | 3.69 | 0.12 | 0.02 | 94.16 |
| C1B4 | 62.75 | 1.12 | 19.33 | 4.75 | 0.07 | 1.40 | 0.23 | 0.93 | 3.09 | 0.14 | 0.02 | 93.84 |
| C1B5 | 65.50 | 1.18 | 21.98 | 1.22 | 0.00 | 0.72 | 0.05 | 0.40 | 3.27 | 0.03 | 0.03 | 94.37 |
| C21 | 54.39 | 1.00 | 19.94 | 4.16 | 0.04 | 1.16 | 0.27 | 0.20 | 2.91 | 0.09 | 0.09 | 84.26 |
| C31 | 57.50 | 0.79 | 12.20 | 13.23 | 0.31 | 2.08 | 0.43 | 0.20 | 1.88 | 0.12 | 0.03 | 88.76 |
| C41 | 41.59 | 0.65 | 12.46 | 5.65 | 0.14 | 5.05 | 10.81 | 0.28 | 2.67 | 0.18 | 0.72 | 80.18 |
| C51 | 58.84 | 0.97 | 20.68 | 7.10 | 0.07 | 0.94 | 0.19 | 0.27 | 3.52 | 0.05 | 0.03 | 92.66 |
| C52 | 65.94 | 1.06 | 17.79 | 3.85 | 0.02 | 1.29 | 0.13 | 0.36 | 3.33 | 0.11 | 0.03 | 93.90 |
| C61 | 56.88 | 0.96 | 20.47 | 7.16 | 0.07 | 1.98 | 0.31 | 1.70 | 3.76 | 0.16 | 0.02 | 93.47 |
| C71 | 55.52 | 0.94 | 20.23 | 6.87 | 0.08 | 1.89 | 0.54 | 1.30 | 2.53 | 0.14 | 0.02 | 90.06 |
| C82 | 48.74 | 0.84 | 19.48 | 12.67 | 0.21 | 2.21 | 0.65 | 0.15 | 3.46 | 0.15 | 0.04 | 88.62 |
| C83 | 64.65 | 1.03 | 17.01 | 5.40 | 0.10 | 1.51 | 0.31 | 1.18 | 2.83 | 0.12 | 0.06 | 94.19 |
| C92 | 15.60 | 0.25 | 6.74 | 9.69 | 0.34 | 0.58 | 0.81 | 0.14 | 1.02 | 0.42 | 0.04 | 35.65 |
| C101 | 64.67 | 1.07 | 19.96 | 3.38 | 0.02 | 1.25 | 0.14 | 0.41 | 3.92 | 0.07 | 0.02 | 94.90 |
| C111 | 50.45 | 0.59 | 23.35 | 4.19 | 0.06 | 1.48 | 0.37 | 0.42 | 5.13 | 0.14 | 0.02 | 86.21 |
| C112 | 63.61 | 0.97 | 15.44 | 6.45 | 0.15 | 1.37 | 0.56 | 1.24 | 3.44 | 0.12 | 0.05 | 93.40 |
| C121 | 52.50 | 0.70 | 23.89 | 6.41 | 0.11 | 1.62 | 0.28 | 0.18 | 4.57 | 0.14 | 0.04 | 90.44 |
| C122 | 49.86 | 0.90 | 25.10 | 4.33 | 0.08 | 0.90 | 0.16 | 0.08 | 2.18 | 0.08 | 0.02 | 83.69 |
| C131 | 43.28 | 0.90 | 24.53 | 6.14 | 0.13 | 0.64 | 0.51 | 0.40 | 1.59 | 0.20 | 0.02 | 78.35 |
| C132 | 63.24 | 1.02 | 19.22 | 3.42 | 0.05 | 0.69 | 0.17 | 0.80 | 2.06 | 0.08 | 0.02 | 90.79 |
| C133 | 54.59 | 1.28 | 28.89 | 1.55 | 0.01 | 0.33 | 0.06 | 0.18 | 1.14 | 0.04 | 0.02 | 88.09 |
| C141 | 55.45 | 0.96 | 13.29 | 9.22 | 0.24 | 1.83 | 0.54 | 0.23 | 3.24 | 0.23 | 0.04 | 91.28 |
| C151 | 58.64 | 1.20 | 22.03 | 5.54 | 0.07 | 0.94 | 0.21 | 0.29 | 2.43 | 0.07 | 0.04 | 91.47 |
| C161 | 32.07 | 0.65 | 13.61 | 24.11 | 0.58 | 1.89 | 1.08 | 0.26 | 1.78 | 0.35 | 0.02 | 76.39 |
| C171 | 63.61 | 0.98 | 14.91 | 7.65 | 0.18 | 1.49 | 0.46 | 1.13 | 2.39 | 0.14 | 0.02 | 92.96 |
| C172 | 64.78 | 1.04 | 16.44 | 5.89 | 0.10 | 1.23 | 0.28 | 1.02 | 2.58 | 0.12 | 0.02 | 93.52 |
| C181 | 57.76 | 1.06 | 21.92 | 5.52 | 0.06 | 1.48 | 0.24 | 0.63 | 2.05 | 0.07 | 0.03 | 90.80 |

Table 5.8. Table of corrected XRF data.

| Sample. | Rutile. | Apatite. | Haematite. |
|---|---|---|---|
| Ca11 | 1 | 0.3 | 7.9 |
| Ca12 | 0.9 | 0.3 | 5.6 |
| Ca13 | 0.8 | 0.3 | 8.9 |
| O11 | 0.8 | 1.7 | -------- |
| O12 | 0.9 | 0.4 | -------- |
| O21 | 1 | 0.3 | -------- |
| O31 | 1 | 0.2 | -------- |
| S11 | 1 | 0.2 | -------- |
| S31 | 1 | 0.7 | -------- |
| S32 | 0.8 | 0.6 | -------- |
| D11 | 1 | 0.5 | 5.1 |
| D12 | 0.8 | 0.3 | 5.6 |
| D21 | 0.8 | 0.3 | -------- |
| C1B1 | 0.5 | 0.5 | -------- |
| C1B2 | 1 | 0.4 | -------- |
| C1B4 | 1.1 | 0.5 | -------- |
| C1B5 | 1.2 | 0.1 | -------- |
| C21 | 1 | 0.3 | -------- |
| C31 | 0.8 | 0.4 | -------- |
| C41 | 0.6 | 0.6 | -------- |
| C51 | 1 | 0.2 | -------- |
| C52 | 1.1 | 0.4 | -------- |
| C61 | 1 | 0.6 | -------- |
| C71 | 0.9 | 0.5 | -------- |
| C82 | 0.8 | 0.5 | -------- |
| C83 | 1 | 0.4 | -------- |
| C92 | 0.2 | 1.5 | -------- |
| C101 | 1.1 | 0.2 | -------- |
| C111 | 0.6 | 0.5 | -------- |
| C112 | 1 | 0.4 | -------- |
| C121 | 0.7 | 0.5 | -------- |
| C122 | 0.9 | 0.3 | -------- |
| C131 | 0.9 | 0.7 | -------- |
| C132 | 1 | 0.3 | -------- |
| C133 | 1.3 | 0.1 | -------- |
| C141 | 1 | 0.8 | -------- |
| C151 | 1.2 | 0.2 | -------- |
| C161 | 0.6 | 1.2 | -------- |
| C171 | 1 | 0.5 | -------- |
| C172 | 1 | 0.4 | -------- |
| C181 | 1.1 | 0.2 | -------- |

Table 5.9. Quantification of rutile, apatite and haematite.

## 5.9. Determination of Apatite, Rutile and Haematite.

These two minor minerals occur in mudrocks and may be recalculated directly from the XRF results, apatite (flourapatite) from $P_2O_5$ and rutile from $TiO_2$ (Campbell, 1993). These two minerals were generally not noted on the XRD whole rock scans as they occur in quantities too small to be detected.

Apatite is recalculated by multiplying the phosphate percentage by 1.5 to give $P_3O_{7.5}$, then multiplied by 2.37 (molecular weight flourapatite ÷ molecular weight $P_3O_{7.5}$). The percentage of rutile is assumed to equate directly with the XRF determined percentage of $TiO_2$. The results for apatite and rutile are presented in Table 5.9.

In addition to the detected mineral phases, haematite was detected on the XRD traces for some of the geologically older samples. The quantity was determined for the appropriate samples using the same approach adopted for feldspar determinations as presented in Section 5.4. A reference intensity of 0.947 was used, which was obtained from Baylis (1986). The results are presented in Table 5.9.

## 5.10. Methylene blue adsorption test.

The methylene blue adsorption test is a method of determining the cation exchange capacity of clays, it is a measure of the mudrocks potential reactivity due to its clay mineral composition. It is intended to see how it correlates with engineering behaviour. It has been used for many years by the drilling industry for testing the quality of drilling mud mixes. Fairburn and Robertson (1956) showed that there was a remarkably good positive correlation between the methylene blue index value and the Atterberg limits of soils. It has also been found by workers such as Taylor (1967), Stapel and Verhoef (1989) and Cokca and Birand (1993) that as a index test, the methylene blue index is a simple, reproducible means of characterising the clay mineralogy in a whole rock sample. The method is not without its problems as, according to Taylor (1985), the methylene blue molecule is large, and anomalous results can be obtained when dealing with untreated smectites.

Clay minerals carry a negative electrical charge, and broken bonds around clay surfaces also give rise to an unbalanced charge. This charge on clay mineral surfaces creates potential adsorption sites for cations. With maturation of clay minerals due to diagenetic processes, the exchange capacity becomes lower due to recrystallization and cation fixation. Methylene blue is an organic base in combination with an acid, the formula in its dried state being: $C_{16}H_{18}N_3SCl$ - mol.wt. (319.9 g/mol) (Stapel and Verhoef, 1989). The molecule exists as a monomer when made up to a low concentration in solution. In contrast to the reversible exchange of inorganic cations methylene blue replaces natural cations on clays in an irreversible process as follows:-

Ca/Na Clay + Methylene blue hydrochloride $\Rightarrow$ Methylene blue clay + Ca/Na chloride
(Taylor, 1985)

Since indurated mudrocks are being investigated in this study the clay mineralogy will be relatively mature with relatively large clay mineral platelets, therefore the $\sim 1.3 \rightarrow 1.35$ nm large size of the methylene blue molecule is not considered to be a problem. Since smectite is only present in two of the samples, and at a very low concentration, it was not considered likely that anomolous results would occur.

The methylene blue adsorption index and cation exchange capacity was calculated for all the samples to see if this simple index test, which is a reflection of the reactivity of the clay species in a mudrock sample correlates with engineering properties. It was decided to use a combination of Stapel and Verhoef (1989) and ASTM C837 (1986) test methods. TEMA mill powdered samples were used with minimum of sample preparation except for low temperature ashing on samples containing high organic carbon,. The methodology is described in Appendix A10, and the results for the methylene blue adsorption index (MBI) and cation exchange capacity (CEC) are presented in Table 5.10.

## 5.11. Discussion and conclusions of the mudrock mineralogies.

The mineral phases of the samples have been grouped together into main mineral catagories for comparative purposes, the data are presented in Table 5.11. It can be seen from the mineralogical data set that ~75% of the 41 samples analysed can be classed as average mudrocks when compared to the extensive data sets presented by Shaw and

| Sample. | MBA [g%] | CEC [mEq/100g] |
|---|---|---|
| Ca11 | 0.29 | 0.90 |
| Ca12 | 0.21 | 0.66 |
| Ca13 | 0.22 | 0.70 |
| O11 | 2.48 | 7.77 |
| O12 | 2.42 | 7.60 |
| O21 | 0.45 | 1.40 |
| O31 | 0.35 | 1.08 |
| S11 | 2.20 | 6.87 |
| S31 | 0.86 | 2.69 |
| S32 | 0.61 | 1.90 |
| D11 | 0.75 | 2.36 |
| D12 | 2.07 | 6.49 |
| D21 | 0.81 | 2.55 |
| C1B1 | 1.85 | 5.79 |
| C1B2 | 1.05 | 3.27 |
| C1B4 | 1.18 | 3.68 |
| C1B5 | 1.49 | 4.65 |
| C21 | 2.57 | 8.04 |
| C31 | 1.15 | 3.60 |
| C41 | 2.35 | 7.36 |
| C51 | 1.96 | 6.14 |
| C52 | 1.54 | 4.81 |
| C61 | 2.01 | 6.28 |
| C71 | 1.78 | 5.58 |
| C82 | 2.66 | 8.32 |
| C83 | 2.00 | 6.26 |
| C92 | 1.65 | 5.17 |
| C101 | 2.23 | 6.98 |
| C111 | 3.09 | 9.67 |
| C112 | 1.48 | 4.62 |
| C121 | 1.75 | 5.48 |
| C122 | 1.49 | 4.68 |
| C131 | 1.49 | 4.66 |
| C132 | 1.27 | 3.98 |
| C133 | 1.85 | 5.79 |
| C141 | 2.49 | 7.78 |
| C151 | 2.20 | 6.88 |
| C161 | 1.41 | 4.40 |
| C171 | 2.06 | 6.45 |
| C172 | 1.21 | 3.78 |
| C181 | 1.47 | 4.59 |

**MBA = Methylene blue adsorption. CEC = Cation exchange capacity.**

**Table 5.10. Methylene blue adsorption test results.**

Weaver(1965) and Taylor(1988). The exceptions are based only on mudrocks with above average contents of carbonate and organic material, these phases are of importance when considering illite ‘crystallinity’ values. As discussed in Chapter 3, both high carbonate and organic carbon contents within mudrocks tend to inhibit the progressive changes in illite ‘crystallinity’ values up to the onset of the anchizone, with increasing diagenetic processes such as burial. These adverse mineral phases, which for carbonates will be taken as quantities greater than ~8% and organic carbon as quantities greater than ~4% (based on data from Shaw and Weaver(1965) and Taylor(1988)), are important to note in the evaluation of ‘crystallinity’ data and are presented as controlling mineralogical prefixes in Table 5.12.

The mudrocks have been classified according to their mineralogies using the scheme proposed by Spears (1980) and modified by Taylor (1988). The scheme is based upon their quartz contents, which is considered to comprise the silt sized fraction. In this study feldspar contents have also been determined, and as feldspars together with quartz contribute to the silt sized fraction, a combined quartz and feldspar content is used as the basis of mudrock classification presented in Table 5.12. The mudrock samples have been grouped into one of three catagories, claystone (which Spears (1980) and Taylor (1988) refer to as very fine grained mudstones), mudstone and siltstone. The term shale has not been used for classification for the reasons discussed in Chapter 2, although as fissility plays a major roll in the engineering performance of mudrocks, it cannot be ignored. Descriptive data regarding fissility and lamination is presented in Table 5.12. The total proportion of mixed-layer clays present within the various samples has also been calculated on a whole rock basis and is presented in Table 5.12. The data for mixed- layer clays is considered in Chapter 9 in term of the extent to which the presence of this mineral phase controlls the swelling and slaking properties of indurated mudrocks.

The mineralogical analysis of the samples did not produce any anomolous data except for samples D.1.1 and D.1.2, which both were found to contain traces of smectite.These samples otherwise had a relatively mature clay mineral suite with an appropriate degree of illite ‘crystallinity’ apparent on the XRD trace. In situ these deposits contained quartz mineral veins and it is expected that this secondary mineralization phase along with the circulating waters precipitated authigenic clay minerals including the smectite detected.

| Sample | Quartz% | Feldspar% | Clays% | Pyrite% | Calc.% | Org. C% | Other% |
|---|---|---|---|---|---|---|---|
| Ca11 | 15.7 | 25.6 | 48.5 | 0.5 | 0.3 | 0.2 | 9.2 |
| Ca12 | 19.3 | 35 | 35.7 | 2.3 | 0.8 | 0.1 | 6.8 |
| Ca13 | 20.2 | 41.4 | 27.0 | 1.3 | -------- | 0.1 | 10.0 |
| O11 | 9.4 | -------- | 78.6 | 6.6 | 2.7 | 0.2 | 2.5 |
| O12 | 7.4 | 3.8 | 77.9 | 7.1 | 2.2 | 0.3 | 1.3 |
| O21 | 22.8 | 15.9 | 56.4 | 3.1 | -------- | 0.5 | 1.3 |
| O31 | 18.1 | 15.6 | 63.8 | 0.4 | 0.5 | 0.4 | 1.2 |
| S11 | 18.9 | 12.5 | 61.7 | 4.1 | 1.3 | 0.3 | 1.2 |
| S31 | 18.8 | 12.6 | 60.8 | 3.3 | 2.2 | 0.6 | 1.7 |
| S32 | 25.8 | 17.8 | 49.7 | 3.5 | 1.1 | 0.7 | 1.4 |
| D11 | 17.5 | 4.2 | 55.1 | 3.9 | 12.2 | 0.5 | 6.6 |
| D12 | 11.0 | 3.7 | 54.6 | 4.3 | 19.5 | 0.2 | 6.7 |
| D21 | 10.0 | 6.2 | 79.0 | 3.5 | -------- | 0.2 | 1.1 |
| C1B1 | 3.1 | 1.2 | 66.2 | 2.1 | 11.4 | 15.0 | 1.0 |
| C1B2 | 12.5 | 6 | 73.0 | 2.1 | 4.3 | 0.7 | 1.4 |
| C1B4 | 19.8 | 8.7 | 56.8 | 8.2 | 4.2 | 0.7 | 1.6 |
| C1B5 | 24.3 | 4.2 | 66.0 | 3.4 | -------- | 0.8 | 1.3 |
| C21 | 17.5 | 4.2 | 62.3 | 3.9 | 3.3 | 7.5 | 1.3 |
| C31 | 34.7 | 7.7 | 28.2 | 2.3 | 24.7 | 1.2 | 1.2 |
| C41 | 5.3 | -------- | 51.7 | 6.9 | 32.2 | 2.7 | 1.2 |
| C51 | 16.3 | 6.4 | 65.9 | 3.3 | 6.5 | 0.4 | 1.2 |
| C52 | 30.4 | 16.4 | 50.2 | 1.9 | 0.3 | 0.3 | 1.5 |
| C61 | 11.1 | 8.2 | 70.5 | 5.3 | 2.4 | 0.9 | 1.6 |
| C71 | 14.9 | 9.0 | 64.4 | 4.1 | 3.2 | 3.0 | 1.4 |
| C82 | 7.3 | -------- | 74.9 | 0.1 | 15.2 | 1.2 | 1.3 |
| C83 | 24.1 | 15.8 | 49.6 | 1.9 | 5.0 | 2.2 | 1.4 |
| C92 | 2.7 | 1.2 | 29.7 | 5.6 | 17.6 | 41.5 | 1.7 |
| C101 | 20.7 | 5.5 | 66.3 | 5.6 | -------- | 0.6 | 1.3 |
| C111 | 5.4 | 2.4 | 78.8 | 4.1 | 2.2 | 6.0 | 1.1 |
| C112 | 23.4 | 6.5 | 56.6 | 1.2 | 10.2 | 0.8 | 1.4 |
| C121 | 6.8 | 2.1 | 75.1 | 2.8 | 10.6 | 1.4 | 1.2 |
| C122 | 8.1 | 2.6 | 73.8 | 4.7 | 3.5 | 6.1 | 1.2 |
| C131 | 3.9 | 0.8 | 77.4 | 1.9 | 4.6 | 9.8 | 1.6 |
| C132 | 21.8 | 3.6 | 64.1 | 2.1 | 6.0 | 1.1 | 1.3 |
| C133 | 10.2 | 0.7 | 82.5 | 3.2 | -------- | 2.0 | 1.4 |
| C141 | 14.8 | 5.8 | 65.1 | 6.9 | 3.5 | 2.1 | 1.8 |
| C151 | 17.4 | 3.4 | 71.7 | 0.9 | 4.3 | 0.9 | 1.4 |
| C161 | 5.4 | 3.0 | 40.6 | 5.3 | 37.5 | 6.4 | 1.8 |
| C171 | 33.9 | 23.7 | 30.0 | 0.9 | 9.0 | 1.0 | 1.5 |
| C172 | 26.7 | 8.1 | 52.3 | 4.8 | 5.9 | 0.8 | 1.4 |
| C181 | 16.6 | 8.5 | 64.8 | 4.1 | 3.5 | 1.2 | 1.3 |

Calc = Calcareous mineral content.

Table 5.11. Table of mudrock mineralogies.

The geochemical analyses of the samples were performed and as such were not used for any quantitative mineral recalculations except for rutile and apatite. The direct chemical approaches were adopted to eliminate the assumption generally involved with bulk mineralogy recalculations. The geochemical data were useful as an indicator to what non-silicate phases were possibly present in large quantities. Loss on ignition indicates the volatile content which comprises carbonates ($CO_2$), pyrite (S), structural water and organic matter ($CO_2$). These constituents were evident in samples O12, S31, C1B1, C21, C31, C41,C82 , C92 , C111 , C122 , C131 and C161 suggesting either organic matter or one of the other volatile components. Further analysis of the data showed high values of $Fe_2O_3$ for samples O12, S31, C1B1, C31, C82, C161, which could be attributed to the presence of either pyrite or siderite. Sample C41 had high values for MgO and CaO indicating the presence of dolomite and sample D12, had a high value for CaO indicating calcite. These results were useful as an indicator as to which samples contained high proportions of certain volatile constituents and thus precautions could be taken as to the quantity of sample tested in the various chemical methods. The XRF results were primarily intended as a control for the selected samples used for the weathering experiments to see which components were affected by the different chemical additives, as will be described in Chapter 8.

The methylene blue test results for cation exchange capacities tend to be relatively low (<10% mEq/100g). Since the mudrocks are indurated they tend to contain more stable clay mineral assemblages which result in lower cation exchange values. The test was performed as an index to identify the samples which would be susceptable to slaking by nature of their reactive clay mineral phases, which have higher cation exchange capacities. The test is simple, rapid, reliable and cheap to carry out and as such is a useful index test. It is found that higher CEC values were measured for the samples identified in Chapter 6 as being more prone to slaking. Correlations presented in Chapter 9 show that the CEC values correlate with mixed-layer clay contents of the samples, so the test reflects a samples susceptability to slaking and swelling with respect to its mineralogy. The clay mineral phases present within mudrocks tend to be a reflection on their state of diagenetic alteration since smectites and immature kaolinite have the highest cation exchange capacities. These phases tend to be altered to more stable clay mineral phases such as illite and chlorite with increasing diagenesis. Such minerals have much lower cation exchange capacities so the methylene blue test could be used to evaluate the diagenetic rank of the mudrock. This is explored further in Chapter 9.

| Sample | Mudrock classification | Adverse Mins. | Fissility/Lam. | % Total MLC |
|---|---|---|---|---|
| Ca11 | Siltstone. | ---------- | ---------- | 0 |
| Ca12 | Siltstone. | ---------- | ---------- | 0 |
| Ca13 | Siltstone. | ---------- | ---------- | 0 |
| O11 | Claystone. | ---------- | ---------- | 28.8 |
| O12 | Mudstone. | ---------- | Laminated. | 28.0 |
| O21 | Mudstone. | ---------- | ---------- | 0 |
| O31 | Mudstone. | ---------- | ---------- | 0 |
| S11 | Mudstone. | ---------- | Laminated. | 18.4 |
| S31 | Mudstone. | ---------- | Fissile. | 0 |
| S32 | Siltstone. | ---------- | ---------- | 0 |
| D11 | Mudstone. | Calcareous. | ---------- | 0.5 (Sm) |
| D12 | Mudstone. | Calcareous. | ---------- | 4.7 (Sm) |
| D21 | Mudstone. | ---------- | Laminated | 0 |
| C1B1 | Claystone | Organic./Calc. | Fissile. | 8.2 |
| C1B2 | Mudstone. | ---------- | Laminated | 9.7 |
| C1B4 | Mudstone. | ---------- | Laminated | 8.6 |
| C1B5 | Mudstone. | ---------- | ---------- | 13.6 |
| C21 | Mudstone. | Organic. | Fissile. | 16.6 |
| C31 | Siltstone. | Calcareous. | Laminated | 6.7 |
| C41 | Claystone | Calcareous. | Laminated | 17.9 |
| C51 | Mudstone. | ---------- | ---------- | 35.5 |
| C52 | Siltstone. | ---------- | Laminated | 10.0 |
| C61 | Mudstone. | ---------- | ---------- | 18.7 |
| C71 | Mudstone. | ---------- | ---------- | 19.1 |
| C82 | Claystone | Calcareous. | Fissile. | 31.1 |
| C83 | Siltstone. | ---------- | Laminated | 7.3 |
| C92 | Claystone | Organic/Calc. | Laminated | 10.3 |
| C101 | Mudstone. | ---------- | ---------- | 17.7 |
| C111 | Claystone | Organic. | Fissile. | 30.3 |
| C112 | Siltstone. | Calcareous. | ---------- | 17.6 |
| C121 | Claystone | Calcareous. | ---------- | 14.7 |
| C122 | Mudstone. | ---------- | Fissile. | 3.3 |
| C131 | Claystone | Organic. | Fissile. | 5.6 |
| C132 | Mudstone. | ---------- | Laminated | 7.2 |
| C133 | Mudstone. | ---------- | ---------- | 13.3 |
| C141 | Mudstone. | ---------- | Laminated | 17.2 |
| C151 | Mudstone. | ---------- | ---------- | 17.1 |
| C161 | Claystone | Calc./Organic. | Fissile. | 4.2 |
| C171 | Siltstone. | ---------- | Laminated | 4.9 |
| C172 | Mudstone. | ---------- | ---------- | 13.2 |
| C181 | Mudstone. | ---------- | Fissile. | 8.2 |

Sm = Smectite.

Table 5.12. Mineralogical classification of the mudrock samples.

# Chapter 6.

# Physical and engineering characterization - methods, relevance of the properties and results.

## 6.1. Introduction.

Mudrocks can be characterized in terms of mineralogy, chemistry and physical properties. Although a mineralogical/chemical investigation provides knowledge of the mineral suite present, this cannot in itself be used to predict the engineering behaviour of the rock. Mudrocks are found in various stages of induration where the principal variables are consolidation and cementation. The latter are a reflection of burial and diagenetic history of the material. Consolidation of mudrocks leads to changes to their bulk physical properties, including, for example, reductions of void space and increases in dry density. These changes are associated with recrystallisation and cementation of grains, these textural properties will be dealt with in more detail in Chapter 7.

It is stated by Bell (1992 -b) that there are no fundamental mechanical properties which can be used to characterize a particular variety of intact rock. However, there are a number of simple physical tests which can be used to determine rock properties. These index tests frequently give good correlations between one other. Index tests must satisfy certain criteria before they are useable. For instance, they must be inexpensive to perform, simple and rapid to carry out, the test results must be reproducible and the results must be relevant to the engineering requirement. It was stated by Oliveira (1993) that parameters measured from tests on intact samples of weak rock such as mudrocks, are often relevant to the mass behaviour to a far greater degree than is the case for stronger rocks where discontinuities normally have a relatively greater impact. One of the objectives of this study is to use an appropriate range of index tests to characterize in detail the physical properties of the samples, evaluate the applicability of the tests and where necessary modify them as appropriate.

In terms of durability, mudrocks may possess desirable or undesirable engineering properties, depending upon their degree of compaction. (Mead, 1936), distinguished between compaction and cementation mudrocks, the latter mudrocks being the more durable. The principal problems in engineering situations associated with mudrocks is their unique tendencies to swell and slake when exposed to water. Slaking or physical breakdown which is a function of wetting and drying under atmospheric conditions takes two forms, physical and physiochemical (Taylor, 1988). In less indurated or uncemented mudrocks, it has been found that a few cycles of wetting and drying caused rapid breakdown. This is attributed by Taylor (1988) to air breakage within voids and along discontinuities together with negative pore water pressure formation on drying which leads to tensile failure of weak intercrystalline bonds (Kennard et al., 1967). Russell (1982) in his study of Ordovician mudrocks, discovered that the degree of microfracturing represents an important role in the rate of breakdown of mudrocks, as during wetting and drying, breakdown is initiated along the fractures by air breakage due to capillary suction of water (Badger et al., 1956). Certain species of clay minerals such as smectites have been attributed to giving mudrocks their swelling and slaking tendencies, but Taylor & Smith (1986) point out that many British mudrocks of Carboniferous and older age do not contain discrete smectite phases and yet these properties still persist. They attribute the factor controlling expansion to be the cation types present in clay minerals. However, it is clear that voids including pores and microfractures also govern swelling, as they provide the access routes for water to gain access to clay minerals (Dick and Shakoor, 1992). Morgenstern & Eigenbrod (1974) found that there is a direct correlation between strength loss during weathering of mudrocks and changes to the initial void ratio, bulk density and initial moisture content. It therefore can be seen that the engineering properties of swelling, slaking and strength in mudrocks are controlled to a large extent by physical factors such as porosity, void ratio, dry density and moisture content as well as the bulk mineralogy. So it is intended to determine these physical properties and relevant diagenetic parameters for a suite of samples and evaluate and to discuss their relative importance in terms of mudrock breakdown.

## 6.2. Bulk physical properties.

Moisture conditions including moisture content, absorption, adsorption, and physical properties such as dry density, porosity and void ratio can be used to express the relative degree of consolidation, and state of weathering in mudrocks (Dick, 1992). In the following section these relevant physical properties shall be discussed including specific gravity and moisture content under various conditions of testing

### 6.2.1. Moisture conditions.

#### *6.2.1.1. Natural moisture content (MC%).*

Moisture content can be used to express the state of weathering in mudrocks, as during surface exposure progressively more voids open up within the material. This creates a greater water retention capacity.

Moisture contents in this study were determined according to the methods described in BS 1377:1990. The determination was carried out in triplicate from which an average value of moisture content was obtained. The determinations were carried out on the rock fragments collected as jar samples as soon as the samples were returned to the laboratory. The determination involves weighing about 10 to 20 grams of the rock fragments to an accuracy of 0.001g, placing them in an oven set at 105°C where they were left to dry for a total of 72 hours, letting them cool down in a desiccator for 1 hour and then re-weighing them. The moisture content is expressed as the loss in weight expressed as a percentage of the original mass of the sample. The average moisture content values are presented in Table 6.1.

#### *6.2.1.2. Water absorption ($MC_{AB}$%).*

Water absorption is an indicator of the degree of consolidation, absorption being the water which during the submergence of a sample fills the void spaces present. In some samples this parameter is overestimated due to adsorption of water onto the surface of clay mineral species.

The water sorption test outlined in ASTM (1987) method C97 was used. This involves the use of regular cubes of rock, and it is presumed that the rocks being tested do not disintegrate when submerged in water, which is not always the case with mudrocks. A modified version of this test was carried out in which 40-50mm cubes of mudrock were submerged in distilled water and left to saturate at atmospheric pressure for a minimum of 72 hours. Since the samples tended to slake, they were tested at their natural water content, which did not entirely eliminate slaking. However, with slaked samples the largest fragments with no evident microfractures were removed for weighing. These fragments, and the original cubes where slaking did not occur were surface dried, weighed, and dried in an oven set at 105°C for 72 hours. On removal from the oven, the samples were cooled in a desiccator, reweighed and the percent absorption calculated as follows:

$$\%MC_{AB} = \left[\frac{\text{Saturated sample weight (g) - dry sample weight (g)}}{\text{dry sample weight}}\right] \times 100$$

The tests were repeated on at least three samples of each mudrock, the results are presented in Appendix B1, and the average water absorption values are given in Table 6.1.

### *6.2.1.3. Water Adsorption ($MC_{AD}$%).*

Water adsorption is referred to as the adhesion of liquid or gas molecules onto the surfaces of solid bodies. Water adsorption is an important property of mudrocks as it is sensitive to the proportion of clay minerals present. Since the durability of mudrocks is partly controlled by the clay mineralogy, water adsorption may correlate well with durability results.

The methodology adopted in this study was devised and used by the National Civil Engineering Laboratory of (LNEC), Portugal (pers.com.). For this 220g of NaCl was combined with 125ml of distilled water and placed in the bottom of a bell jar. The sample rack was then placed in the bell jar and three dried pre-weighed fragments of each mudrock sample were placed on the rack along with a humidity gauge. The bell jar was then sealed. Under these conditions at the test temperature of 20°C, the relative humidity in the bell jar would be 75.5%RH. The samples were left under these conditions for 7 days, then removed and immediately reweighed. The values of water adsorption were calculated as follows:

$$\%MC_{AD} = \left[\frac{\text{Moist weight (g) - dry weight (g)}}{\text{dry weight (g)}}\right] \times 100$$

The results are presented in Appendix B1, and the average water adsorption value for each sample at 75.5%RH is presented in Table 6.1.

### 6.2.2. Density and porosity determinations.

The density of rock is defined as being one of its most fundamental physical properties (Dick, 1992 and Bell, 1992-b), and is closely related to the degree of consolidation. In mudrocks it is strongly affected by diagenetic changes. During compression, as the density of the rock increases the porosity is reduced due to increased packing of the minerals, and re-cementation. As previously mentioned these properties have a control on the engineering behaviour of mudrocks, as they govern the access of water into the rock body.

#### *6.2.2.1. Specific gravity (Gs).*

Specific gravity of the rock powder represents an average density for the assortment of minerals which comprise the rock. It is expressed as the ratio of mass of the rock constituents to that of an equal volume of water at a temperature of 23 °C.

Specific gravity was determined according to BS 1377:1990 in which a powdered sample was prepared using a powered TEMA mill, with further grinding in an agate pestle and mortar. The powdered sample was oven dried, and after cooling in a desiccator about 3-5g was placed in a pre-weighed 50ml density bottle and weighed. De-aired distilled water was then added to the density bottle, just covering the sample and it was then placed into a desiccator to which a vacuum was applied to remove any trapped air. Once the air had been removed from the sample, care being taken to ensure no loss of sample from the bottle due to effervescing the bottle was filled with de-aired distilled water and brought to a constant temperature of 23°C in a water bath, the bottle was then surface dried and weighed.

| Sample. | MC%. Natural. | MC%. Absorption. | MC%. Adsorption. |
|---|---|---|---|
| Ca11 | 0.12 | 0.19 | 0.09 |
| Ca12 | 0.13 | 0.17 | 0.04 |
| Ca13 | 0.11 | 0.15 | 0.08 |
| O11 | 5.18 | 5.34 | 2.04 |
| O12 | 7.14 | 7.16 | 2.47 |
| O21 | 1.03 | 1.04 | 0.32 |
| O31 | 0.69 | 2.18 | 0.17 |
| S11 | 1.68 | 3.97 | 2.05 |
| S31 | 0.78 | 2.32 | 0.54 |
| S32 | 0.74 | 0.91 | 0.12 |
| D11 | 3.70 | 4.76 | 0.53 |
| D12 | 3.64 | 3.68 | 1.22 |
| D21 | 1.57 | 1.58 | 0.65 |
| C1B1 | 2.19 | 2.66 | 1.16 |
| C1B2 | 1.83 | 2.32 | 0.98 |
| C1B4 | 1.48 | 1.51 | 0.80 |
| C1B5 | 1.74 | 2.45 | 0.58 |
| C21 | 2.87 | 9.26 | 1.48 |
| C31 | 0.85 | 1.84 | 0.76 |
| C41 | 4.89 | 6.52 | 1.13 |
| C51 | 5.52 | 8.82 | 1.89 |
| C52 | 4.42 | 4.57 | 0.61 |
| C61 | 3.13 | 3.97 | 1.15 |
| C71 | 1.93 | 5.67 | 1.32 |
| C82 | 5.38 | 6.79 | 1.99 |
| C83 | 1.67 | 3.56 | 0.76 |
| C92 | 2.35 | 2.41 | 0.25 |
| C101 | 2.08 | 5.86 | 1.55 |
| C111 | 2.37 | 12.31 | 2.49 |
| C112 | 1.92 | 4.02 | 1.49 |
| C121 | 1.02 | 5.70 | 1.87 |
| C122 | 1.94 | 2.80 | 1.63 |
| C131 | 4.26 | 5.84 | 2.71 |
| C132 | 0.73 | 3.00 | 1.16 |
| C133 | 1.45 | 4.20 | 0.91 |
| C141 | 2.26 | 10.26 | 1.97 |
| C151 | 3.53 | 4.11 | 1.59 |
| C161 | 4.95 | 6.25 | 0.84 |
| C171 | 1.23 | 4.15 | 1.02 |
| C172 | 2.66 | 2.66 | 0.99 |
| C181 | 2.28 | 3.60 | 1.33 |

**Table 6.1 Results for moisture content determinations.**

The bottle was then emptied and thoroughly cleaned and the procedure repeated using de-aired, distilled water. The specific gravity is derived from the following expression.

$$Gs = \frac{M2 - M1}{(M4-M1) - (M3-M2)}$$

M1 = Mass of density bottle & stopper
M2 = Mass of powder, bottle & stopper
M3 = Mass of powder, bottle, stopper & water
M4 = Mass of bottle, stopper and water

The test was repeated in duplicate. Where the results differed by more than 0.03, BS 1377:1990 recommends that the test is repeated, but this was not found to be necessary in the present study. The results are presented in Appendix B2 and the average specific gravity value is presented in Table 6.2. The specific gravity result is controlled by mineral types present, but in this instance it was determined for the purpose of calculating the total porosity.

#### *6.2.2.2. Dry density determinations.*

According to Hudec (1982), since most mudrocks consist of a similar suite of major mineral components, providing they are not too organic rich, dry density is a valid indicator of consolidation.

Dry density is defined as the mass of mineral aggregate and voids containing air per unit volume. No standard method of determining dry density of mudrocks exists, so a modification of the BS 1377:1990 water immersion method was used. The method is based on Archimedes principle:

$$\rho d = \frac{Ms}{Vs} \ (\mathrm{Mg/m^3})$$

Ms = Mass of dried sample
Vs = Volume of dried sample

where: Vs ($m^3$) = Mass of sample in air (Mg) - Mass of sample in water (Mg),
and the specific gravity of the water is 1 $Mg/m^3$.

Since mudrocks slake when immersed in water, the samples were sprayed with an aerosol acrylic enamel sealant having first been oven dried and cooled. The weight difference of the spray was found to be between 0.1 and 0.05 %, therefore no correction was applied. Once ready the samples were weighed in air and then weighed submerged in water, suspended by a thin nylon line from an analytic balance arm. The test was repeated in triplicate, the results are given in Appendix B2, and average dry density is presented in Table 6.2. The dry density value was also used in the calculation of total porosity.

### *6.2.2.3. Porosity determinations.*

The porosity of a rock is defined as the volume of pore space divided by the total volume expressed as a percentage. Porosity can be divided into two types, total porosity (including occluded pore volume) and relative porosity, which is defined as the ratio of bulk volume to the excess of bulk volume over grain volume and occluded pore volume (Bell, 1992-b). Relative porosity is therefore considered as a measure of the voids which water can access. It is an important parameter since it is a reflection of the degree of compaction. Similarly relative porosity is of importance as it is an indication of the pore space available for water entry to promote air breakage, swelling and slaking.

It is yet to be seen whether the value between these porosity types has any relationship to the maturity of mudrocks, as during diagenetic changes voids, especially pore throats, become blocked by cementation agents and recrystallization of clay minerals.

Total porosity:- The total porosity is determined as the excess of grain density over dry density per unit of grain density (specific gravity), and can be obtained from the following expression (Bell, 1992-b).

$$\text{Total porosity } (n_T) = \left[ 1 - \frac{\text{dry density}}{\text{specific gravity}} \right] \times 100$$

The results for total porosity are presented in Table 6.2.

Relative porosity:- The relative porosity was determined using a Micromeritics Poresizer 9320 housed in the Department of Engineering Materials, University of Sheffield. The pore sizer measures the volume distribution of pores in a material by mercury intrusion. Mercury has a high surface tension and is non-wetting to all materials, with the exception of a few noble elements which do not occur in mudrocks. This property causes a mercury surface in contact with a solid to assume the minimum surface area and largest radius of curvature possible at a given pressure. The test is performed by increasing the pressure in the autoclave by set increments, an increase in pressure on the mercury shifts the balance between surface tension and surface area causing the radius of curvature of the mercury contacting the solid to become smaller. When the radius is equal to that of a pore entrance, mercury fills the pore volume. The size can therefore be evaluated by monitoring the volume of mercury injected into a sample as the mercury pressure is increased. The porosimeter is capable of measuring pore sizes down to a size of 0.006 μm, and is considered to be a good reflection to the pore area accessible to water (Shakoor & Scholer, 1985). However, since in the calculation it is assumed that all pores are cylindrical, which they are not, pore size distribution data are not a true representation of pore size distribution. Furthermore, measurements of the pore size distribution in rocks in which pore throats tend to be much smaller than the pores, have been shown to be biased towards the small pore size because of hysteresis effects in the pore throats (Rootare, 1968; Shakoor & Scholer, 1985). Other problems with this system are the compressibility of the test specimen and the incomplete evacuation of air from the sample prior to mercury intrusion. After evaluating the data and observation of the pore distribution using SEM it was decided only to use the relative porosity data as measured by the mercury porosimeter which is presented along with the value of average pore diameter (see Table 6.2).

One specimen consisting of a chip weighing 8-14g was tested for each sample. Where it was found that microfractures affected the test, it was repeated on another fragment. The testing was limited due to the availability of the equipment, time involved in setting it up and testing, and the cost. The maximum sample size was limited by the volume of the penetrometer cell. All samples were oven dried at 105 °C for 72 hours prior to testing. The samples were not touched by hand to avoid greasing the surfaces which would affect the evacuation of air, and it was found that adequate air evacuation took between 6 to 18 hours depending on the pore size distribution within the sample.

The results of the relative porosity ($n_R$) and average pore diameter are presented in the Table 6.2.

| Sample. | Gs. Ave. | γd. Ave. | $n_T$. | $n_R$. | Ave. Pore Dia.(μm) | e |
|---|---|---|---|---|---|---|
| Ca11 | 2.91 | 2.82 | 3.1 | 0.22 | 28.10 | 0.03 |
| Ca12 | 2.88 | 2.81 | 2.4 | 0.37 | 4.27 | 0.02 |
| Ca13 | 2.88 | 2.83 | 1.7 | 0.50 | 35.26 | 0.02 |
| O11 | 2.82 | 2.64 | 6.4 | 2.63 | 0.01 | 0.07 |
| O12 | 2.80 | 2.61 | 6.6 | 4.48 | 0.03 | 0.07 |
| O21 | 2.88 | 2.71 | 5.9 | 0.59 | 6.06 | 0.06 |
| O31 | 2.85 | 2.68 | 4.6 | 1.48 | 0.01 | 0.06 |
| S11 | 2.77 | 2.56 | 7.6 | 5.17 | 0.03 | 0.08 |
| S31 | 2.83 | 2.67 | 5.7 | 4.10 | 0.02 | 0.06 |
| S32 | 2.82 | 2.73 | 3.2 | 0.56 | 0.15 | 0.03 |
| D11 | 2.79 | 2.62 | 5.4 | 3.60 | 0.01 | 0.06 |
| D12 | 2.75 | 2.62 | 4.7 | 4.84 | 0.02 | 0.05 |
| D21 | 2.77 | 2.59 | 6.5 | 3.86 | 0.10 | 0.07 |
| C1B1 | 2.31 | 2.20 | 4.8 | 0.78 | 0.02 | 0.05 |
| C1B2 | 2.74 | 2.65 | 3.3 | 0.68 | 0.02 | 0.03 |
| C1B4 | 2.76 | 2.66 | 3.6 | 0.60 | 4.31 | 0.04 |
| C1B5 | 2.69 | 2.61 | 3.0 | 1.18 | 0.02 | 0.03 |
| C21 | 2.48 | 2.30 | 7.3 | 2.07 | 0.01 | 0.08 |
| C31 | 2.81 | 2.66 | 5.3 | 1.54 | 6.87 | 0.06 |
| C41 | 2.70 | 2.50 | 7.4 | 2.51 | 0.01 | 0.08 |
| C51 | 2.73 | 2.53 | 7.3 | 4.28 | 0.01 | 0.08 |
| C52 | 2.64 | 2.46 | 6.8 | 7.20 | 0.03 | 0.07 |
| C61 | 2.74 | 2.63 | 4.0 | 1.37 | 0.01 | 0.04 |
| C71 | 2.65 | 2.52 | 5.3 | 3.13 | 0.01 | 0.05 |
| C82 | 2.79 | 2.49 | 10.8 | 4.90 | 0.01 | 0.12 |
| C83 | 2.75 | 2.48 | 9.8 | 7.35 | 0.03 | 0.11 |
| C92 | 1.83 | 1.76 | 3.8 | 2.17 | 0.01 | 0.04 |
| C101 | 2.74 | 2.52 | 8.0 | 4.93 | 0.01 | 0.09 |
| C111 | 2.59 | 2.49 | 3.9 | 2.47 | 0.01 | 0.04 |
| C112 | 2.76 | 2.50 | 9.2 | 6.19 | 0.02 | 0.10 |
| C121 | 2.76 | 2.57 | 6.9 | 1.42 | 0.02 | 0.07 |
| C122 | 2.47 | 2.39 | 3.2 | 1.46 | 0.02 | 0.03 |
| C131 | 2.44 | 2.39 | 2.0 | 2.32 | 0.02 | 0.02 |
| C132 | 2.64 | 2.48 | 6.1 | 4.22 | 0.02 | 0.06 |
| C133 | 2.60 | 2.49 | 4.2 | 2.44 | 0.01 | 0.04 |
| C141 | 2.77 | 2.50 | 9.7 | 4.18 | 0.01 | 0.11 |
| C151 | 2.71 | 2.51 | 7.4 | 3.44 | 0.01 | 0.08 |
| C161 | 2.72 | 2.60 | 4.4 | 11.83 | 0.01 | 0.05 |
| C171 | 2.71 | 2.59 | 4.4 | 5.77 | 0.04 | 0.05 |
| C172 | 2.71 | 2.61 | 3.7 | 2.75 | 0.01 | 0.04 |
| C181 | 2.66 | 2.52 | 5.6 | 4.47 | 0.02 | 0.06 |

Gs = specific gravity. Ave. = average. γd = dry density. $n_T$ = total porosity.
$n_R$ = relative porosity. e = void ratio.

Table 6.2 Table of density and porosity results

### *6.2.2.4. Voids ratio.*

Voids ratio is the ratio of the volume of voids to the volume of solids. It has been shown by Hudec (1982) to be a valid indicator of the degree of consolidation of mudrocks.

The voids ratio was calculated from the measured values of dry density and specific gravity of the solids using the following expression:

$$\text{Voids ratio (e)} = \left[\frac{\text{specific gravity}}{\text{dry density}}\right] - 1$$

The results are presented in Table 6.2.

## 6.3. Engineering characterization.

Engineering characterization of mudrocks concentrates on 3 main types of characteristics:

- Swelling and slaking properties.
- Consistency limits.
- Strength.

Most of the determinations were carried out using standard test methods but, where necessary slight modifications were made to the test procedures to assist with potential interpretation. In addition to various slaking and swelling tests the occurrence of microfractures was assessed, these features have been found in many studies to play an important role in mudrock breakdown (Olivier, 1980; Russell, 1982; Grainger, 1983 and Dick, 1992).

The point load test was selected for the determination of strength, as samples require a minimum of preparation which tends to be problematic in mudrocks, and also the test fails the sample in a tensile mode, which is an important control on mudrock slaking.

### 6.3.1. Slaking tests.

Physical disintegration of mudrocks is considered to be a much more important breakdown process than chemical weathering (Bell, 1992). The principal controls on breakdown are slaking and expansion of clay minerals. Slaking refers to the breakdown of rocks, especially mudrocks by alternate cycles of wetting and drying. Taylor (1988) states that when mudrocks are allowed to dry, air drawn into the outer voids and capillaries produces high suction pressures (Taylor & Smith, 1986). Upon subsequent saturation, entrapped air is pressurised as water is drawn into the mudrock by capilliarity, therefore the slaking process stresses the skeletal framework of the mudrock. This pressure creates a tensile force which acts to enlarge and extend pores when the capacity of the interparticle bonding is exceeded and induced tensile failure occurs (Seedsman, 1986). In certain cases where cements may strengthen a rock fabric such that it does not fail immediately but with the repeated compressive and tensile forces that result from wetting and drying, the cements eventually fail and the sample slakes (Hudec, 1982).

It was observed by Hudec (1982) that due to cementation and clay mineral regrowth, increasing diagenetic rank produces mudrocks which are more indurated, and resistant to slaking. Previously to this it had been noted by Badger et al. (1956) and Taylor & Spears (1970) that as the measured rank of coal seams increased, then the durability of the associated mudrocks they studied increased, so it has been stated that diagenetic change plays a role in the durability of mudrocks. It was also noted by Russell (1982) and Olivier (1990) in their studies that the controlling aspect which separated durable and non-durable but otherwise similar mudrock, was the presence of incipient microdiscontinuities, along which the mudrocks broke during the slaking tests. However, it is not only air breakage in voids and along discontinuities that controls the breakdown of mudrocks since, as stated by Badger et al. (1956) and Smith (1978), disintegration during the slake durability test does not conform to a first order decay law. It was seen that the dispersion of clays susceptible to swelling due to dissociation of ions on the clay surfaces plays a key role. Thus breakdown by slaking is controlled principally by two factors, air breakage in voids and microdiscontinuities and also swelling and dissociation of clay minerals.

Detailed durability research into mudrocks was instigated during the 1950's by the National British Coal Board, principally to investigate high wall and mine roof failure problems (Taylor, 1988). This led to the development of various durability tests, in particular the end-over-end durability test (Badger et al., 1956), which involved the rotation of mudrock fragments in water contained in a sealed glass container. This test eventually evolved into the slake durability test of Franklin & Chandra (1972) which has become the standard test for measuring the slake durability of mudrocks. It was found that the slake durability test lacked sensitivity for very low and very high durability mudrocks and Lutton (1977) proposed the jar slake test to overcome this problem. In contrast to the dynamic slake durability test this is a static test. It involves placing an oven dried fragment of mudrock in water and qualitatively monitoring its breakdown over a 24 hour period, this involves observing the development of fractures and slaking. Both the static slaking and dynamic slaking tests were used to characterize the durability of the mudrocks in this study.

### *6.3.1.1. Slake Durability Test.*

Franklin and Chandra (1972) devised the slake durability test for the evaluation of mudrock breakdown so that an evaluation of their disintegration potential during weathering could be made. The test involves placing ten fragments each weighing between 40 and 60g, preferably equi-dimensional shaped of oven dried mudrock in a test drum constructed of a 2mm exterior mesh housed in a test trough. Water is placed in the test troughs at a level below the drum axle, and the drum is rotated for 200 revolutions at 20 revolutions per minute. The sample that remains in the drum after this treatment and is oven dried for a minimum of 6 hours, cooled and then reweighed, from this the slake durability index (Id) is obtained by the following expression:

$$Id_1 = \left[\frac{B - C}{A - C}\right] \times 100\%$$

A = Initial mass of test drum and rock fragments
B = Mass of drum and retained portion after drying
C = Mass of test drum

This test has been standardised by the International Society for Rock Mechanics (Brown, 1981). Franklin & Chandra (1972) preferred the one cycle test as a basis for classification of durability, Gamble (1971) and the ISRM prefer a two cycle test, whereas Taylor (1988) recommended using a three cycle test to classify mudrocks. In this study it was decided to test over 5 cycles of wetting and drying as has been recommended by Taylor (1988) for more indurated mudrocks. The results are presented in Table 6.3. Taylor & Spears (1981) stated that the test may be insensitive to weaker or stronger mudrocks, as the 2mm test mesh gives little indication of the mode or amount of breakdown of the material. Therefore both the material retained in the test drum, and material passing the 2mm test mesh were sieved and the silt and clay size fractions determined by hydrometer analysis according to the recommendations of BS 5930:1990 to determine the extent of breakdown, the results are presented graphically in Appendix B3. The test was performed twice on each mudrock sample, the results in Table 6.3, are the average of the two determinations which tended to be in good agreement. The particle size distribution graphs presented in Appendix B3 also give a brief description of the sample debris after testing. In terms of shape it was found that the fragments tended to be angular blocky, platy or almond shaped as illustrated in Figure 6.1.

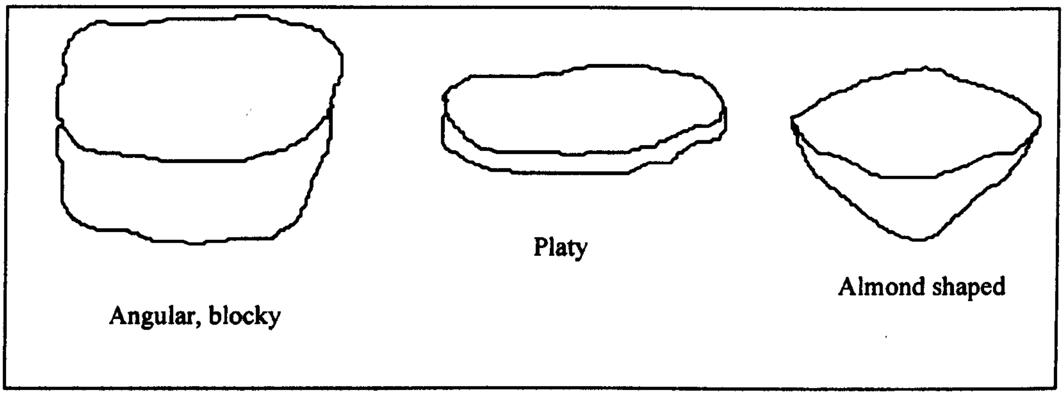


Figure 6.1. Illustration of mudrock fragment breakdown shapes during the slake durability test.

### *6.3.1.2. Jar Slake test (Ij).*

The jar slake test which was initially devised by Lutton (1977) consisted of placing an irregular equidimensional block of oven dried mudrock weighing about 20g in a beaker, submerging the sample in water, and then monitoring the change at frequent intervals for the initial part of the test, and less frequently as the test proceeded. The samples were ranked and described according to the categories presented by Lutton (1977), as seen in Table 6.4.

| Ij | Behaviour |
|---|---|
| 1 | Degrades to a pile of flakes or mud. |
| 2 | Breaks rapidly and/or forms many chips. |
| 3 | Breaks slowly and/or forms few chips. |
| 4 | Breaks rapidly and/or forms several fractures |
| 5 | Breaks slowly and/or develops few fractures |
| 6 | No change |

Table 6.4 Luttons (1977) Classification of slaking in the jar slake test (Ij).

This catagorization was modified by Dusseault et al. (1983) by including descriptions of the murkiness of the water, and presenting a visual estimate of the swelling. In this study which involves indurated mudrocks, it was found that the existing test procedures and classifications was too insensitive and therefore the procedure was again modified.

Modified jar slake test procedure (Ij')

Initially a 40-50cm sided cuboid block of mudrock having one side cut parallel and one perpendicular to the bedding was cut with a dry saw. The sample was then brushed clean of any dust and oven dried at 60°C for 72 hours. Once the sample had cooled it was placed in a 500ml or 1000ml beaker and covered to a level 50mm above its top surface with distilled water, and the stopwatch started. Descriptions of the sample were made at the following elapsed time intervals:- 1 min, 10 mins, 1 hr, 2 hrs, 3hrs, 4 hrs, 6 hrs, 8hrs, 24hrs. If no change was observed in the sample after 24 hours then it was left for a further 24 hours and again described if any change had occurred. The sample state was described according to the classification presented in Table 6.5, which was devised during the course of this study. The scheme is designed to record the development of discontinuities over time, and the extent of slaking. The discontinuities were described according to their length, orientation, spacing and degree of openness. It was found that with flat cut faces the development of fractures could be observed more accurately than on a rough surface. Samples either reacted rapidly within a 4 hour period, or slowly over the 24 hour test duration, therefore the final Ij' values were also designated as fast or slow

| Sample. | $Id_1$ | $Id_2$ | **$Id_3$** | $Id_4$ | $Id_5$ | Durability. |
|---|---|---|---|---|---|---|
| Ca11 | 99.5 | 99.2 | **99.0** | 98.7 | 98.6 | D. |
| Ca12 | 99.6 | 99.5 | **99.4** | 99.3 | 99.2 | D. |
| Ca13 | 99.6 | 99.6 | **99.4** | 99.3 | 99.0 | D. |
| O11 | 86.8 | 74.1 | **56.9** | 46.9 | 36.6 | N.D. |
| O12 | 64.9 | 48.9 | **35.8** | 27.6 | 21.8 | N.D. |
| O21 | 99.4 | 98.6 | **98.5** | 98.2 | 97.9 | D. |
| O31 | 99.3 | 98.7 | **98.4** | 98.2 | 97.8 | D. |
| S11 | 98.4 | 95.9 | **94.6** | 92.9 | 91.5 | D. |
| S31 | 99.6 | 99.2 | **98.6** | 98.2 | 97.8 | D. |
| S32 | 99.2 | 98.7 | **98.2** | 97.9 | 97.7 | D. |
| D11 | 97.4 | 96.5 | **94.9** | 94.1 | 93.0 | D. |
| D12 | 99.2 | 98.1 | **97.6** | 96.4 | 96.0 | D. |
| D21 | 99.3 | 98.8 | **98.4** | 97.9 | 97.6 | D. |
| C1B1 | 99.5 | 98.2 | **97.5** | 96.8 | 96.1 | D. |
| C1B2 | 99.0 | 94.7 | **91.8** | 89.1 | 87.0 | D. |
| C1B4 | 99.2 | 98.0 | **97.5** | 97.3 | 96.9 | D. |
| C1B5 | 97.9 | 89.6 | **85.0** | 81.1 | 78.0 | D. |
| C21 | 91.8 | 66.2 | **46.8** | 39.6 | 34.5 | N.D. |
| C31 | 99.0 | 98.0 | **97.5** | 96.7 | 96.2 | D. |
| C41 | 95.2 | 84.6 | **74.3** | 67.9 | 63.3 | D. |
| C51 | 82.0 | 49.9 | **27.8** | 15.6 | 8.7 | N.D. |
| C52 | 91.2 | 65.1 | **44.8** | 26.6 | 17.2 | N.D. |
| C61 | 89.6 | 68.4 | **56.2** | 46.7 | 41.5 | N.D. |
| C71 | 96.3 | 90.7 | **85.2** | 81.9 | 72.3 | D. |
| C82 | 65.2 | 30.8 | **22.3** | 18.1 | 15.9 | N.D. |
| C83 | 96.5 | 89.1 | **81.7** | 76.3 | 72.0 | D. |
| C92 | 99.4 | 98.8 | **98.0** | 97.5 | 96.9 | D. |
| C101 | 89.6 | 72.3 | **63.2** | 57.1 | 52.9 | D. |
| C111 | 83.1 | 64.1 | **56.9** | 51.8 | 48.0 | N.D. |
| C112 | 94.6 | 86.5 | **81.2** | 76.9 | 74.6 | D. |
| C121 | 90.1 | 79.7 | **75.2** | 71.4 | 68.7 | D. |
| C122 | 95.0 | 88.7 | **85.6** | 83.2 | 81.6 | D. |
| C131 | 76.7 | 49.8 | **41.4** | 35.5 | 31.6 | N.D. |
| C132 | 97.0 | 94.1 | **91.0** | 88.8 | 86.4 | D. |
| C133 | 33.1 | 13.0 | **10.4** | 9.6 | 9.2 | N.D. |
| C141 | 90.7 | 76.5 | **63.3** | 52.6 | 45.1 | D. |
| C151 | 91.8 | 79.5 | **72.4** | 66.3 | 61.6 | D. |
| C161 | 97.3 | 95.4 | **93.8** | 92.2 | 90.8 | D. |
| C171 | 97.0 | 94.0 | **91.1** | 87.8 | 84.5 | D. |
| C172 | 98.6 | 96.6 | **94.8** | 92.8 | 91.1 | D. |
| C181 | 97.6 | 93.9 | **90.7** | 87.2 | 84.2 | D. |

D = Durable. N.D. = Non durable.

Table 6.3 Table of slake durability results over 5 test cycles and durability classification afterTaylor (1988).

**Ij - Jar Slake Classification.**

1. No visible sign of specimen deterioration - air bubbles may be emitted from the sample.

2. No notable specimen deterioration, development of occasional hairline fractures, (usually bedding fractures, or parallel to bedding) air bubbles generally emitted from these fractures.

3. Slight specimen deterioration, generally consisting of extremely closely spaced (10 - 20mm), hairline to (≤1mm) open fractures, usually parallel to bedding with up to 5% slaking, usually from the sample corners.

3i. Same as 3. but fractures tend to be randomly orientated.

4. Moderate specimen deterioration, generally consisting of many extremely closely spaced (5-10mm) hairline to (≤2mm) open fractures, usually with up to 10% slaking of the sample consisting of gravel sized fragments and shards.

4i. Same as 4. but fractures tend to be randomly orientated.

5. Moderate to high specimen deterioration, generally consisting of many extremely closely spaced (2-10mm) generally open (1-4mm) fractures, generally parallel to bedding. Sample block integrity still maintained, although the single block may have split into a few free-standing blocks. Sample/s block/s have a general appearance of heavy desiccation, with upto 25% slaking.

5i. Same as 5. but fractures tend to be randomly orientated.

6. High degree of sample deterioration, only a partial block shape retained, usually in the form of multi free-standing blocks, or block within a pile of slaked debris. Sample block/s have a general appearance of heavy desiccation, and appear unstable. Fractures extremely closely spaced (2-6mm) and generally open (2mm+),usually parallel to bedding with occasional crossed fractures, with up to 50% slaking.

7. The sample block shape largely to completely destroyed. The slaked debris generally consists of a pile of angular gravel sized shards or blocky fragments, and occasionally with free-standing fragments of the original sample block.

8. Total sample disintegration consisting of a pile of soil like debris ie. high proportion of sub-gravel sized debris and some fine to medium gravel sized fragments.

Table 6.5 Modified jar slake classification scheme.

depending on the rate at which the slaking proceeded. The results for the jar slake test (Ij') are presented in Table 6.6, including the overall (Ij') value and rate. These results are considered further in Chapter 9 which includes cross correlation of recorded diagenetic features.

Time.

| Sample. | 1m. | 10m. | 30m. | 1hr. | 2hr. | 3hr. | 4hr. | 6hr. | 8hr. | 24hr. | Rate. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca11 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1-2 | slow |
| Ca12 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1-2 | slow |
| Ca13 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | slow |
| O11 | 3i | 5i | 6 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | fast |
| O12 | 4i-5i | 5i | 5i-6 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | fast |
| O21 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | slow |
| O31 | 1 | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | fast |
| S11 | 1 | 3 | 3 | 3-4 | 4 | 4 | 4 | 4 | 4 | 5 | fast |
| S31 | 1 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3-4 | fast |
| S32 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | fast |
| D11 | 1 | 2 | 2 | 3 | 3 | 4 | 4-5 | 5 | 5 | 5 | slow |
| D12 | 1 | 2 | 2 | 3 | 3 | 3 | 4 | 4-5 | 5 | 5 | slow |
| D21 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | fast |
| C1B1 | 1 | 2 | 2-3 | 3 | 4 | 4 | 5 | 6 | 6 | 6 | slow |
| C1B2 | 1 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | fast |
| C1B4 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 | 3 | 3-4 | slow |
| C1B5 | 1 | 2 | 3i | 4i | 5i | 5i | 5i | 5i | 6 | 6 | slow |
| C21 | 3 | 5 | 5 | 5-6 | 7 | 7 | 7 | 7 | 7 | 7 | fast |
| C31 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 3 | 3-4 | slow |
| C41 | 3 | 5 | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | slow |
| C51 | 1 | 3 | 5 | 5-6 | 6 | 7 | 7 | 7 | 7 | 7 | fast |
| C52 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 3 | slow |
| C61 | 1 | 4 | 4 | 5 | 5 | 6 | 6 | 6 | 6 | 6 | fast |
| C71 | 1 | 2 | 4 | 5 | 5 | 6 | 6 | 6 | 6 | 6 | fast |
| C82 | 3 | 5 | 6 | 6-7 | 7 | 7 | 7 | 7 | 7 | 7 | fast |
| C83 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | fast |
| C92 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | fast |
| C101 | 1-2 | 2-3i | 3i-4i | 4i | 4i-5i | 5i | 5i-6 | 5i-6 | 5i-6 | 6 | slow |
| C111 | 3i | 4i | 5i-6 | 6 | 6-7 | 7 | 7 | 7 | 7 | 7 | fast |
| C112 | 1 | 2 | 2-3 | 2-3 | 3 | 3 | 3 | 3 | 3-4 | 3-4 | slow |
| C121 | 4 | 6 | 6-7 | 6-7 | 7 | 7 | 7 | 7 | 7 | 7 | fast |
| C122 | 1 | 2-3 | 2-3 | 3 | 3 | 3-4 | 4 | 4 | 4 | 4 | fast |
| C131 | 2 | 4-5 | 5 | 5 | 5 | 5 | 6 | 6 | 6 | 6 | fast |
| C132 | 1 | 2-3 | 3i | 3i | 3i | 3i | 4i | 4i | 4i | 4i | fast |
| C133 | 1 | 3i | 3i-4i | 4i | 4i-5i | 5i | 5i | 5i | 5i | 5i-6 | slow |
| C141 | 3 | 5 | 5-6 | 6 | 6 | 6 | 6-7 | 6-7 | 6-7 | 7 | slow |
| C151 | 1 | 2 | 3i | 4i | 4i | 5i | 5i | 5i-6 | 5i-6 | 5i-6 | fast |
| C161 | 1 | 3 | 3 | 4 | 4 | 4-5 | 4-5 | 4-5 | 4-5 | 5 | fast |
| C171 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 3-4 | 4 | 4 | slow |
| C172 | 1 | 2 | 2-3 | 3i | 4i | 4i | 4i | 4i | 4i-5i | 4i-5i | slow |
| C181 | 1 | 2 | 3 | 4 | 4 | 5 | 5 | 5 | 5 | 5 | fast |

Table 6.6 Modified jar slake test results. (Ij')

### 6.3.2. Swelling tests.

Swelling in mudrocks results from the same processes as slaking, and as such slaking tends to be the physical outcome of swelling. The two main mechanisms which control swelling are respectively physiochemical and mechanical processes (Taylor & Smith, 1986 and Bell et al., 1993).

The physiochemical process involves the expansion of clay mineral species such as smectites and mixed layer clays. The swelling is caused by a diffused layer next to the clay platelets. Due to this diffusion layer, the minerals present exhibit a net repulsion, as when the double layers overlap there is an excess cation concentration between the clay platelets (see Fig 6.2). Equilibrium is restored by free water being drawn into the system from adjacent pores and capillaries therefore creating osmotic swelling which promotes unloading, this process tends to be controlled by electrolyte concentration, cation valency, temperature and the dielectric constant (Taylor & Smith, 1986; Hungxi, 1993; Bell et al., 1993).It has been stated by Bell et al. (1993) that not only expansive clay species react in this way, since some clay species such as illite naturally occur in a hydrated state where a diffused layer of ordered water molecules and cations occupy spaces between crystals. An increase in water content reduces the cation concentration of the pore fluid which increases the electrostatic repulsion between particles and so swelling restores the balance by increasing the number of cations present in the inter-crystalline spaces.

Mechanical swelling is caused by elastic and time dependent stress unloading and textural features. It has been found by many workers (Venter, 1981; Sarman & Shakoor, 1990; Erol & Dhowian, 1990; and Sharman, Shakoor & Palmer, 1994) that fracture development plays a more important role in more indurated mudrocks and that a poor relationship exists between the expansive clay content and the swelling properties of mudrocks.The importance of textural features has been discussed by Sarman and Shakoor (1990) who found that volumetric increase is more related to fabric in mudrocks than it is to mineral composition.

Laminations are an important controlling feature as water can easily enter along them causing greater expansion. Lo et al. (1978) found that expansion is also controlled by the clay fabric in particular clay mineral orientation, so if the clay platelets lie parallel to the bedding then the majority of the expansion is parallel to the bedding due to the effects of double layer and interlayer cation hydration swelling in the Z crystallographic axis. Hungxi (1993) states that diagenetic history plays an important part in the swelling potential of mudrocks, since the mineralogical and physical changes resulting from diagenetic changes generally make the mudrocks less susceptible to swelling.

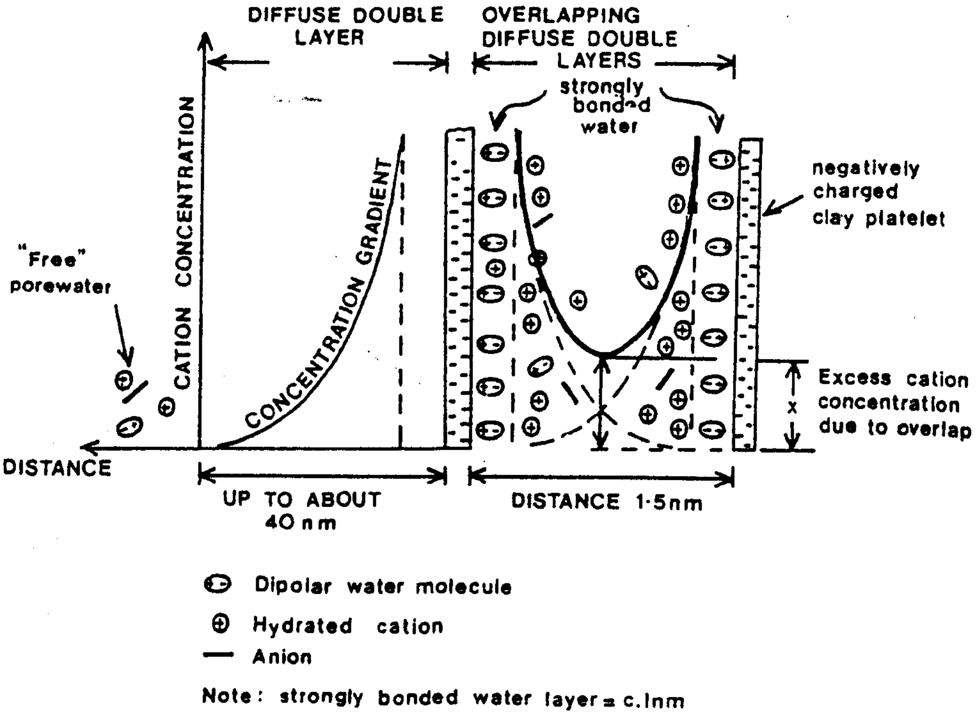


Fig 6.2 Model of double-layer (osmotic) swelling of two clay mineral platelets. Double-layer formed by negatively charged mineral surfaces attracting cations and polar water (from Taylor & Smith, 1986).

There are two main approaches to measuring volumetric strain in mudrocks, these being confined and unconfined tests. Since it is too difficult to machine mudrocks because of their brittle nature and susceptibility to swelling and slaking when water is used for coring, the confined oedometer test is usually less suitable, and so unconfined tests generally prove to be the only course of action. Duncan et al. (1968) introduced the uniaxial strain test, which involves placing a piece of core or prism of mudrock in a trough with a dial gauge positioned against its top surface. Then the sample is submerged in distilled water and the swelling monitored. Due to its simplicity this method is commonly used, although only the swelling along one axis is monitored per test. The ISRM (Brown, 1981) specify a triaxial swelling cell for measuring the strain on all three axis during expansion, which is the method employed in this study. In addition, the powder free swell test (Gibbs & Holtz, 1956) was also performed, this test eliminates any structural controls on the swelling and crudely measures the influence of mineralogy on swelling.

### *6.3.2.1. Unconfined triaxial free swell test.*

This test is intended to measure the swelling strain development when an unconfined, undisturbed mudrock specimen is immersed in water. The test determines the swelling potential of particular specimens, and gives an indication as to how a rock will behave under changed or particular environmental conditions, but as such the test cannot be used to predict the amount of swelling a rock will undergo in a particular situation.

The method adopted was suggested by the ISRM, (Brown, 1981) and involves a cubic test cell with dial gauges reading to 0.002mm accuracy positioned on three sides of the cell. These are connected to plungers extending into the cell which are positioned against the centre of each of the three faces of the test specimen (see Fig 6.3).

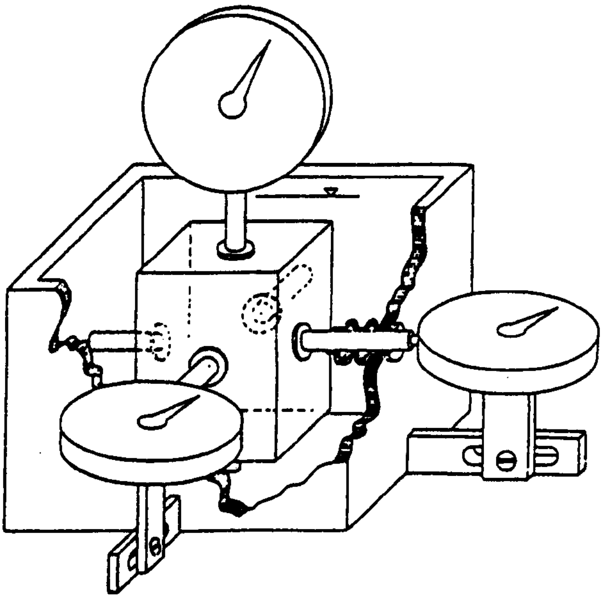


Fig 6.3 Cell and specimen assembly for unconfined swelling tests.

The mudrock samples were pre-cut cubes of between 40-50mm side lengths, two faces were parallel to the bedding. The samples were oven dried at 60°C for 72 hours prior to testing. The cell plungers had 25mm diameter perspex pads attached to them so that a representative area on all three sides of the cube could be monitored. Once the specimen was ready for testing, the dimensions between the gauge points were measured using a micrometer. The specimen was then placed in the test cell, the bearing plates and plungers where then positioned against the sample, the cell lid was securely fastened, and the cell flooded with distilled water. The expansion was measured at regular intervals, the test duration varied from sample to sample, the minimum being 7 hours, and the maximum being 250 hours due to an especially slow response. One test per sample was performed. The results are presented in Table 6.7, where they are presented as maximum strain per axis, total volumetric strain and time duration to ceasation of swelling. The graphs for time versus strain for each sample are presented in Appendix B4.

The unconfined swelling strain for each axis was calculated from the following expression:-

$$\text{Unconfined swelling strain in direction X (Ex)} = \left[\frac{d}{L}\right] \times 100\%$$

x = test axis
d = maximum swelling recorded (mm)
L = initial gauge point distance (mm)

and the volumetric strain from the following expression:-

$$Ev = \frac{(Ex + Ey + Ez)}{3}$$

### *6.3.2.2. Powder free swell test.*

This simple index test first proposed by Gibbs & Holtz (1956) and was intended to measure the swelling susceptibility of clay minerals in soils. It was decided to carry out this test on the samples as it gives an indication of the swelling potential due only to mineralogical effects as the state of the sample eliminates any structural and textural controls.

The test involves placing 10ml of dried powdered rock sample in a 100ml measuring cylinder, adding distilled water to the 100ml mark, thoroughly mixing the contents and then allowing the sample to settle, the final volume of sample being measured after a 24 hour period. Initially the tests were performed using distilled water, but it was found that many of the samples containing organic material did not settle out. The tests were then repeated using a calgon solution which was made by dissolving 33g of sodium hexametaphosphate and 7g of sodium carbonate in 1000ml of distilled water. It was found that the same results were obtained for the samples that settled out in water as in the calgon solution therefore it is considered that calgon has no detrimental effect on the results except to promote total settlement of organic rich samples.

The powder volumetric free swell value was obtained from the following expression:-

$$E_{PD}\,\% = \left[\frac{V_2 - V_1}{V_1}\right] \times 100$$

$V_1$ = volume of sample used in the test.
$V_2$ = volume of settlement of the sample in calgon.

The tests were run in duplicate and good repeatability was found. The average results for powder free swell are presented in Table 6.7.

### 6.3.3. Fracture index.

Microfractures are a common textural feature found in lithified mudrocks. There are generally two types of fractures which are recognised, rough surface microfractures, and slickensided microfractures (Dick, 1992). The effects of microfractures on mudrock durability have been noted by Olivier (1980), Russell (1981), Grainger (1983), Dick & Shakoor (1990) and Dick (1992) who consider these planes of weakness to contribute to weathering and breakdown of mudrocks due to an increase in exposed surface area. Microfractures appear due to the effects of stress relief on mudrocks, and internal discontinuities caused by grain inter-relationships.

The method for quantifying the degree of microfracturing was suggested by Dick (1992) and termed the "microfracture frequency index - $I_{MF}$". The procedure requires the dry cutting of four slabs of the mudrock sample, two parallel and two perpendicular

| Sample. | Ex % | Ey % | Ez % | Ev % | Duration. | $E_{PD}$% |
|---|---|---|---|---|---|---|
| Ca11 | 0.016 | 0 | 0 | 0.005 | 72hr. | 7 |
| Ca12 | 0.046 | 0 | 0 | 0.015 | 150hr. | 7 |
| Ca13 | 0.08 | 0 | 0.008 | 0.029 | 148hr. | 9 |
| O11 | 2.1 | 3.41 | 0.7 | 2.07 | 4hr. | 45 |
| O12 | 4.35 | 0.01 | 0.083 | 1.73 | 7hr. | 33 |
| O21 | 0.102 | 0 | 0 | 0.03 | 79hr. | 10 |
| O31 | 0.43 | 0.04 | 0.024 | 0.165 | 77hr. | 10 |
| S11 | 2.52 | 0.39 | 0.33 | 1.08 | 24hr. | 42 |
| S31 | 1.13 | 0.006 | 0.15 | 0.43 | 95hr. | 7 |
| S32 | 0.07 | 0 | 0.002 | 0.024 | 69hr. | 10 |
| D11 | 1.31 | 0.066 | 0.006 | 0.46 | 54hr. | 0 |
| D12 | 3.25 | 0 | 0 | 1.17 | 129hr. | 52 |
| D21 | 0.57 | 0 | 0 | 0.19 | 12hr. | 30 |
| C1B1 | 2.51 | 0.11 | 0.004 | 0.875 | 56hr. | 50 |
| C1B2 | 4.04 | 0.24 | 0.79 | 1.69 | 28hr. | 30 |
| C1B4 | 0.85 | 0.15 | 0.05 | 0.35 | 45hr. | 33 |
| C1B5 | 3.33 | 0.72 | 0.91 | 1.65 | 196hr. | 45 |
| C21 | 7.76 | 1.31 | 0.303 | 3.12 | 32hr. | 65 |
| C31 | 1.81 | 0.08 | 0.003 | 0.63 | 58hr. | 18 |
| C41 | 3.0 | 0.23 | 0.23 | 1.15 | 23hr. | 59 |
| C51 | 4.87 | 2.86 | 0.64 | 2.79 | 14hr. | 55 |
| C52 | 0.74 | 0.024 | 0.096 | 0.285 | 97hr. | 35 |
| C61 | 3.81 | 0.002 | 0.66 | 1.49 | 9hr. | 40 |
| C71 | 5.09 | 1.31 | 1.26 | 2.55 | 101hr. | 30 |
| C82 | 8.11 | 1.06 | 1.00 | 3.39 | 93hr. | 91 |
| C83 | 0.64 | 0.23 | 0.08 | 0.32 | 128hr. | 45 |
| C92 | 0.64 | 0.026 | 0 | 0.22 | 191hr. | 32 |
| C101 | 4.24 | 0.78 | 0.57 | 1.86 | 74hr. | 65 |
| C111 | 16.6 | 1.79 | 0.50 | 6.3 | 1hr. | 42 |
| C112 | 0.78 | 0.055 | 0 | 0.28 | 32hr. | 69 |
| C121 | 8.66 | 1.77 | 0.95 | 3.79 | 51hr. | 60 |
| C122 | 1.74 | 0.28 | 0.07 | 0.7 | 29hr. | 37 |
| C131 | 5.74 | 0.71 | 0.08 | 2.18 | 24hr. | 33 |
| C132 | 1.73 | 0.097 | 0 | 0.61 | 119hr. | 6 |
| C133 | 2.52 | 0.82 | 1.26 | 1.53 | 4hr. | 55 |
| C141 | 6.99 | 1.36 | 0.42 | 2.92 | 11hr. | 70 |
| C151 | 0.93 | 0.63 | 0.92 | 0.83 | 215hr. | 70 |
| C161 | 0.57 | 0.023 | 0.19 | 0.26 | 29hr. | 55 |
| C171 | 1.85 | 0.16 | 0.51 | 0.84 | 24hr. | 33 |
| C172 | 0.62 | 0.14 | 0.22 | 0.33 | 60hr. | 30 |
| C181 | 1.99 | 0.35 | 0.26 | 0.87 | 35hr. | 37 |

Ex = x axis(perpendicular to bedding). Ey/z = axis perpendicular to the x axis.
$E_{PD}$ = powder free swell test.

Table 6.7 Table of swelling test results.

to bedding, these should have a minimum dimension greater than 50mm. The slabs are then smoothed with fine sandpaper, wiped free of dust and oven dried at 60°C for 72 hours. Dick (1992) found problems with some samples crumbling during cutting and drying, in this study no problems resulted during the dry cutting stage, but some of the samples were found to crumble during oven drying. It was decided to place the sample slabs in small metal trays, and secure them laterally with wooden blocks, this did not prevent the microfractures from opening, but did prevent the samples from falling apart. Once the samples had been dried and cooled, six linear traverses were drawn on the samples, three being at right angles to the other three, and regularly spaced. The traverses were then surveyed and the number of microfractures counted. The microfracture index was expressed as the number of fractures per unit length (f/cm). On a limited number of samples, generally the more durable ones where no microfractures were encountered, the microfractures were recorded following a cycle of submergence of the sample in water for 15 minutes and further oven drying. This was intended to promote the opening of any potential fractures. It failed to produce any further fractures in the most durable material, but in less durable samples, fracture development was promoted. This wetting cycle value is referred to as the "wetting cycle microfracture index - $I_{1MF}$". The data for the microfracture index parallel and perpendicular to bedding, and results for the wetting cycle fracture index are presented in Table 6.8.

### 6.3.4. Point load test.

The point load test is an index strength test for rocks. It is a form of tensile test from which the results can be converted to a uniaxial compressive strength value by means of applying empirical conversion factors.

The point load test has been used for many years for laboratory based research into strength testing. Broch & Franklin (1972) reported experimental results which provided the basis for introducing the test as an economic and reliable index test. They state that the test is a form of indirect tensile test for rock, being a point rather than a linear version of the 'Brazilian' cylinder-splitting test. The test is not strictly a tensile test, as a compressive component is involved during loading, and it is found that the tensile strength of rock in direct pull apart tests is approximately 80% of the point load tensile strength of rock in direct pull apart tests is approximately 80% of the point load index result (ISRM, 1985). The test procedure and equipment has been standardized by the ISRM (1985), and as such their methodology was adhered to.

| | | | | 1 Cycle results. | |
|---|---|---|---|---|---|
| Sample. | ⊥ f/cm. | ∥ f/cm. | Ave $I_{MF}$ | ⊥ f/cm. | ∥ f/cm. |
| Ca11 | 0.09 | 0 | 0.04 | ------- | ------- |
| Ca12 | 0 | 0 | 0 | 0 | 0.04 |
| Ca13 | 0 | 0 | 0 | 0 | 0 |
| O11 | 1.3 | 1.6 | 1.45 | ------- | ------- |
| O12 | 1.4 | 1.5 | 1.45 | ------- | ------- |
| O21 | 0.39 | 0 | 0.19 | ------- | ------- |
| O31 | 0.26 | 0 | 0.13 | ------- | ------- |
| S11 | 0.37 | 0.36 | 0.36 | 2.52 | 1.81 |
| S31 | 0.31 | 0.10 | 0.20 | ------- | ------- |
| S32 | 0.12 | 0.15 | 0.13 | ------- | ------- |
| D11 | 0.2 4 | 0.28 | 0.26 | ------- | ------- |
| D12 | 0.15 | 0 | 0.07 | ------- | ------- |
| D21 | 0.11 | 0.11 | 0.11 | ------- | ------- |
| C1B1 | 0.63 | 0.12 | 0.37 | ------- | ------- |
| C1B2 | 0.28 | 0.4 | 0.34 | ------- | ------- |
| C1B4 | 0.31 | 0.16 | 0.23 | ------- | 0.16 |
| C1B5 | 0.62 | 0.22 | 0.42 | 1.05 | 0.34 |
| C21 | 0.80 | 0.46 | 0.63 | 2.74 | 1.87 |
| C31 | 0.28 | 0.39 | 0.33 | 0.36 | ------- |
| C41 | 1.02 | 0.48 | 0.75 | 3.55 | 2.32 |
| C51 | 0.80 | 0.87 | 0.83 | ------- | ------- |
| C52 | 0.13 | 0 | 0.06 | 0.13 | ------- |
| C61 | 0.30 | 0.25 | 0.27 | 2.45 | 0.54 |
| C71 | 0.21 | 0.10 | 0.15 | ------- | ------- |
| C82 | 0.55 | 0.41 | 0.48 | 3.91 | ------- |
| C83 | 0.07 | 0 | 0.03 | 0.07 | 0 |
| C92 | 0.53 | 0.26 | 0.39 | ------- | ------- |
| C101 | 0.12 | 0.14 | 0.13 | 1.98 | 0.78 |
| C111 | 0.59 | 0.13 | 0.36 | ------- | ------- |
| C112 | 0.15 | 0 | 0.07 | ------- | ------- |
| C121 | 1.10 | 0.67 | 0.88 | ------- | ------- |
| C122 | 0.24 | 0.02 | 0.13 | 1.63 | 0.49 |
| C131 | 0.77 | 0.30 | 0.53 | 1.72 | 1.82 |
| C132 | 0.06 | 0.23 | 0.14 | 0.83 | ------- |
| C133 | 0.13 | 0.24 | 0.18 | ------- | ------- |
| C141 | 0.76 | 0.48 | 0.62 | 3.24 | ------- |
| C151 | 0.50 | 0.14 | 0.32 | 1.67 | 0.99 |
| C161 | 0.32 | 0.19 | 0.25 | ------- | ------- |
| C171 | 0.10 | 0.02 | 0.06 | 0.44 | 0.02 |
| C172 | 0.09 | 0.10 | 0.09 | 0.18 | 0.14 |
| C181 | 0.44 | 0.16 | 0.30 | ------- | ------- |

⊥ = perpendicular to bedding. ∥ = parallel to bedding. f/cm = fractures per cm.
Ave. = average $I_{MF}$ of the sample over both axis.

Table 6.8 Results of the microfracture index determinations ($I_{MF}$).

In view of the controlling influence of tensile failure in slaking processes, the test results were considered to be highly relevant in this study. The test was performed on each sample to determine its relative strength in terms of point load index values ($I_s$) rather than being converted to UCS values. Norbury (1986) states that the point load value is a recognisable quotable measured rock strength value (see Table 6.9) and that when the value is converted to a UCS value using empirical multipliers then the results may become unreliable as the values for the multiplier quoted in the literature range between 8 and 45. Pells (1975) recommends that if $I_S$ results are to be converted to UCS values then actual UCS tests should be carried out on the rocks concerned as a check.

| Strength | Point load strength index (MPa) |
|---|---|
| Extremely high strength | >10 |
| Very high strength | 3 - 10 |
| High strength | 1 - 3 |
| Medium strength | 0.3 - 1 |
| Low strength | 0.1 - 0.3 |
| Very low strength | 0.03 - 0.1 |
| Extremely low strength | <0.03 |

Table 6.9 Point load strength classification (Broch & Franklin, 1972)

The test procedure involves loading a block or core section of rock by the application of a compressive stress through two opposing curved steel surfaces until it fails in tension. The ELE portable test rig which was used (Courtesy of Mr A Deaves of Sheffield City Works Department) utilises two steel cones which apply compressive stress in opposite directions at the contact of the cone point and the specimen. The load is applied continually by a hydraulic hand pump, and the pressure at failure recorded from a hydraulic dial gauge. The ISRM (1985) suggest that the pressure be applied at a rate that will cause the sample to fail within 60 seconds of commencing the test, and also they provide the guidelines as to the test sample dimensions shown in Figure 6.4.

The point load determinations were performed on dry cut blocks of mudrocks. After cutting, the sample blocks were oven dried at 60°C for 72 hours. Since the test is a dry point load index it only measures the truly tensile component of the rock with no additional influence from pore water, therefore making the results more comparable

| Sample. | $I_S$ ⊥ (MPa) | $I_S$ ⇈ (MPa) | $I_A$ | UCS⊥(MPa) | UCS⇈(MPa) |
|---|---|---|---|---|---|
| Ca11 | 14.6 | 4.5 | 3.2 | 229 | 194.2 |
| Ca12 | 15.8 | 8.0 | 2.0 | 272.3 | 255.5 |
| Ca13 | 21.5 | 7.5 | 2.9 | 343 | 295 |
| O11 | 2.6 | 1.1 | 2.4 | ------- | ------- |
| O12 | 2.1 | 0.1 | 21.0 | ------- | ------- |
| O21 | 14.0 | 1.2 | 11.7 | ------- | ------- |
| O31 | 16.4 | 1.9 | 8.6 | 168 | 79 |
| S11 | 4.1 | 1.6 | 2.6 | ------- | ------- |
| S31 | 6.9 | 1.0 | 6.9 | ------- | ------- |
| S32 | 10.8 | 7.7 | 1.4 | 187 | 88 |
| D11 | 10.6 | 1.9 | 5.6 | ------- | ------- |
| D12 | 10.2 | 1.7 | 6.0 | ------- | ------- |
| D21 | 7.5 | 0.9 | 8.3 | ------- | ------- |
| C1B1 | 3.3 | 0.4 | 7.2 | ------- | ------- |
| C1B2 | 7.2 | 1.1 | 6.5 | ------- | ------- |
| C1B4 | 9.2 | 2.2 | 4.2 | ------- | ------- |
| C1B5 | 5.7 | 1.1 | 5.2 | ------- | ------- |
| C21 | 4.1 | 0.9 | 4.5 | ------- | ------- |
| C31 | 14.8 | 8.7 | 1.7 | 228 | ------- |
| C41 | 0.4 | 0.2 | 2.0 | ------- | ------- |
| C51 | 1.3 | 0.5 | 2.6 | ------- | ------- |
| C52 | 4.1 | 1.1 | 3.7 | ------- | ------- |
| C61 | 2.2 | 0.9 | 2.4 | ------- | ------- |
| C71 | 4.3 | 1.3 | 3.3 | ------- | ------- |
| C82 | 0.6 | 0.2 | 3.0 | ------- | ------- |
| C83 | 5.5 | 3.5 | 1.6 | ------- | ------- |
| C92 | 4.0 | 1.4 | 2.8 | ------- | ------- |
| C101 | 4.5 | 2.2 | 2.0 | ------- | ------- |
| C111 | 1.3 | 0.2 | 6.5 | ------- | ------- |
| C112 | 5.1 | 1.6 | 3.2 | ------- | ------- |
| C121 | 4.2 | 0.6 | 7.0 | ------- | ------- |
| C122 | 3.8 | 0.6 | 6.3 | ------- | ------- |
| C131 | 2.9 | 0.7 | 4.1 | ------- | ------- |
| C132 | 4.8 | 2.0 | 2.4 | ------- | ------- |
| C133 | 3.6 | 2.1 | 1.7 | ------- | ------- |
| C141 | 2.1 | 0.8 | 2.6 | ------- | ------- |
| C151 | 2.8 | 0.9 | 3.1 | ------- | ------- |
| C161 | 3.9 | 0.5 | 7.8 | ------- | ------- |
| C171 | 4.3 | 0.7 | 6.1 | ------- | ------- |
| C172 | 5.5 | 1.1 | 5.0 | ------- | ------- |
| C181 | 4.6 | 0.3 | 15.3 | ------- | ------- |

$I_S$ = Point load index ⊥ = Perpendicular to bedding. ⇈ = Parallel to bedding.
$I_A$ = Point load anisotropy. UCS = Unconfined compressive strength.

Table 6.10 Rock strength results from point load and UCS testing.

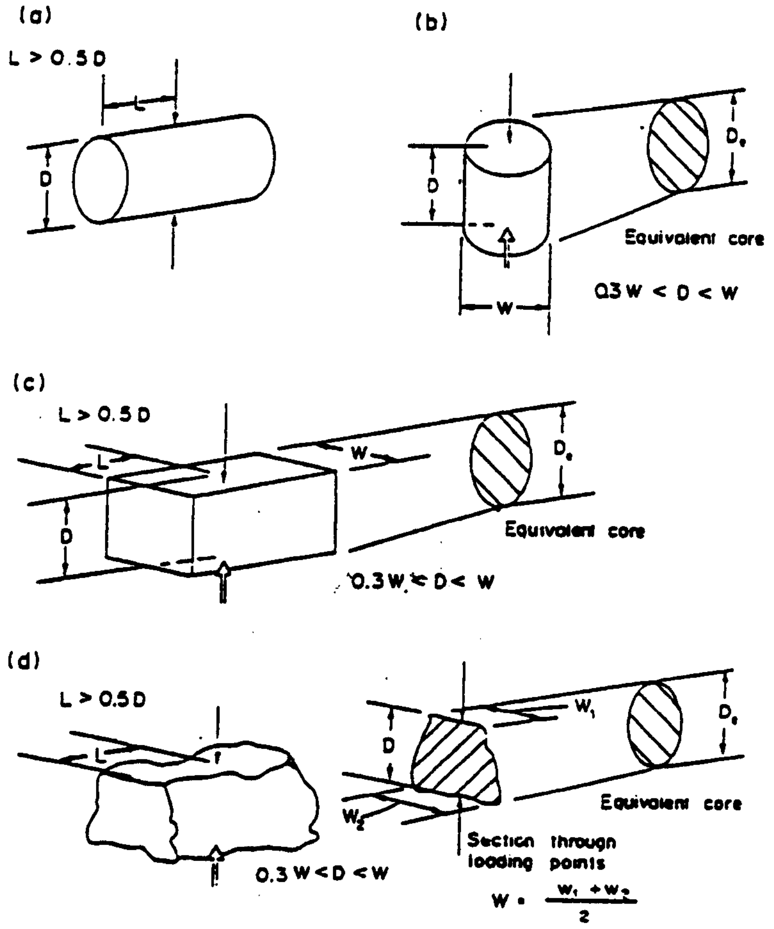


Figure 6.4. Specimen shape requirements for (a) diametral test (b) axial test (c) block test, and (d) irregular lump test, for point load index determinations (ISRM, 1985).

between different mudrock samples. The determinations were performed both parallel (⇑) and perpendicular (⊥) to the bedding direction. For each sample a minimum of twenty determinations was made, ten per direction, and the point load index for each direction was calculated from the average five results to avoid erroneous results using the following expression.

$$I_s = \frac{P}{d^2}$$

P = applied load in (N)
d = distance between loading platterns
at failure in (mm).

The results are presented in Table 6.10 together with the calculated anisotropy index, which is calculated from the $I_s$ ($\perp$) divided by $I_s$ ($\Uparrow$) value.

It was attempted to perform UCS tests on the samples as a check, but most of the samples tended to deteriorate during the preparation stage. The only samples from which testable core specimens were obtained are:- Ca.1.1; Ca.1.2; Ca.1.3; 0.3.1; S.3.2; and C.3.1, the average UCS values for these samples are presented in Table 6.10. This was determined according to the suggested method of ISRM (Brown, 1981)

## 6.4. Discussion of results.

The significances and interelationships of the physical and engineering properties are analysed in detail in Chapter 9, here it is intended to present a short discussion of the tests and results.

Moisture conditions:

Natural moisture content results generally reflect the in situ weathering states of samples. When the results in Table 6.1 are compared with water absorption results it is seen that data for samples O11, O12, O21, D12, D21, C1B4, C52, C92 and C172 have values of natural moisture content which closely resemble values for water absorption (as seen in Figure 6.5) suggesting that these samples were all found in a near saturated state. These samples were all collected from near zones of water seepage which will influence their natural moisture contents. Sample C92 had been exposed for 3 - 4 months and had probably been affected by weathering and rainfall. Results for water absorption and water adsorption as seen in Figure 6.6, appear to have similar trends for the data set. The samples with the greatest values for both these parameters are O11, O12, C21, C41, C51, C82, C101, C111, C121, C131, C141, and C161. Controls on water absorption tend to be both physical such as effects of voids and discontinuities and mineralogical controlled by adsorption by water susceptable clay mineral phases. On the other hand adsorption tends to be controlled just by the mineral phases in particular the amount and type of clay present, this relationship is demonstrated by the close trend of the two parameters. The effects of clay mineral species moisture adsorption also affects the natural moisture content of mudrock samples as can be seen in Figure 6.7.

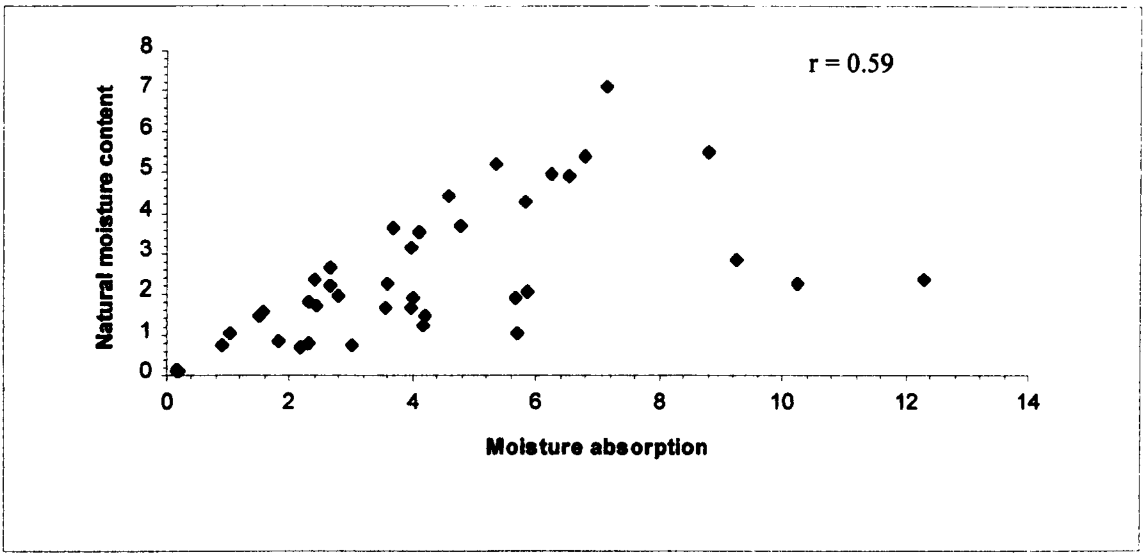


Figure 6.5. Relationship between natural moisture content and moisture absorption.

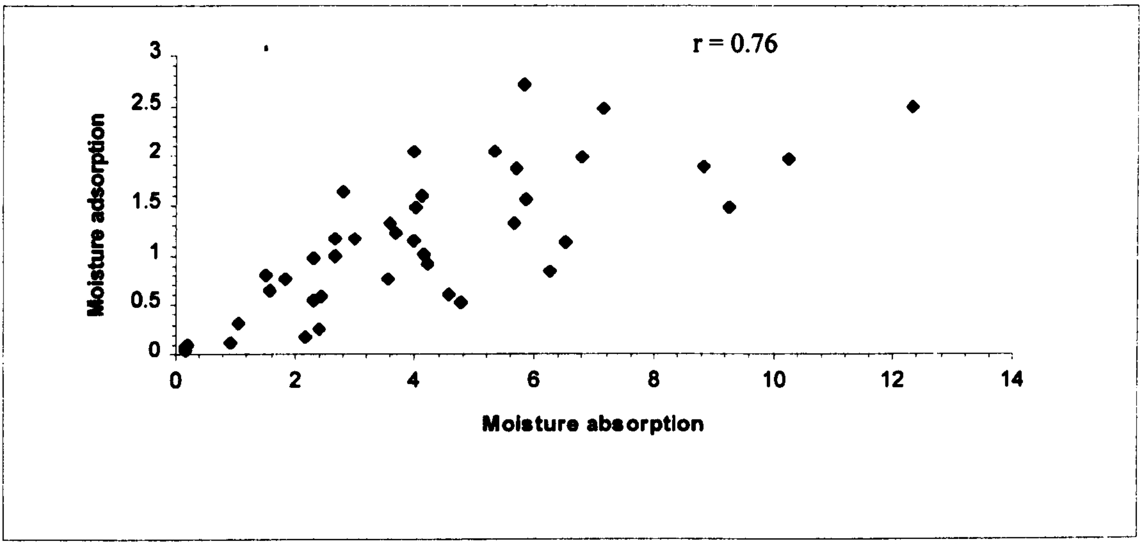


Figure 6.6. Relationship between moisture absorption and moisture adsorption.

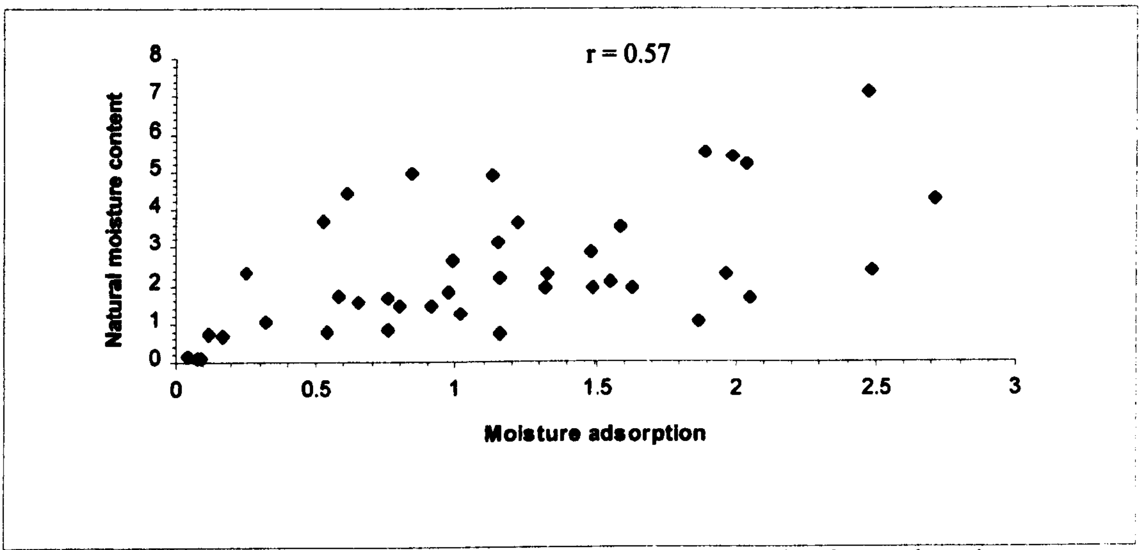


Figure 6.7. Relationship between natural moisture content and moisture adsorption.

## Porosity determinations:

As shown in Table 6.2, the total porosities of the samples are relatively low ranging from 1.7% - 10.8%, which is a range expected in a suite of indurated mudrocks that have been affected by cementation, mineral recrystallization and compression reducing pore space. Generally a weak relationship exists between the total and relative porosity values as seen in Figure 6.8. The relative porosity values are lower than the total porosity values since diagenetic processes such as recrystallization and cementation tend to isolate pore space which is not measured when determining relative porosity. Sample C52 has a relative porosity value which is slightly larger than its total porosity value, this sample is a siltstone which may have contained a microfracture on the fragment tested for relative porosity, therefore producing the anomolous result. There must also be slight inaccuracy in the determination of both of the porosity parameters. Sample C161 shows a value for relative porosity which is much greater than total porosity. This may have arisen due to to a non-representative weathered sample having been used for the relative porosity determination. The results for average pore sizes range from 0.01 - 0.04μm with exceptions being sample D21 - 0.10μm and sample S32 - 0.15μm. These results probably reflect the sizes of the connecting pore capilliaries as opposed to actual pore sizes. This is seen in Figure 6.9, which shows a linear distribution of pore size values ranging between 0.1 to 0.3 μm for the majority of samples analysed which have a range of relative porosity values between 0.5 to 12%. Samples Ca11, Ca12, Ca13, O21 and C1B4 have large average pore size values, these are probably due to microfratures being present in samples which otherwise have negligable relative porosity values. The relationship between moisture absorption and total porosity seen in Figure 6.10, presents a poor correlation in values. It would be expected that a strong correlation should exist between these two parameters, since moisture absorption is an indirect measure of void distribution, but in mudrocks the development of microfractures on exposure to water controls the water absorption.

## Slaking tests:

Five cycle slake durability determinations were carried out for all the samples, but the results in Table 6.3 show no drastic sample slaking beyond the third test cycle.

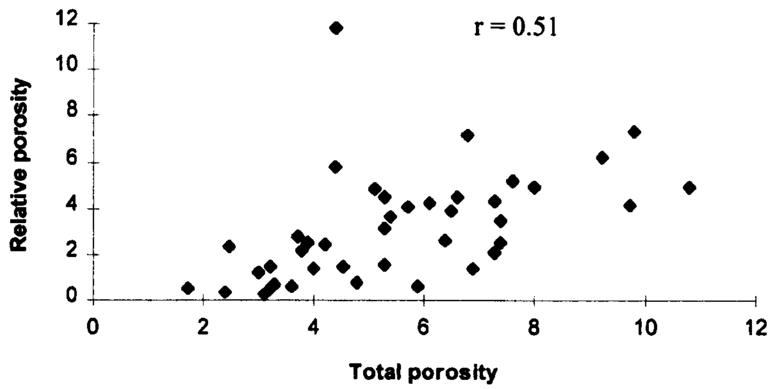


Figure 6.8. Relationship between total and relative porosity results.

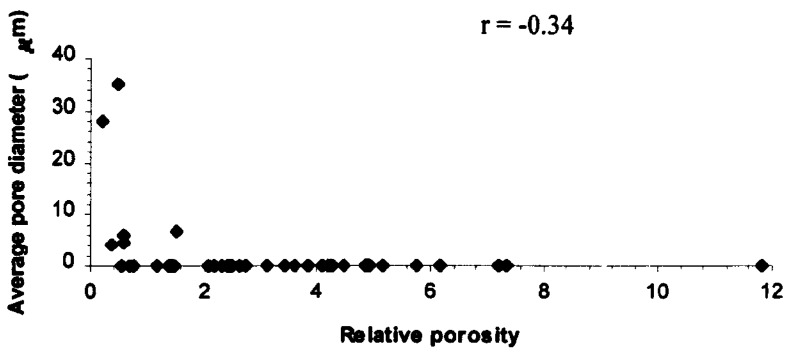


Figure 6.9. Relationship between the average pore diameter and relative porosity results.

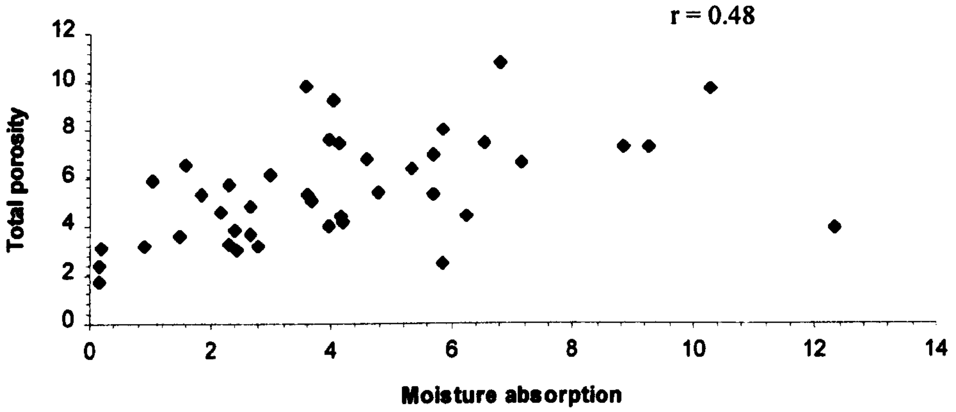


Figure 6.10. Relationship between total porosity and moisture absorption.

Based on Taylor's (1988) durability classification scheme which uses the value from the third test cycle, samples O11, O12, C21, C51, C52, C61, C82, C111, C131 and C131 can be classed as non-durable, the rest of the samples being classed as durable. Particle size analysis was performed on the samples to evaluate the extent of breakdown during the slake durability test and the data are presented in Appendix B3. It was found that the very durable samples in the data set with $Id_3 > 95\%$, namely Ca11, Ca12, Ca13, O21, O31, S31, S32, D11, D12, D21, and C1B4 produced negligable breakdown debris therefore particle size analysis was not carried out. It can be seen from the particle size distribution curves for samples C1B5, C41, C61, C71, C111, C121, C122, C141, C151, C161, C172 and C181 which are also classed as durable, that there was considerable sample breakdown within the size range of 2 - 19mm suggesting that these samples are liable to slaking. This is not evident from the results of the slake durability test as the standard mesh size for the classification of slake durability is 2mm and the breakdown produces fragments larger than this. The particle size distribution curves suggest that the fragment sizes produced by the slake durability test tend to be sand sized, in the region of 0.06 - 2mm which for the non-durable samples ranges from 46 - 87% of the resulting debris. . This is a reflection on the bias of the test to reduce fragments to this size range rather than reduce the material to its fundamental particles. The grain size distribution curves for all the samples show that none of the samples produced >10% material in the <2μm size fraction. In Figure 6.11 a positive relationship ($r = 0.80$) is seen between the mean grain size of the slake durability sample debris and the slake durability test especially for the less indurated mudrocks. This suggests that less durable material tends to be more loosely held by diagenetic bonds such as cementation and recrystallization therefore producing greater breakdown of the samples down to a smaller aggregate size within the sand to silt size range. This would confirm the argument that it is futile to base the classification of indurated mudrocks on grain size distribution data as the dissaggregation process produces material in the silt to sand size range.

Results from the modified jar slake test also show that the samples classified as being non-durable based on the slake durability test tend to have a high static slake susceptibility of 7 achieved at a fast rate. Samples C1B5, C41, C71, C101, C121,

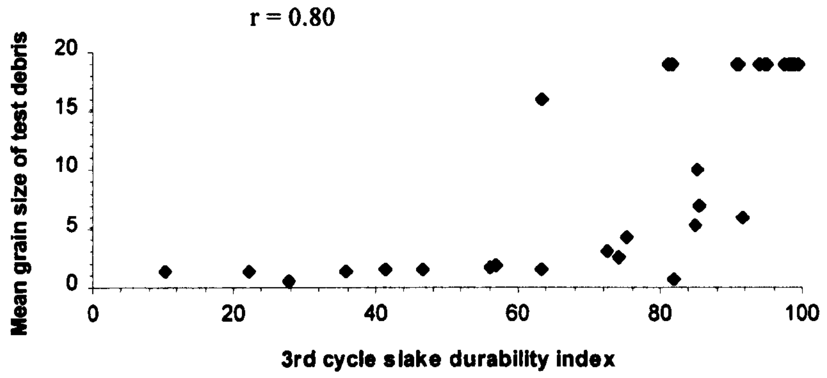


Figure 6.11. Relationship between $Id_3$ and mean grain size of the slaked debris.

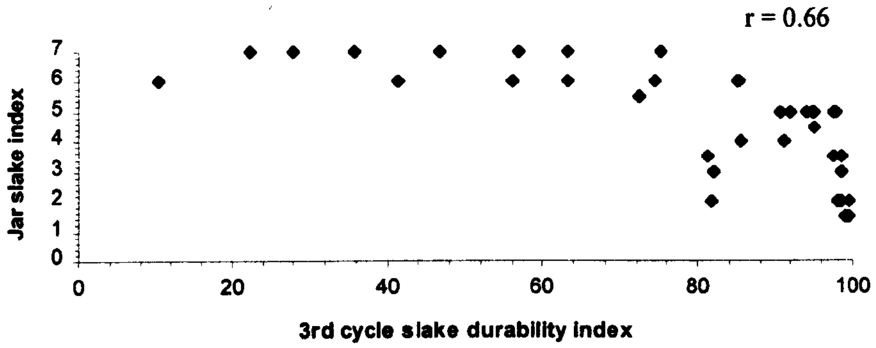


Figure 6.12. Relationship between $Id_3$ and the jar slake index.

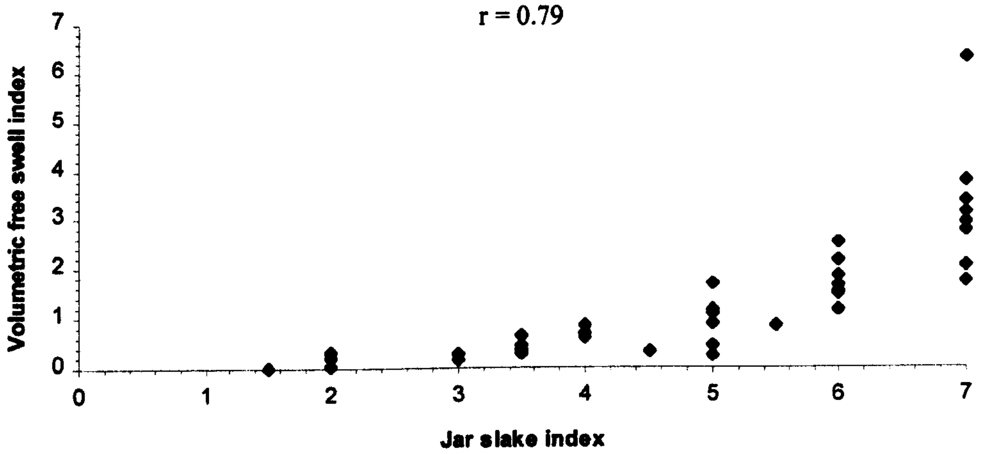


Figure 6.13. Relationship between volumetric free swell and jar slake index.

C141, and C151 have jar slake values showing them also to be prone to slaking, but at a slow rate. These samples are all classed as being durable based on their $Id_3$ value with results between 63 - 85%. From the size distribution curves there is breakdown of particles within the size range of 2 - 19mm within the test drum but this is not evident evident from the durability results. The results from the modified jar slake test demonstrate the advantages of using the jar slake test in conjunction with the slake durability test for durability classification of mudrocks. In Figure 6.12 a clear trend is seen to exist between values of Ij and $Id_3$ with low durability samples having low values of $Id_3$ and high values of Ij and durable samples having high $Id_3$ values and low Ij. This relationship is investigated further in Chapter 9.

Swelling tests:

The unconfined swelling test results show that samples identified as having high slaking susceptibilities from the jar slake test also tend to have the highest volumetric swelling values ranging from $E_v$ = 1 - 6.5%. This link between results from the unconfined swelling test and jar slake test as seen in Figure 6.13, is to be expected as they are both being controlled by expansion along discontinuities as seen by the relationships with microfracture index presented in Figures 6.14 to 6.16, also suggesting that less durable samples have higher swelling capacities. From the 18 samples identified as having high volumetric swelling results and high jar slake values, only 9 are classed as being non-durable based on results of the slake durability determinations. This shows the limitations of the slake durability test at identifying samples proned to swelling and slaking. This can be seen in Figure 6.17 which shows much scatter of data points along a obvious trend line. This is a reflection of the constraint due to the drum mesh used in the slake durability test on which the classification is based. It can be seen from the triaxial swelling plots presented in Appendix B4, that in all the samples the most prominent and, in some cases the only, direction of swelling tends to be perpendicular to the bedding direction. This highlights the control that lithological effects such as lamination and preferred clay mineral orientation exert upon the presence and orientation of discontinuities. Samples C71, C82 and C121 tend to have significant swelling capacities (generally in excess of 1%) in all three of the axial directions and

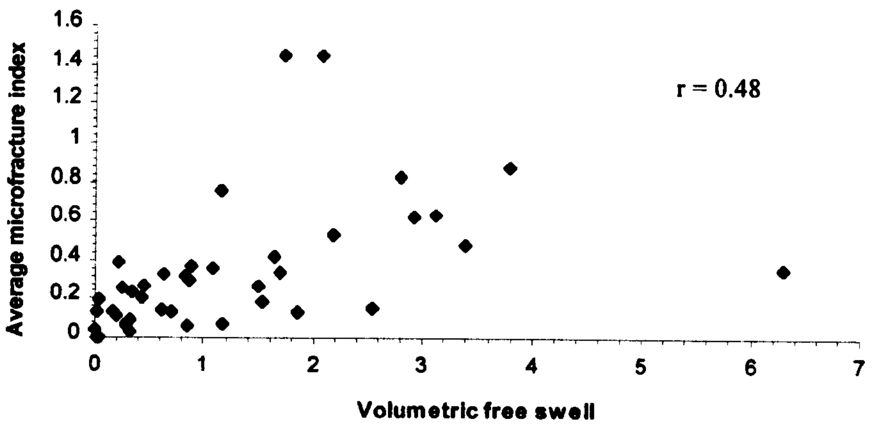


Figure 6.14. Relationship between volumetric free swell and average microfracture index.

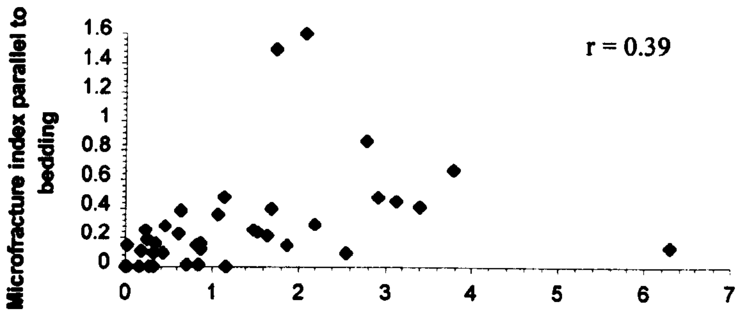


Figure 6.15. Relationship between volumetric free swell and microfracture index parallel to bedding.

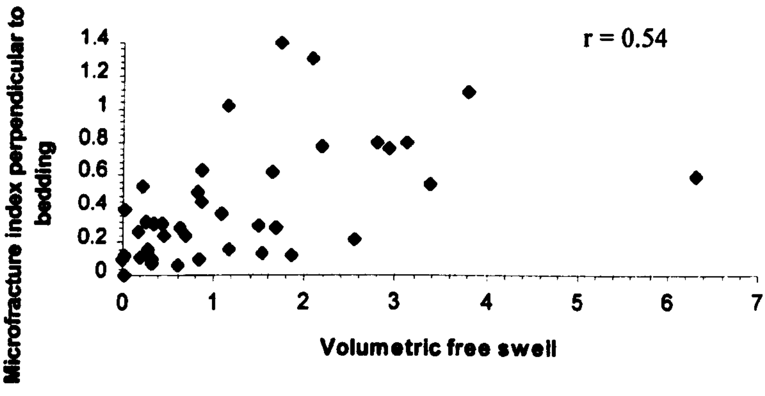


Figure 6.16. Relationship between volumetric free swell and microfracture index perpendicular to bedding.

samples O11, C21, C51, C111, C131 and C141 in two of the axial directions, these samples tend to have poorly developed laminations or slight fissility but the swelling results suggest they have more random arrangements of clay minerals. This is confirmed by the SEM study data presented in Chapter 7.

The powder free swell test is intended to provide a rapid indication of the swelling susceptibility of clay minerals present within the samples since all structural constraints within the mudrocks have been removed during the grinding process. The results from this test show that samples with large powder swelling results tend to be those with high jar slake susceptibilities and triaxial free swell values as from Figure 6.18. This suggests that for these samples, mineralogical as well as lithological controls, govern their engineering performance.

Microfracture index:

Fracture index counts are generally greater when measured on rock slabs which have been cut perpendicular to the bedding. Microfractures develop both along internal rock discontinuities and as a result of stress relief. The average microfracture index count, which is the average of fracture count results obtained parallel and perpendicular to the bedding direction is considered as a more valid parameter than single direction fracture measurements. The average microfracture index result will give an indication of the possible extent of breakdown of a sample as controlled by small internal discontinuities. The average $I_{MF}$ values range from 0 - 0.88 f/cm, with the exception of samples O11 and O12 both of which have values of 1.45 f/cm. Some of the samples identified as being non-durable in the slake durability test tend to have high $I_{MF}$ values, usually >0.45 f/cm, but there does not seem to be a strong relationship between jar slake susceptibility and high $I_{MF}$ counts. The standard microfracture index count only determines existing microfractures which would normally be very difficult to observe on a unprepared mudrock sample block. The wetting cycle $I_{MF}$ test, which was only carried out on a limited number of samples, produces a much closer correlation with jar slake results. This is evident in samples Ca12, Ca13, C31, C171 and C172 which have low 1 cycle $I_{MF}$ counts and low slake susceptibilities, and samples S11, C21, C41, C61, C82, C101, C131, C141, and C151 which have high slake susceptibilities and also large 1 cycle microfracture counts.

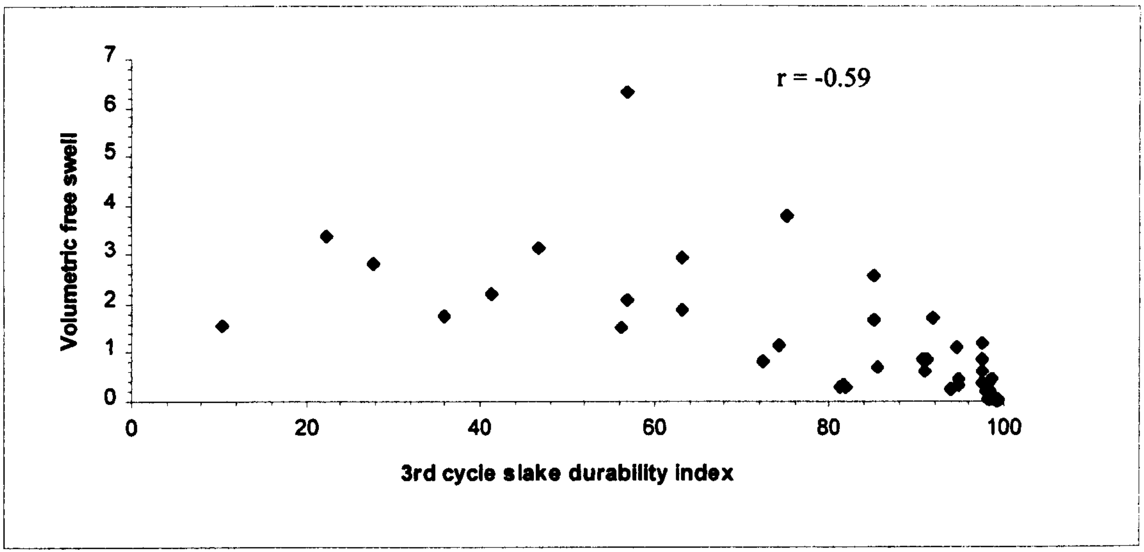


Figure 6.17. Relationship between Id$_3$ and volumetric free swell.

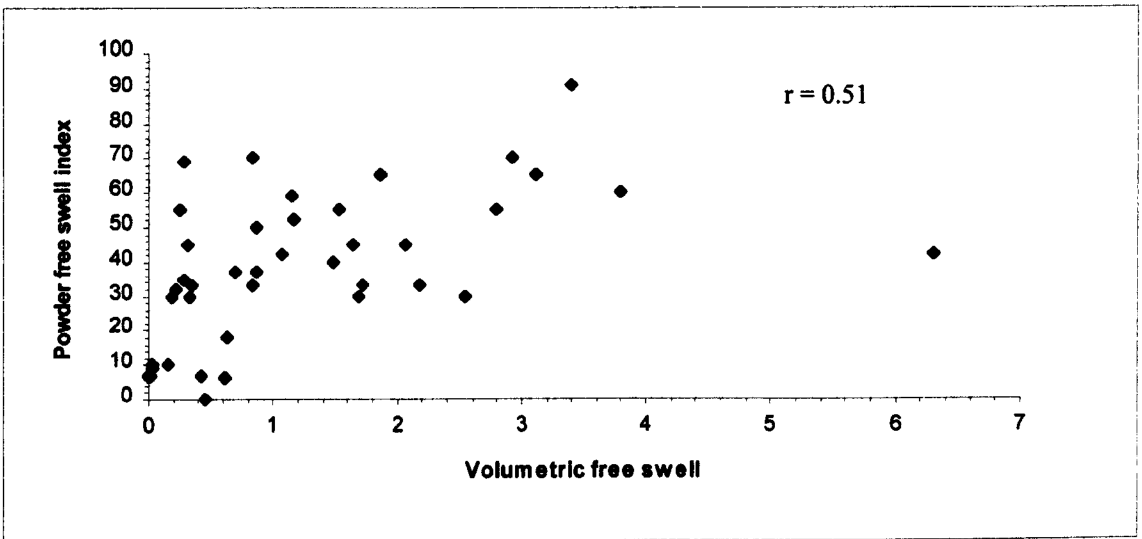


Figure 6.18. Relationship between volumetric free swell and powder free swell.

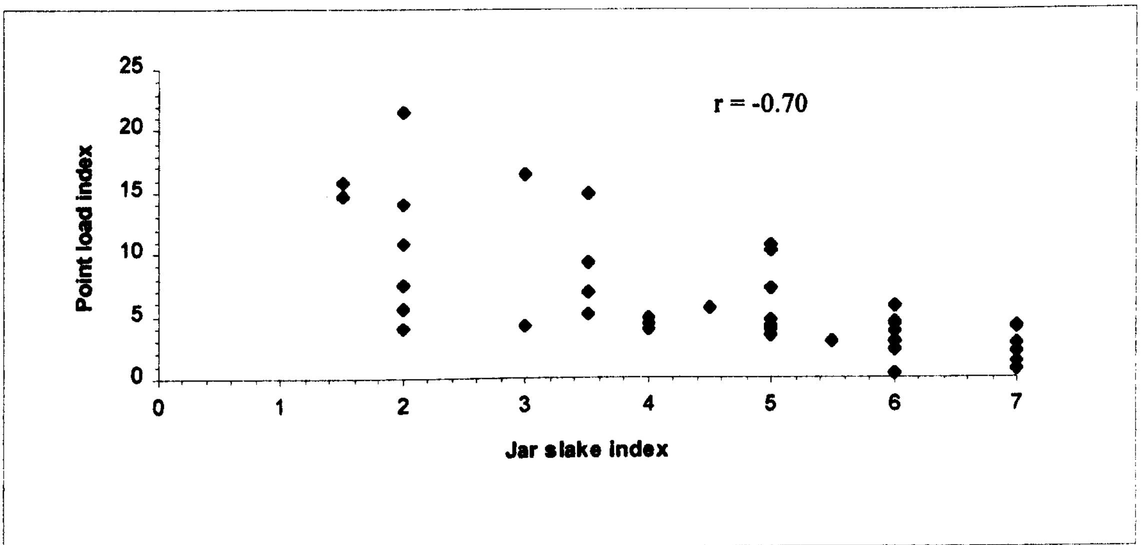


Figure 6.19. Relationship between point load strength and jar slake index.

Rock strength testing:

The data from the point load strength test based on the strength classification presented in Table 6.12 which are applied to test results obtained normal to laminations shows that the samples range from medium strength to extremely high strength mudrocks.

As expected, the samples with low slaking and swelling susceptabilities tend to be grouped in the extremely high strength category, with the remaining samples ranging from very high strength to medium strength. It can be generally seen that the stronger samples tend to be those less susceptible to slaking showing that higher tensile strengths tends to reduce susceptibility to slaking, since the tensile strength must be exceeded before slaking commences. The relationship between strength and jar slake index is presented in Figure 6.19. The ISRM (1985) suggest that a point load anisotropic strength index ratio of approximately 1.0 is indicative of quasi-isotropic rocks, whereas higher values suggest that the material is anisotropic. Results indicating samples approaching almost quasi-isotropic conditions are seen for samples S32, C31, C41, C83 and C133 whose results range between a ratio value of 1 - 2. Samples S32, C31, and C83 are laminated siltstones and as is evident from the SEM analysis data presented in Chapter 7, silica cementation and carbonate cementation in the case of C31 has resulted in an almost quasi-isotropic condition. Sample C41 is a non-laminated highly calcareous mudstone ( see Table 5.12) and sample C133 is a non-laminated, massive kaolinitic seatearth (see Table 5.12). The anisotropic index ratio values for most of the

| **Point load strength classification catagories.** | **Samples.** |
|---|---|
| Extremely high strength: >10 MPa. | Ca11, Ca12, Ca13, O21, O31, S32, D11, D12, C31. |
| Very high strength: 3 - 10 MPa. | S11, S31, D21, C1B1, C1B2, C1B4, C1B5, C21, C52, C71, C83, C92, C101 C112, C121, C122, C132, C133, C161, C171, C172, C181. |
| High strength: 1 - 3 MPa. | O11, O12, C61, C111, C131, C141, C151. |
| Medium strength: 0.3 - 1 MPa. | C41, C82. |

Table 6.12 Point load test strength classification of the mudrock samples.

remaining samples range from 2 - 9 with higher values corresponding to samples that are evidently fissile or laminated. Samples O11, O12, C181 have values between 10 - 20, these are laminated samples which have undergone a degree of weathering which has probably caused weakening along the lamination plains since all three were obtained from sites suffering from water logged conditions.

In general it can be concluded that influences do exist between different rock properties which influence their durabilities. It can be seen that the higher porosities and fracture index values are associated with samples of low durability, which also tend to have higher swelling potentials and lower strength values. The low sensitivity of the slake durability test has been shown, and therefore its use should be restricted just to distinguish between durable and non-durable material. The slake durability test should be conducted in conjunction with the modified jar slake test which is more sensitive to the rate and extent of slaking development in mudrocks.

# Chapter 7.

# Diagenetic and textural studies.

## 7.1. Introduction.

The diagenetic rank and history of a mudrock is important as it enables the compositional and compaction history to be placed in context with the weathering and engineering behaviour of the rock.

With increasing depth of burial there is an increase in overburden pressure related to the thickness of the sediment and temperature increases which relates to the local geothermal gradient and thermal conductivity of the rock. With consolidated clays maximum burial depth can be estimated from the laboratory loading curves measured by the oedometer test (Smith, 1978 and Campbell, 1993). Unfortunately this is not possible for mudrocks which have undergone geological ageing which results in cementation and recrystallization. As a sedimentary column increases in thickness, clay minerals undergo a series of diagenetic changes in composition and crystal size (crystallinity) in response to the increase in temperature and confining pressures. The most impressive reaction is the progressive illitization of smectite clay species via intermediate stages of mixed-layer illite-smectite. It is a process that has been recorded in numerous basinal studies (Weaver, 1959; Dunoyer de Segonzac, 1970; Foscolos and Kodama, 1974; Pearson et al, 1982 etc.). This clay mineral change has been used as a means of estimating the depth of sediment burial, but for such estimations it is invariably assumed that the starting mineralogy is pure smectite, which is not necessarily the case (Jeans, 1989). In most sedimentary basins with an average geothermal gradient of ~30°C/km (Merriman and Kemp, 1996) the conversion to ~60-80% illite in mixed-layer illite-smectite occurs by a depth of around 3-4 km, after which difficulties arise in interpreting the X-ray diffraction curves as the smectite component occurs as a shoulder on the 10Å illite peak. At this point illite 'crystallinity' becomes a useable and sensitive measure of burial diagenesis. It is important to appreciate that the final mineralogy depends on the sedimented mineral assemblage as well as such processes which give rise to changes in mineralogy.

Another significant qualitative reaction controlled by temperature is the maturation of organic material. This is of importance to the hydrocarbon industry, as at burial depths of ~3-4 km, changes take place distilling the organic constituents into oil, and by ~6-8 km depth of burial the increased temperature 'cooks' the oil leaving only gas as the hydrocarbon component (Merriman and Kemp, 1996). These changes are also relevant to the coal industry in the conversion of organic matter from low grade lignitic coal with a high volatile content to high grade anthracitic coals with very low volatile contents (Stach et al, 1982). Progressive maturation has been found to be associated with increases in the reflectance of vitrinite. Vitrinite which consists of cell wall material, is the most commonly occurring organic component. Studies of vitrinite reflectance have wide acceptance in the evaluation of hydrocarbon reservoirs and values of coal rank. It has been applied to many diagenetic studies to determine the rank of organic bearing sediments, and in most cases has worked well when used in conjunction with illite 'crystallinity' studies (Kisch, 1980; Hillier and Clayton, 1989; Pearce et al, 1991; Spotl et al, 1993; Velde and Lanson, 1993, etc.).

Estimates of burial depths can be based on estimates of temperature and pressure conditions as indicated by mineralogical studies, but for more indurated mudrocks including geologically mature and non-remouldable material as has been used in this study, such methods do not provide reliable estimates of burial depth.

From the point of deposition due to progressive burial, the fabric of clays and mudrocks is continually changing. Initially, depending upon the electrolytic condition of the depositional environment (Van Olphen, 1963; Moon and Hurst, 1984) clays are deposited as flocs or individual grains. In these two types of deposition, clay particles which are platy in shape are formed into edge-to-edge or face-to-face arrangements depending on the electrolyte concentration and cation valency. This gives the resulting deposit a relatively high porosity and water content. Compaction associated with deep burial destroys such structures, so the resultant clays develop tighter packing. This reduction in porosity is associated with rotation and reorientation of clay particles so that the crystallographic C axes tends towards a parallel arrangement with the major principle stress, where the latter generally acts vertically. These textural changes, including recrystallization and cementation, play an important role in the weathering performance and engineering behaviour of the subsequent mudrocks (Taylor, 1988; Dick and Shakoor, 1992; Dick, 1992). With standard petrographic thin section analysis it is difficult to obtain much information from mudrocks (Blatt et al., 1980). In thin section observation of the silt and clay size fractions are usually limited to observations of grading or recrystallization/dissolution of the silt sized quartz fraction. Clay minerals cannot be seen in thin section apart from appearing as a brown amorphous mass due to their small grain size. Scanning electron microscopy (SEM) can resolve individual mineral grains down to a resolution of $10^{-3}$ microns (Lee, White and Ingles, 1983), so mineral inter-relationships, orientations, packing and voids can be studied, but it is difficult to distinguish between the clay mineral types as they tend to occur as similar appearing anhedral masses or broken grains. The use of backscatter secondary electron analysis (BSE) during SEM work allows mineral species to be distinguished. The technique operates on the basis of density contrasts produced by chemically induced differences in the absorption or reflection of electrons. Using BSE, mineral species and cementation can be studied down to a submicron level. A complete characterisation of mudrocks requires the application of all three of the above mentioned microscopic techniques in combination. These techniques have formed the basis of textural investigations of the mudrocks in this study. The individual techniques are described in greater detail in Section 7.4.

## 7.2. Illite 'crystallinity'.

### 7.2.1. Introduction.

Many of the deep burial studies which map out clay mineralogy changes with depth have been carried out on Cenozoic and Mesozoic sedimentary basins (Weaver, 1989), which have not been affected by excessive burial beyond ~3-4 km, nor uplift, thrusting or other major tectonic events. In mudrocks which have been subjected to burial depths in excess of 4 km, it becomes progressively more difficult to estimate the percentage of illite in illite/smectite. The smectite component no longer appears as a discrete peak on the X-ray diffraction trace, but as a shoulder on the high portion of the

10Å illite peak. Since the crystallite thickness increases, illite 'crystallinity' can be used to monitor these progressive changes. The mudrocks in this study are indurated types which now possess less than 15% smectite in the mixed-layer illite/smectites. Illite 'crystallinity' has therefore been chosen as one of the diagenetic rank parameters.

Weaver (1960) was the first to observe the modifications to the shape of the 10Å illite X-ray diffraction peak in relation to increasing diagenetic and metamorphic grade in mudrocks. He defined this as the 'sharpness ratio', which is the ratio of the height intensities of the 10Å and 10.5Å positions of the illite peak above background. It was found by Kubler (1968) that this method worked well in low grade mudrocks but as the grade increased, the errors increased due to difficulties in accurately determining the heights of narrow peaks. Kubler proposed an index which is the width, expressed as °2θ, of the 10Å illite X-Ray diffraction peak at half height above background. He defined three zones of very low grade metamorphism based on the values of this Kubler index:-

| Zone |  | °2θ |
|---|---|---|
| Diagenetic | = | >0.42 |
| Anchizone | = | 0.42-0.25 |
| Epizone | = | <0.25 |

Kubler (1967) defined illite 'crystallinity' as the degree of ordering in a crystalline lattice, but omitted to specify what he meant by ordering. Subsequently, Kubler (1984) therefore proposed changing the term, but since it had gained such wide acceptance, Frey (1987) proposed the term be retained but the term 'crystallinity' be placed within inverted commas.

The mechanisms of illite 'crystallinity' are still not clearly understood and several theories have been proposed. Eberl & Srodon (1988), and Beavins & Robinson (1992), based upon the TEM work, proposed an Ostwald ripening mechanism by which illite-smectite expandability decreases as a result of the growth of thicker illite crystallites at the expense of thinner ones, usually by dissolution. Ahn and Peacor (1986) who based their findings upon TEM studies and suggested a diffusion mechanism in which packets of illite grow within a smectite matrix. The reaction mechanism shows that illite-smectite expandability and illite 'crystallinity' represent an indirect measure of reaction extent rather than specific pressure-temperature-depth conditions (Pearce, Clayton and Kemp, 1991). It is primarily controlled by temperature and time, with other controlling factors being pore-fluid chemistry, initial smectite composition and porosity/permeability conditions of the rock. It is this development of larger, thicker crystals (crystallite thickness) with advancing grade which is measured by the Kubler index. Unfortunately the index loses sensitivity within the epizone (Beavins and Robinson, 1992; Merriman and Kemp, 1996) which is generally beyond a burial depth of 12 km by which stage mudrocks have generally been converted by regional metamorphism to slates. As such they tend to become durable engineering material having lost their propensity for shrink-swell and slaking behaviour. Work by Frey (1987) indicates that illite 'crystallinity' measurements need careful interpretation. There are factors that affect the measurements in illite crystallite thickness:

- Temperature - believed to be the most important control mechanism.
- Fluid pressure - considered to be of negligible importance.
- Pressure- found to occasionally play a role, as shown by Robertson and Merriman (1985) in an analytical study on a regional scale in North Wales.
- Time - From the large amount of evidence it is evident that time influences 'crystallinity', where it is suggested that the longer illite remains at a constant temperature, the better the development of crystallinity.
- Lithology - this is an important control, coarse grained sediments tend to develop better crystallinity values due to the detrital, more mature illite/muscovite content, and also due to the porosity allowing unrestricted space for the growth of authigenic illite crystals. This promoted by the free circulation of interstitial water and increases in the concentration of pore fluids. Sandstones and siltstones tend to have higher 'crystallinity' values than the associated mudstones even though their burial depth is exactly the same. In carbonates the values of 'crystallinity' may be retarded due to the deficiency of potassium, and smectite may therefore persist into epizonal material. Retardation may also be found in sediments with a high organic matter content (Kubler, 1968). Dunoyer de Segonzac (1970) states that the influence of lithology diminishes with increasing diagenetic rank and is negligible by the time anchizone conditions are reached.

- Illite chemistry - increases in the potassium content of the illite leading to better crystallinity (Weaver and Beck, 1971). Potassium may come from the destruction of K-feldspars, muscovite or biotite.
- Interference - in the anchizone/epizone minerals such as paragonite, pyrophyllite and margarite which cause an overlap on the X-ray diffraction trace at around 9.7 - 9.8Å. These minerals develop at the expense of kaolinite and occasionally at the expense of mixed-layer illite-smectite (Frey, 1978).
- Experimental conditions - methods of sample preparation and X-ray conditions play a very important role, which has lead to the standardization of the technique, this is covered in greater detail in Section 7.2.2.

Therefore Frey (1987) states that at the present level of knowledge, illite 'crystallinity' cannot be used for geothermometric purposes, but it remains a most useful technique for characterizing burial depth in very low grade metamorphic and diagenetic clastic sedimentary rocks.

### 7.2.2. Experimental determinations of illite 'crystallinity'.

The recommendations suggested to standardise the technique are described and this is followed by a presentation of the methodology used in this study.

#### *7.2.2.1. Recommendations for sample preparation and diffractometer settings.*

Frey (1987) states that over one hundred authors have successfully applied illite 'crystallinity' in their studies, but either many of the findings were not comparable, or the boundaries of the anchi- and epi- zones do not correspond with Kubler's (1968) original values. As shown by Kisch (1990, Table 1), these variations are due to variations in both preparation techniques and X-ray diffractometer settings and scanning conditions. To overcome these problems, and help to standardize the technique; the illite 'crystallinity' working group was set up in 1989, and at a workshop in 1990 agreed on a set of recommendations. The discussions and recommendations for preparation and analysis are detailed in Kisch (1991). The main were as follows:-

a) Sample grinding:- Initially the sample should be reduced using a jaw crusher, or hammer with further reduction performed in an agate pestle and mortar. Disc or swing mills are to be avoided as they can cause 'amorphization' of the clay minerals and if employed a grinding period of less than 3 minutes should be used.

b) Ultrasonic disaggregation:- No studies have shown deleterious effects but probes should not be used and only low frequency tanks and a duration of less than 30 minutes should be used.

c) Size separation:- No method other than sedimentation or centrifugation is suggested, as long as the <2 μm clay size fraction is separated.

d) Cation saturation and ethylene glycol solvation: - Calcium saturated air dried samples is recommended, as this is particularly useful for poorly crystalline illites containing expandable layers. When cation saturation is carried out, grain size separation should use sodium rather than ammonium as a dispersing agent. For broad peaks it may be desirable to run glycolated samples, and if so, both air dried and glycolated values must be presented.

e) Slide preparation:- The quality of the mounted surface is apparently the main source of error in crystallinity determinations, both smear and sedimented slides can be used, and thin slides should be avoided. The slides should contain at least 3 mg/cm$^2$ of sample.

f) Diffractometer settings:- Measurements should be preferably carried out on diffractometers without monochromators. The amount of peak broadening for a given receiving slit is similar for different scan rates as long as the time constant (TC) conforms to the following formula:-

$$\text{TC (sec)} \leq 0.5\left[\frac{\text{receiving slit width } (^\circ)}{\text{scan rate } (^\circ\text{min}^{-1})}\right] \times 60 \qquad \text{(Kisch, 1990)}$$

g) Illite 'crystallinity' standards: Since some laboratories will depart from the recommended instrument setting as given in (f) it is suggested that interlaboratory standards be used. These standards should range from the diagenetic to anchizone, not require preparation by the user, be simple to insert into the diffractometer and be homogenous and available in large volumes.

### *7.2.2.2. Experimental methodology used in the study.*

The recommended preparation procedures and instrument running conditions were adhered as far as was possible in this study. Some minor deviations in the adopted procedure were as follows:

a) The sample was initially crushed using a flypress down to millimetric sized fragments, these were then oven dried. The sample was then further ground in a tungsten carbide disc mill for a period of 10 seconds to further reduce the size of the fragments to a submillimetric size. The powdered sample was further ground in an agate pestle and mortar using distilled water as a lubricant for a period of one minute.

b) The ground sample was transferred into a plastic beaker, a 'pinch' of sodium hexametaphosphate was added and the contents placed in an ultrasonic bath for a period of 20 minutes.

c) After sonification the <2μm clay sized fraction was collected by centrifugation according to the times provided in Appendix A1.

d) Once the clay size fraction had been collected, the sample was cation exchanged with calcium as detailed in section 5.2.3.1, and the sample left overnight to flocculate.

e) Once the sample had flocculated, the slides were prepared using the millipore transfer method as detailed in section 5.2.3.2,. According to Kisch and Frey (1987), this method produces the best quality sample slides as it eliminates sample segregation provides a high degree of preferred clay orientation and leaves a flat surface exposed to the X-ray beam.

f) Once the samples were dried they were X-rayed at least twice under the same experimental conditions as adopted for clay mineralogy determinations with slit settings of :-

Divergent slit = 1°
Receiving slit = 0.1°
Scatter slit = 1°

A monchromator was not used. A scan speed of 0.5°/min with 0.02° step intervals and scanning from 6-11 °2θ was adopted. This conforms to the time constant formula mentioned in f) above:

$$\text{TC (sec)} \leq 0.5 \; \frac{0.1}{0.5} \; \text{x } 60 \qquad \text{therefore TC} = 6 \text{ sec}$$

A time constant (TC) of 1 second was used.

The peak widths were measured off the printed diffractometer traces. After a background was drawn on with a french rule, the half height was measured with an engineering rule, and the peak width at half height measured with a planimeter. It was found that the duplicate scans were all within an accuracy of ≤0.01 Δ°2θ, which was probably due to the high quality surfaces produced on the sample slides. The average results are presented in Table 7.1.

To calibrate the procedures, four rock standard slides prepared from samples collected and available from Warr and Rice (1994) were used. These samples, which were prepared and kindly loaned by Dr. R. Merriman of the British Geological Survey, were also run under the same experimental conditions. The expected values and measured values are presented in Table 7.2, along with the plot of the results seen in Figure 7.1.

| Sample (standard) | Actual Ic (°2θ) | Measured Ic (°2θ) |
|---|---|---|
| SW1 | 0.63 | 0.45 |
| SW2 | 0.47 | 0.33 |
| SW4 | 0.38 | 0.27 |
| SW6 | 0.25 | 0.25 |

Table 7.2 Actual and Measured Ic values for 'crystallinity' rock standards

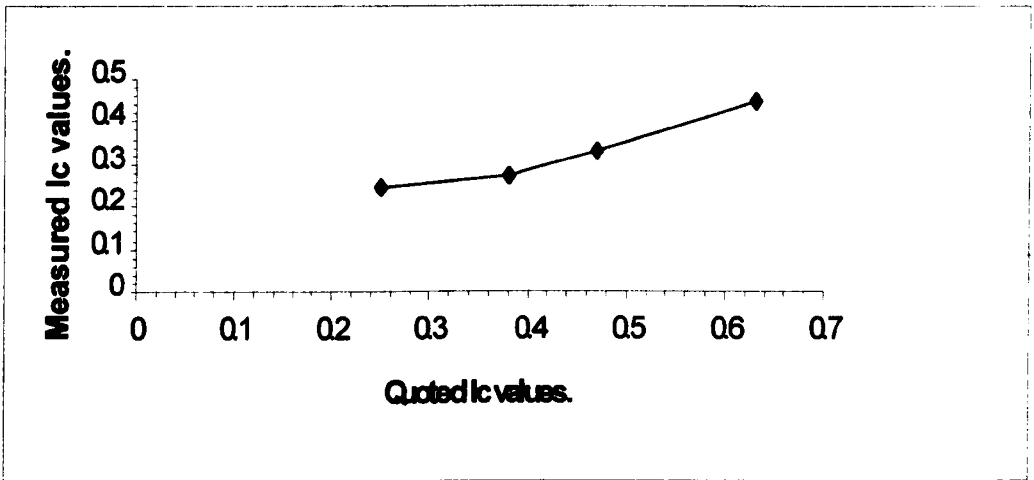


Fig. 7.1 Plot of expected to actual measured 'crystallinity' values from the rock standards.

From Fig. 7.1 it can be seen that above an Ic value of 0.30°2θ, there is a difference between actual and measured 'crystallinity' values with a linear relationship, for which the relationship for correcting results for Ic >0.30°2θ is:-

Ic (corrected) = [Ic (measured) x 1.375] + 0.015

The measured values were corrected using the above expression to standardise the results, so the values obtained could be correlated against engineering properties on a more universal scale. The corrected Ic (corr) values are presented in Table 7.1, and correlations with engineering properties are discussed in Chapter 9. Additionally, the samples were run after treatment for 12 hours with ethylene glycol, these results and their corrected values are also presented in Table 7.1. The ratios of glycolated and air dried Ic values are also expressed in Table 7.1. This ratio is indicative of the smectite component.

## 7.3. Vitrinite reflectance.

### 7.3.1. Introduction.

During the process of coalification, which is the diagenetic conversion of deposited organic matter through devolatization into coal, the stages of development has been found to follow rank stages of :- peat ⇒ lignite ⇒ sub-bituminous coal ⇒ bituminous ⇒ anthracite ⇒ meta-anthracite (Stachs et al, 1975). The conversion involves, chemical and physio-structural changes, including a decrease in porosity and moisture content as well as optical properties. During higher stages of diagenesis the changes are predominantly chemical and optical, as moisture content decreases the calorific value of coal increases. The loss of moisture depends on the decrease in porosity and decomposition of hydrophilic functional groups such as OH groups, carboxyl groups, methoxyl groups and carbonyl groups which split off leading to an increase in carbon content. After the sub-bituminous stage the last remnants of lignin and cellulose are transformed into humic acid which condenses in to larger molecules. It looses its acidic character and forms alkali-soluble humins. This is seen petrographically as vitrinization of the humic substances forming coal and by this stage lignite to bituminous coal has formed and the lowest reflectance values (%Ro) of ~0.35-0.38% are recorded. During the bituminous stage, volatile matter decreases and the reflectivity of the material rises as $CH_4$ and $CO_2$ is released. By the anthracite stage the hydrogen content decreases, resulting in %Ro values >2.5.

In coals and sedimentary rocks the organic matter, commonly referred to as phytoclasts (Bostick 1974) as it is derived from land plants, reacts very sensitively to the rise of rock temperature and pressure. The process is also very sensitive to the heat duration time (Stachs et al., 1975; Teichmuller, 1987). Since this process is irreversible, it plays an important role in diagenetic and metamorphic rank determinations of mudrocks. The organic matter is divided into 3 maceral groups; vitrinite, liptinite and inertinite. Vitrinite is the most commonly occurring organic material in sedimentary rocks and coals (Teichmuller, 1987), and its changes during diagenesis are relatively uniform.

Weaver (1989) states that vitrinite properties are affected by microbial activity, pore fluid composition, thermal history, fluid movement, sediment mineralogy and pressure history of the rock. Therefore he argues that there is no reason why organic material should provide more accurate palaeo-temperature data than do clay minerals. However many authors have shown good relationships between coal rank and diagenetic-metamorphic rank of the associated rock (Teichmuller et al.,1979; Frey et al., 1980; Kisch, 1983). Teichmuller et al., (1979) state that in West German coal basin work no simple relationship between illite 'crystallinity' and coal rank existed, each region studied was characterized by its own relationships. Frey (1980) states that good correlation exists between the two parameters in certain areas of the European Alps, but no general correlation can be reached. This may be due to variations in lithology which affects illite 'crystallinity' values. In certain cases retardation of vitrinite rank can occur when rocks with high heat conductivity such as sandstones are involved (Teichmuller, 1987). Since vitrinite reflectance is dependant on maximum heating temperature and heating duration, there should be a gradual increase with burial depth, but when sandstone horizons are encountered they can cause a retardation of rank increase, as there is a damming of heat in the less conductive overlying mudrocks.

Vitrinite reflectance is not totally without problems, but it is a widely used, and relatively accurate rank parameter and, since most mudrocks contain organic material, the technique is very widely applicable. Unfortunately, in pre-Devonian mudrocks there is no classic vitrinite as landplants had not extensively evolved, but coalification of microfossils can be used for comparative reflectance and has generally been found to give good correlations with illite 'crystallinity'.

Vitrinite reflectance has been used in association with illite 'crystallinity' in this study to help establish a general diagenetic history for the samples.

### 7.3.2. Preparation of sample blocks.

Reflectance of vitrinite is performed on polished samples set in epoxy resin, using a reflectance microscope with an oil immersion objective lens, and fitted with a photomultiplier. Two approaches had to be adopted in the sample preparation stage for vitrinite reflectance work:-

1. For the majority of the Carboniferous samples, the associated coal seams were sampled. The coal samples were prepared using a method similar to that of BS 6127 Part 2 (1981). For this the coal samples were crushed to an upper limit of 1mm in an agate pestle and mortar and stored in labelled plastic vials. Using a disposable plastic beaker, 10ml of Metset epoxy resin and hardener were mixed together in accordance with the manufacturers recommendations. Approximately 10g of the coal sample was added to the prepared resin and stirred thoroughly using a clean spatula, further sample was added until the mixture was a thick paste that would only just adhere to the container walls. The mixture was then poured into a plastic mould, and further epoxy resin was poured over the top making the block thickness a total of 25-30mm. The moulds were then allowed to stand on a hot plate set at 60°C overnight. Once the epoxy resin had hardened the block was ejected from the mould using a metal plunger. The ends of the blocks were then levelled using a bench lathe which reduced the thickness of the blocks to ~20-25mm. They were then labelled and stored ready for polishing.

2. For samples that were older than Carboniferous in age, and samples C.1.B1, C.1.B2, C.1.B4, C.1.B5, C.6.1, C.7.1, no organic material was collected on site. Organic material had therefore to be extracted from the powdered mudrocks for the preparation of reflectance blocks. This involved placing ~20-40g of the TEMA crushed mudrock sample into plastic beakers, then treating with concentrated HCl to remove any carbonates. After carbonate dissolution, which took about 2 days, the samples were washed free of acid and residue by water decantation, this process took a period of 4 days. Once the samples were free of HCl residue a quantity of 36% HF acid was added to remove any silicates present in the sample. The samples were stirred twice daily, and the acid replaced on a weekly basis. This treatment tended to take between 4-12 weeks depending upon the state of induration of the sample. Once it was visibly evident that most of the sample had dissolved leaving the organic debris in the beaker, the contents were washed by water decantation over a period of 6 days. The solid material was then sieved using a 10μm nylon mesh sieve and the remaining fraction air dried ready for mounting within epoxy resin blocks.

Since a limited quantity of organic material was collected by acid treatment, standard mounts could not be prepared so a modified version of Irdi and Booher's (1995) technique was adopted. The organic fraction was mixed with a small quantity of prepared epoxy resin as mentioned in (a). The paste was then transferred into 10mm diameter plastic sample vials, and covered with further epoxy resin. These were then allowed to cure overnight on a hot plate set at 60°C. Once the resin had cured, the plastic vials were cut away from the 10mm diameter sample blocks. The 10mm diameter sample blocks were then placed in standard cylindrical moulds, surrounded with epoxy resin and left to cure. Once the resin had set the blocks were prepared as described in section (a).

The prepared blocks were ground and polished. For this they were secured in specimen holders attached to polishing laps, and ground using silicon carbide paper with a medium grain size of 50μm, the abrasive surface was continually flushed with water during grinding, this process usually took ~2 minutes. Once the sample surface was washed free of any debris, grinding continued using silicon carbide paper of 15μm approximate mean grain size, again with a continuous water flush until a flat surface virtually relatively free of deep scratches had been achieved. The specimens were removed from the specimen holders and thoroughly washed prior to polishing. A slurry of 1μm alumina powder was prepared and poured onto a lap cloth on which the sample blocks were then polished for 2 minutes. Whilst the lap was still rotating, the cloth was flooded with water to remove any alumina slurry. The specimen blocks were removed from their holders, washed under a jet of cold water and allowed to air dry. The sample surface was then examined using a reflected light microscope, fitted with a dry objective lens of x10 magnification. If the sample surface was relatively free of deep scratches, flat and adequately polished, they were retained for analysis, if not then they were reground and repolished.

### 7.3.3. Measurement of random reflectance of vitrinite.

In lower rank coals, up to low volatile bituminous coals, the three maceral groups can be identified by different grey levels of reflectivity, the liptinite macerals are dark grey and low reflecting, the vitrinite macerals are medium grey and medium reflecting and inertinite macerals are light grey to white and highly reflecting. However, with increasing rank an overall convergence of the chemical and physical properties of the macerals occurs and the difference in reflectance between macerals diminishes. So in high rank coals like anthracite it is impossible to differentiate between maceral types from the vitrinite and inertinite groups based on reflectance (Booth, 1996).

For the reflectance work a Leitz Ortholux reflecting microscope adjusted for Köhler illumination (BS 6127, part 3 (1981)) and set up for random reflectance using a photomultiplier was used. It was allowed to stabilise for about a minimum of 1 hour before use. The microscope was calibrated using the following standards: Sapphire :- %Ro = 0.59; Glass :- %Ro = 1.24; Glass :- %Ro = 1.67. Once the instrument was calibrated the sample block was mounted on a micrometer stage and measurements on separate pieces of vitrinite in the block were carried out on over linear traverses. The measurements were carefully carried out on sections of vitrinite that were free from cracks or scratches, otherwise the results would have been affected. After each 50 measurements the instrument was re-calibrated, and if the measured values of the standards differed by more than 0.2% from the quote value, the readings were discarded, the instrument re-calibrated and the procedure repeated. If the instrument was stable after calibration then a further 50 readings were obtained. Rather than the 500 recommended by BS6127, part 5 (1981) a total of 100 reflectance measurements per sample were made because organic particles are not abundant in mudrock extracts. As pointed out by Bustin et al., (1985) the reflectance of coal can be accurately determined with only 100 measurements, therefore it is not worth while obtaining more readings. After the measurements were obtained from the polished blocks, the readings were grouped in categories each representing a 0.1% change, equivalent to a full V-step. From these groupings the mean random reflectance and standard deviation of the distribution could be calculated using the following equations:

$$\%\,Ro = \frac{\Sigma\,(RiXi)}{n} \qquad Sd = \sqrt{\left[\frac{\Sigma\,(Ri^2Xi) - nRo^2}{(n-1)}\right]}$$

Where:-

%Ro = mean random reflectance

Ri = mid value of the step

Xi = number of reflectance measurements in the V-step

n = total number of reflectance readings taken

Sd = standard deviation

The results for %Ro and Sd obtained from the analysis are presented in Table 7.1. For certain older samples (Ca.1.1, Ca.1.2, Ca.1.3, O21, D11, D12), as no organic material was extracted, reflectance measurements were not possible.

## 7.4. Textural analysis.

### 7.4.1. Introduction.

Rock fabric exerts a significant control over the responce of mudrocks to environmental changes, textural studies therefore are relevant in the interpretation of the engineering behaviour of these materials (Bell, 1993; Yumei et al., 1993). For example, due to the affect on porosity and microstructure the inter-relationships between the clay mineral and clastic constituents affect the swelling and slaking properties. In a clay or mudrock with randomly oriented clay minerals or pockets of randomly oriented clay

| **Sample.** | $I_{c'}$(°2θ) | $I_{c(co)}$ (°2θ) | $I_{cg'}$(°2θ) | $I_{cg(co)}$ (°2θ) | $I_{c(co)}$- $I_{cg(co)}$ | %$R_o$ /(Sd) |
|---|---|---|---|---|---|---|
| **Ca.1.1** | 0.22 | 0.22 | 0.22 | 0.22 | 1 | --------- |
| **Ca.1.2** | 0.20 | 0.20 | 0.20 | 0.20 | 1 | --------- |
| **Ca.1.3** | 0.19 | 0.19 | 0.19 | 0.19 | 1 | --------- |
| **O.1.1** | 2.16 | 2.98 | 0.41 | 0.58 | 5.1 | 0.45(0.45) |
| **O.1.2** | 2.10 | 2.90 | 0.44 | 0.62 | 4.7 | 0.45(0.45) |
| **O.2.1** | 0.22 | 0.22 | 0.22 | 0.22 | 1 | --------- |
| **O.3.1** | 0.20 | 0.20 | 0.20 | 0.20 | 1 | 4.82(0.25) |
| **S.1.1** | 1.66 | 2.30 | 0.56 | 0.78 | 2.9 | 0.96(0.09) |
| **S.3.1** | 0.44 | 0.62 | 0.35 | 0.49 | 1.3 | 0.77(0.08) |
| **S.3.2** | 0.39 | 0.55 | 0.30 | 0.30 | 1.8 | 0.77(0.08) |
| **D.1.1** | 0.22 | 0.22 | 0.22 | 0.22 | 1 | --------- |
| **D.1.2** | 0.22 | 0.22 | 0.22 | 0.22 | 1 | --------- |
| **D.2.1** | 0.21 | 0.21 | 0.21 | 0.21 | 1 | 3.73(0.43) |
| **C.1.B1** | 0.80 | 1.11 | 0.43 | 0.60 | 1.85 | 1.73(0.17) |
| **C.1.B2** | 0.33 | 0.48 | 0.30 | 0.30 | 1.6 | 1.71(0.13) |
| **C.1.B4** | 0.69 | 0.96 | 0.46 | 0.64 | 1.5 | 1.71(0.18) |
| **C.1.B5** | 1.30 | 1.80 | 0.57 | 0.80 | 2.25 | 1.71(0.18) |
| **C.2.1** | 0.84 | 1.17 | 0.37 | 0.52 | 2.25 | 0.54(0.09) |
| **C.3.1** | 0.76 | 1.06 | 0.43 | 0.60 | 1.8 | 1.67(0.13) |
| **C.4.1** | 1.70 | 2.35 | 0.85 | 1.18 | 2.0 | 0.72(0.12) |
| **C.5.1** | 0.50 | 0.70 | 0.42 | 0.59 | 1.2 | 0.68(0.07) |
| **C.5.2** | 0.46 | 0.64 | 0.34 | 0.48 | 1.3 | 0.68(0.07) |
| **C.6.1** | 0.64 | 0.89 | 0.41 | 0.57 | 1.6 | 1.03(0.16) |
| **C.7.1** | 2.51 | 2.90 | 0.61 | 0.85 | 3.4 | 1.13(0.17) |
| **C.8.2** | 0.64 | 0.89 | 0.39 | 0.55 | 1.6 | 0.71(0.07) |
| **C.8.3** | 0.40 | 0.56 | 0.34 | 0.48 | 1.2 | 0.71(0.07) |
| **C.9.2** | 0.67 | 0.93 | 0.44 | 0.62 | 1.5 | 0.61(0.07) |
| **C.10.1** | 0.65 | 0.91 | 0.40 | 0.56 | 1.6 | 1.03(0.17) |
| **C.11.1** | 0.47 | 0.66 | 0.45 | 0.63 | 1.05 | 0.91(0.05) |
| **C.11.2** | 0.50 | 0.70 | 0.36 | 0.51 | 1.4 | 0.74(0.05) |
| **C.12.1** | 0.54 | 0.75 | 0.38 | 0.53 | 1.4 | 0.66(0.06) |
| **C.12.2** | 0.62 | 0.86 | 0.42 | 0.59 | 1.4 | 0.66(0.06) |
| **C.13.1** | 2.04 | 2.82 | 0.50 | 0.70 | 4.02 | 0.60(0.05) |
| **C.13.2** | 1.95 | 2.69 | 0.43 | 0.60 | 4.48 | 0.54(0.04) |
| **C.13.3** | 2.50 | 2.89 | 0.42 | 0.59 | 2.30 | 0.54(0.04) |
| **C.14.1** | 0.51 | 0.72 | 0.36 | 0.51 | 1.4 | 0.56(0.06) |
| **C.15.1** | 2.01 | 2.78 | 0.55 | 0.77 | 3.6 | 0.70(0.07) |
| **C.16.1** | 0.67 | 0.93 | 0.41 | 0.58 | 1.6 | 0.56(0.06) |
| **C.17.1** | 0.46 | 0.64 | 0.35 | 0.49 | 1.3 | 0.71(0.06) |
| **C.17.2** | 0.49 | 0.69 | 0.38 | 0.53 | 1.3 | 0.65(0.08) |
| **C.18.1** | 2.33 | 3.20 | 0.40 | 0.56 | 5.7 | 0.48(0.04) |

Table.7.1. Illite 'crystallinity' and vitrinite reflectance data.

mineral domains, water usually causes isotropic swelling. In addition microfractures randomly oriented around the clay minerals or domains will give the material a tendency to slake rapidly into small fragments. Clay mineral rotation during consolidation of a clay sediment can produce a laminar microstructure with clay minerals arranged face to face in a direction of preferred orientation normal to the overburden pressure. By reducing void size this orientation reduces the access routes for incoming water, such that swelling is restricted and occurs mainly in a horizontal direction. During consolidation and diagenesis, porosity decreases with compaction and recrystallization, this aids to increase the strength of the rock and make it more durable. Shallow burial is associated with low temperature changes and applied lateral stress causes extensive particle rotation with little recrystallization. At greater burial depths, recrystallization is a more dominant responce to applied stress (Weaver and Associates, 1984). Such recrystallization tends to destroy opportunities for microfractures to develop in the resulting rock, making it more resistant to weathering processes.

Textural studies of mudrocks enable direct observations to be made of voids, the effects of recrystallization, cementation, mineral packing, mineral orientation and the relationships between clastic grains such as quartz grains which when touching impart extra strength to the rock. From such observations, assessment of the potential durability of the material and also their state of diagenetic maturity can be made. The interrelated effects of crystal growth and maturity have been demonstrated by White, Huggett and Shaw (1984), who observed a relationship between clay mineral growth and increase in illite 'crystallinity' in a series of 7 samples.

Only limited studies of mudrock microstructure are possible using standard petrographic microscope techniques. Direct observation of the clay mineral structure is not possible, due to resolution which is limited to about 2000 Å (2 μm), with this equipment (Krinsley, Pye and Kearsley, 1983). However, the SEM allows a greater resolution and depth of view of the sample such that mineral orientations and the distribution of voids can be observed. The disadvantage of the SEM compared with petrographic microscopy, is that it does not allow ready identification of mineral species. However, this problem is overcome by the use of the SEM backscatter electron mode which enables the abundances of specific chemical elements to be determined so that all mineral phases, including clay minerals may be identified. This is a relatively that all mineral phases, including clay minerals may be identified. This is a relatively modern application of this method (Krinsley, et al, 1993) which has rarely if ever, until now been applied especially in the field of engineering geology. In this study it was decided to evaluate the textural features of the samples using a combination of standard petrographic techniques, and SEM analysis using both backscatter imagery and energy dispersive X-ray analysis which allows mineral identification by elemental analysis in the SEM mode.

### 7.4.2. Petrographic thin section analysis.

Petrographic thin sections were produced by first cutting thin slices (<5mm thick) of each mudrock sample perpendicular to the bedding using a dry saw. These slabs were then oven dried at 60 °C for 72 hours and then ground flat on both sides using a fine grade wet and dry abrasive paper in a dry condition. The slabs were then mounted on large (30mm × 60mm) petrographic glass slides using 'canada balsam' adhesive. They were then ground to a 30μm thickness on a rotating lap and finished by hand (which was gauged by determining the refractive index of quartz in the samples), using a non-aqueous alcohol based solvent as a cooling medium and grinding lubricant. Once the thin sections of a suitably flat finish were produced they were washed with methylated spirit to remove any grinding residue, and cover slips were attached using 'Lakeside' adhesive labelled and stored. Examination of the slides was carried out using a Nikon Lobophot - Pol petrographic microscope with camera attachment. As expected, only limited information could be obtained from the thin sections due to the lack of resolution of the fine material. However, the mica grain orientation was observed and where present, microlaminations described, also inter-relationships and distribution of any clastic grains such as quartz, and cement were described. Photomicrographs taken of each sample are presented in Section 7.4.4 which also provides a description of each sample.

## 7.4.3. SEM textural analysis using the backscatter electron mode.

### *7.4.3.1. Introduction to the electron microscope.*

A scanning electron microscope consists of an electron gun which produces a stream of electrons to which an accelerating voltage is applied. The beam passes through a series of electromagnetic lenses which, under applied vacuum conditions, results in a small (<10nm) demagnified image of the electron source. Before the beam passes through a final electromagnetic lens, a scanning roster deflects the electron beam so that it scans the surface of the specimen. The scan is synchronised with that of a cathode ray tube and a picture is built up of the scanned area of the specimen surface. Contrast in the cathode ray picture is due to variation in reflectivity across the surface of the specimen. Electrons striking the sample surface are reflected as high energy back scattered electrons (BSE) and low energy secondary electrons (SE). These electrons, mainly the secondary electrons, are collected by a scintallator which emits a pulse of light at the arrival of an electron. This light is then converted to an electrical signal and amplified by a photomultiplier, after further amplification the signal passes to the cathode ray tube grid. In scanning electron mode it is generally difficult to distinguish mineral phases from each other. Sometimes shape can be used as an identifying feature but, since most components of mudrocks tend to be anhedral or fragmented, morphological identification is usually impossible. When the electron beam strikes the specimen surface secondary X-rays are given off, which can be used for X-ray micro-analysis of the target area using an energy dispersive X-ray analysis system (EDX). This provides a chemical analysis at a specific location about 1µm in diameter.

### *7.4.3.2. Backscatter electron imagery (BSI).*

Both low energy secondary electrons and backscattered electrons are produced. The latter electrons actually penetrate the sample surface, and are reflected along a linear path, whereas secondary electrons reflect back off the sample surface in a curved pattern. The higher energy backscattered electrons are collected using detectors which are set higher above the sample than the secondary electron detectors such that they lie beyond the travel range of secondary electrons. When backscatter electrons hit a sample surface the depth of penetration depends on the atomic number of the chemical elements present in the mineral phase. The lower the atomic number, the deeper the electrons penetrate, and so reflection energy is lost (Lloyd, 1987). The degree of backscattering is measured in terms of the back-scattered electron coefficient defined as:-

$$\eta = \frac{\text{No. of electrons scattered out}}{\text{No. of incident electrons}}$$ (White, Shaw & Huggett, 1984)

(η) is related to the atomic number (z) of the mineral relative to the weight fraction of constituent mineral atoms given in Table 7.3. Therefore the higher the mean atomic number of the mineral, the brighter the mineral appears on the screen.. It is possible to distinguish between minerals with a difference of only (z) as small as 0.1.

| Mineral | Z | η |
|---|---|---|
| Mg chlorite | 10.17 | 0.124 |
| Kaolinite | 10.24 | 0.125 |
| Smectite | 10.40 | 0.127 |
| Albite | 10.71 | 0.132 |
| Quartz | 10.80 | 0.132 |
| Dolomite | 10.87 | 0.133 |
| Illite | 11.16 | 0.136 |
| Muscovite | 11.33 | 0.138 |
| Orthoclase | 11.85 | 0.145 |
| Calcite | 12.57 | 0.150 |
| Biotite | 14.59 | 0.174 |
| Fe chlorite | 16.05 | 0.188 |
| Siderite | 16.47 | 0.190 |
| Rutile | 16.93 | 0.195 |
| Heamatite | 20.59 | 0.238 |
| Pyrite | 20.65 | 0.247 |

**Table 7.3 Mean atomic numbers and calculated back-scattering coefficients for some common minerals found in mudrocks. (White, Shaw and Huggett,1984)**

The analysis is normally performed on back scatter mode photomicrographs. The minerals are identified by calibrating the grey tones on the image against known phases such as quartz, pyrite or calcite, which are identified by their characteristic morphologies, or analysed using EDX in the SEM mode. Care is required in sample preparation for BSI analysis, a high level of flatness or polish is necessary on the thin section surface, for the emission of the backscattered electrons is highly directional, so if the sample surface is not perfectly flat the shallower angles reduce electron penetration and scatter angles giving misleading results.

### *7.4.3.3. Sample preparation and analysis using BSI.*

Analysis was performed on the same thin sections prepared for the petrographic studies with the cover slips removed. The thin sections were further polished using an automatic lap and 1μm diamond paste. When a suitable polished flat surface was achieved, the sample was cut down to a size that would fit onto the aluminium mounting stubs, which are 25mm in diameter. The samples were carefully washed with acetone to remove any traces of the polishing medium, dried under a warm air blower, and mounted onto the aluminium stubs using silver paint, which also aids the conductivity of the assembly. Once the paint had dried, the samples were carbon coated under vacuum conditions in a splutter evaporator. A carbon coat of approximately 100 Å was applied to the sample surface to eliminate any charging by increasing the conductivity of the sample. Carbon coating was used in preference to gold/palladium as they decrease the image quality for BSI compared with carbon (Reynolds and Gorsline, 1991). The samples were then analysed using a Camscan series 2 scanning electron microscope in BEI mode, with a Link AN10000 EDX spectral analysis unit for microscope elemental analysis. Initially 12 of the samples were analysed using a JEOL.6400 scanning electron microscope in BEI mode equipped with a LINK EDX spectral analysis unit.

The samples were examined in BSI mode, initial interpretations were made on the microscope monitor screen, and photomicrographs were obtained for the samples for further detailed analysis, the different mineral phases distinguishable by colour contrast on the grey scale were calibrated in the SE mode using the LINK EDX microprobe. Photomicrographs were also taken in the SE mode, these were found not to be useful for textural analysis since polishing had affected the mineral morphologies, but they were used for distinguishing organic constituents from voids both of which appear black regions on the BSI photomicrographs.

The principal aim of the analysis was a textural evaluation of the mudrock samples. Many workers (Primmer and Shaw, 1985; Krinsley, Pye and Kearsley, 1983;

White, Shaw and Huggett, 1984; Huggett, 1985; Shaw and Primmer, 1991, etc.) have used backscatter imagery for observational studies in mudrocks. Their primary objectives were usually the diagenetic interpretations of certain mineral phases, including in most cases clay minerals, carbonates and pyrite. Textural relationships were never really considered in these studies. However, Krinsley et al., (1993) presented data backing up their suggestion that BSI is one of the most useful tools available for textural analysis of mudrocks. In their studies on samples ranging from Cambrian to Eocene in age they observed 7 common textural categories, as follows:-

a) Microlaminations - including mineral orientation and packing.
b) Fossil form - including the state of cement replacement.
c) Pyrite - describes the form and physical relationship to surrounding mineral grains.
d) Clay minerals and micas - state of these phases including breakage and orientations.
e) Chemical and physical alterations - corrosion rims, authigenic growths and orientation of clay minerals and quartz grains.
f) Presence of Glauconite.
g) Porosity - 2D shape, size and orientation of microporosity.

In addition to this textural analysis check list presented by Krinsley et al (1993), Moon and Beattie (1995) presented photomicrographic descriptions of Eocene mudrock textures based on SEM analysis. These textural data were based on observations of laminations and clay mineral orientation as follows:-

a) Laminar microstructure - the mineral grains are well oriented and the clay minerals lie in a linear face to face arrangements.
b) Turbostratic microstructure - this is a continuous matrix type microstructure where the clay minerals have a slightly undulating linear arrangement, the clays may be either arranged face to face or at a low angle end to face arrangements.
c) Skeletal structure - this consists of a discontinuous matrix where the minerals occur in discrete pockets or domains which are bridged by randomly oriented clay minerals, giving essentially a granular structure with connecting clay bridges.

Moon and Beattie (1995) state that the progression of clay mineral orientation passes from skeletal ⇒ turbostratic ⇒ laminar microstructure, with increasing compaction, they also found that there was no relationship between the type of microstructure and the resulting durability of the mudrocks. Moon and Beattie (1985) also state that the extent of clastic grain contact (i.e. quartz grains) is an important textural factor in mudrock microstructural analysis, as they found that increasing clastic grain contact correlated very well with increasing strength and durability.

It was decided to adopt a check list for the routine description of the BSI photomicrographs, in addition to the general observations such as mineralogy and mineral phase relationships. This consists of 4 categories, each with a ranking system for the development or extent of the physical state being described, the intention being to rank texturally the mudrocks so that relationships could be examined for texture, durability and measures of diagenetic rank such as illite 'crystallinity'. The overall rank (4-12) was defined as the sample sum of the ranks (1-3) for each catagory. It is presented in Table 7.4.

The photomicrographs, their descriptions and textural ranking are presented in Section 7.5.

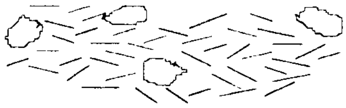
| | **Feature.** | **Rank.** | **Visual description.** |
|---|---|---|---|
| **1.** | Density/ Mineral packing. | 3. | Dense: Closely packed minerals, with evident clay wrap around clastic grains, rare to occasional voids present. |
| | | 2. | Moderately dense: No general clay wrap around, occasional voids present, |
| | | 1. | Loose to moderately dense: Occasional to moderate amount of voids and occasional microfractures evident. |
| **2.** | Clay mineral orientation. | 3. | Laminar clay mineral orientation.<br> |
| | | 2. | Turbostratic clay mineral orientation, generally low angle face-face or end-face contacts.<br> |
| | | 1. | Continuous matrix, consists of discrete clay mineral pockets generally of randomly orientated clay mineral grains, with occasional clay mineral bridging.<br> |
| **3.** | Clastic contact (quartz). | 3. | Much clastic point grain contact evident. |
| | | 2. | Some clastic point grain contact evident. |
| | | 1. | No clastic point grain contact evident. |
| **4.** | Degree of cementation. | 3. | Much cementation and / or recrystallization of clay mineral species evident. |
| | | 2. | Some cementation evident, or slight traces of clay mineral recrystallization. |
| | | 1. | No evident cementation or clay mineral recrystallization, although discrete carbonate grains may be present. |

Table 7.4 Rank description categories for textural analysis of mudrocks.

## 7.5. Petrographic and BSI sample descriptions.

Photomicrograph descriptions and ranking values.

Ca11 -Plate 7.1:- Petrographic description - [x100mag - XPL]. Fined grained groundmass of well orientated phyllositicates including muscovite. Much opaque haematite staining around mineral grains. Fine grained silt sized quartz grains evident, with minimal clastic grain contact, larger grains of moderately euhedral plagioclase feldspar present (Kf) possibly authigenic. Well developed cleavage.

-Plate 7.2:- BSI analysis - [x750mag] - Very dense packing, occasional voids, generally < 5μm in diameter. High degree of compaction evident by tight wrap around of phyllosilicates consisting of chlorite and muscovite around slightly corroded fine to medium silt sized (<20μm) quartz grains (Q). Bedding trending NW-SE in the photomicrograph, with laminar phyllosilicate arrangement trending 5-10° off from bedding, presenting a well defined cleavage (CI). Some clastic grain contact. Iron oxide (white) cement evident, and notable phyllosilicate recrystallization. Many evident rutile/anatase acicular crystals (R). = Slate (fine grained)

Ranking: A = 3; B = 3; C=2; D=3→ 11

Ca12 -Plate 7.3:- Petrographic description - [x100mag - XPL]. Fine grained groundmass of well oriented phyllosilicates including muscovite. Much opaque haematite staining around mineral grains. 20-30% of medium grade silt size fraction consisting of oriented quartz (oQ), plagiclase feldspars and pyroxenes (Py). Grains oriented in parallel to cleavage (pQ).

-Plate 7.4:- BSI analysis - [x500mag]. Very close packing, occasional voids present. High degree of compaction evident by well developed phyllosilicate wrap around texture surrounding clastic grains consisting of quartz (Q) and feldspars (F) up to 30μm in size. Well developed laminar cleavage. Phyllosilicate recrystallization evident in chlorite/moscovite intergrowths (I). Occasional cementation by haematite (H). Evident clastic grain contact (Qo), Slate.

Ranking: A = 3; B = 3; C=3; D=3→ 12

Ca13 -Plate 7.5:- Petrographic description - [x100mag. XPL]. Fine grained groundmass of well oriented phyllosilicates and fine grained quartz. Much haematite staining around grains. Clastic quartz grains with preferred orientation in the direction of cleavage. Recrystallization evident in phyllosilicate and quartz intergrown pods (B) [Plate 7.6:- x22mag. XPL].

-Plate 7.7:- BSI analysis - [x500mag]. Very dense packing, occasional natural voids present. Slight crenulated arrangement of phyllosilicates due to imposed cleavage. Most clastics consisting of quartz (Q) and occasional feldspar less than 10μm in size, with evidence of slight dissolution. Clastic point contact evident (P), and recrystallization of phyllosilicates (C). Much haematite cement evident (H). Slate.

Ranking: A = 3; B = 3; C=3; D=3→ 12

0.1.1 -Plate 7.8:- Petrographic description - [x100mag. XPL]. Very fine groundmass of clay minerals and clay to fine silt sized quartz. Lamination trending in a north-south direction on the photomicrograph with secondary staining trending in a E-W direction possible zones of late stage iron staining or penetrative weathering.

-Plate 7.9:- BSI analysis [x300mag]. Densly packed, with occasional voids (V). Clays laminated in a wavy turbostratic arrangement with face-face and low angle end-face contacts, clays locally in large discrete pockets, showing slight recrystallization (P). Well to moderately compacted with clay wrap around seen on quartz grains (Q). Early formed pyrite fromboids seen (Py) with clay minerals wrapped around suggesting growth prior to compaction. Voids generally along laminations, possible effect due to weathering. No clastic grain contact = slightly weathered <u>Claystone</u>

Ranking: A = 2; B = 1½; C=1; D=2 →6½

0.1.2 -Plate 7.10:- Petrographic description - [x100mag. XPL]. Very fine groundmass of clay minerals and clay to silt sized quartz. Thin laminae seen in a N-S trend, with superimposed brown laminae possibly due to iron staining or penetrative weathering.

-Plate 7.11:- BSI analysis [x500mag]. Moderately densely compacted with occasional to many voids parallel to direction of lamination, with many evident microfractures (M) generally parallel to lamination. Clay minerals laminated in an undulose turbostratic face-face and low angle end-face manner. Sample has been well compacted as seen by the high level of clay wrap around on clastic/carbonate grains (W). Carbonate locally cementing minerals (C) and pyrite fromboids are evident (Py), this appears to be of diagenetically late stage as there is no effect on the clay minerals. Locally clays occurring in discrete pockets of randomly oriented grains (D). No clastic grain contact, but occasional discrete quartz grains (Q). Slightly weathered <u>Claystone</u>

Ranking: A = 1½; B = 1½; C=1; D=2→ 6

0.2.1 -Plate7.12:- Petrographic description - [x100mag. XPL]. Very fine grained groundmass of clay minerals and clay to silt sized quartz. Phillosilicates and quartz grains with a well developed cleavage parallel, to bedding in an E-W trend. Quartz grains have a well developed wrap around texture of phyllosilicates (Q). Graded bedding evident with coarser fraction developed to the base of the photomicrograph, occasional quartz grains with sutured contacts (Qp).

-Plate 7.13:- BSI analysis [x500mag]. Very densly compacted, with occasional voids. Phyllosilicates with laminar face to face arrangement, and well developed wrap around texture surrounding quartz grains (W). Quartz grains occasionally touching (Q). High proportion of clay minerals with lighter chlorite and darker muscovite recrystallized pockets (I-Ch). Quartz grains fine grained silt size generally <15-20 μm maximum size. <u>Argillite</u>.

Ranking: A = 3; B = 3; C=2½; D=3→ 11½

0.3.1 -Plate 7.14:- Petrographic description - [x100mag. XPL]. Very fine grained groundmass consisting of phyllosilicates and fine to medium silt sized quartz grains, locally thin clay rich laminae evident (L). Phyllosilicates with well developed orientation and poorly developed cleavage, elongated and quartz grains generally with an E-W orientation in the direction of cleavage. Larger quartz grains evident (Q) with no preferred orientation, but with compression coronas evident.

-Plate 7.15:- BSI analysis [x500mag]. Very densly packed groundmass of phyllosilicates with occasional voids. Phyllosilicates with moderately well developed orientation occasionally with low angle end-face arrangement, but generally with face-face arrangement in the direction of poorly developed cleavage, phyllosilicates locally recrystallized in to pockets (30μm) (P). Quartz grains generally fine grained <15μm in size, with high degree of phyllosilicate wrap around (Q). Occasional clastic grain contacts (CI). Moderate amount of haematite and pyrite (Py) cementation binding the groundmass. Argillite.

Ranking: A = 3; B = 3; C=2; D=3→ 11

S.1.1. -Plate 7.16:- Petrographic description - [x100mag. XPL]. Consists of many medium silt sized subangular to subrounded quartz clasts in a fine grained clay matrix. No evident lamination. Micas (muscovite) present tend to be randomly oriented. Moderate degree of compaction with no evident wrap around textures.

-Plate 7.17:- BSI analysis [x200mag]. Moderately dense with some small voids present within the matrix (V) moderately poorly oriented clay groundmass, generally with a turbostatic low angle end-face and face-face arrangement. Many subangular medium silt sized quartz grains often with dissolution haloes (Q), generally not touching but matrix supported. Many pockets of intergrown mica-chlorite (M-Ch) up to 80μm long generally with a random orientation, and relatively intact. Large clasts of calcium carbonate (<120μm) present within the silt sized clastic fraction, occasionally cementing the clay minerals together (C). Rare pockets of organic debris present (O), no evident clay mineral recrystallization. - Silty Mudstone.

Ranking: A = 2; B = 2; C=1; D=2→ 7

S.3.1 -Plate 7.18:- Petrographic description - [x100mag. XPL]. Fine groundmass of clay minerals, muscovite mica and fine silt sized quartz grains enclosing coarser rounded chlorite pods and occasional subangular quartz grains, preferred orientation in direction of lamination. [Plate7.19 - x 200 mag. XPL]. Showing pods consisting of chlorite locally intergrown with muscovite, with fracture development along cleavage direction.

-Plate 7.20:- BSI analysis - [x500mag.]. Moderately dense groundmass with occasional voids consisting of turbostratic low angle face-end and end-end clay grains, mainly illite and chlorite (I-Ch). Occasional quartz fragments up to 30μm in size, showing evidence of dissolution (Q). Many large subrounded chlorite pockets showing evidence of leaching as dark bands (Ch), suggesting weathering. No clastic grain contact evident. Small quantity of disseminated pyrite evident as cementing medium. Large chlorite pods show some evidence of recrystallization as interaction with the surrounding groundmass (G). Slightly weathered, clayey Mudstone.

Ranking: A = 2; B = 2; C=3; D=3→ 10

S.3.2 -Plate .21:- Petrographic description - [x100mag. XPL]. Sample consists of densely packed fine to coarse silt sized, subangular quartz, weathered plagioclase feldspar and muscovite grains in a fine clay matrix. Much evidence of clastic grain contact and suturing.

-Plate 7.22:- BSI analysis [x500mag]. Moderately dense with some voids between grains. Consists of many subangular to subrounded fine to medium sized quartz grains (Q) supported in a illitic matrix. Larger clasts consist of chlorite pockets (Ch), locally fractured wrapping plagioclase feldspar clasts (F), evident clastic grain contact (Qc). Clay minerals generally with turbostratic microstructure, locally showing recrystallization, and occasional pockets of possible authigenic illite (I). Siltstone.

Ranking: A = 2; B = 2; C=3; D=3→ 10

D.1.1 -Plate 7.23:- Petrographic description - [x100mag. XPL]. Very densly packed fine grained and fine silt sized quartz groundmass, oriented in direction of well developed cleavage parallel to bedding. Grading evident, coarsening towards the base of the photomicrograph. Quartz vein evident above the centre of the photomicrograph trending in a E-W direction. Much opaque possibly iron rich material present.

-Plate 7.24:-BSI analysis [x500mag]. Very densly packed with occasional small voids present. Groundmass consisting of mainly well oriented laminar phyllosilicates and fine silt sized quartz grains, with a slight crenulated cleavage being defined by intergrowths of chlorite/muscovite grains (I/Ch) trending a few degrees from the bedding (Cl). Occasional quartz grains evident with a wrap around texture and no evident clastic point contact (Q). Moderate degree of clay recrystallization and many lighter coloured pockets of iron oxide and iron carbonate cement. Argillite.

Ranking: A = 3; B = 3; C= 1; D=3→ 10

D.1.2 -Plate 7.25:- Petrographic description - [x100mag. XPL]. Densely packed fine grained groundmass of phyllosilicates and occasional quartz grains. Well oriented with developed cleavage. Phyllosilicate wrap-around quartz grains locally evident. Many opaque pockets of iron oxide cement. Lamination/vein of opaque material with occasional phyllosilicate and carbonate grains evident in SW corner of the photomicrograph.

-Plate7.26:- BSI analysis [x500 mag]. Densly packed fine phyllosilicate groundmass with some voids parallel to mineral orientation direction. Phyllosilicates well oriented in laminar arrangement, defining the cleavage. Occasional fine to medium silt sized quartz grains showing phyllosilicate wrap around (Q). Muscovite grains evident with cleavage fractures suggesting some weathering (M), also seen on edges of chlorite grains (Ch). No clastic grain contact. Much evident siderite cementation (S). Slightly weathered Argillite.

Ranking: A = 2½; B = 3; C=1; D=3→ 9½

D.2.1 -Plate 7.27:- Petrographic description - [x100mag. XPL]. Consists of dense interlaminated fine and course laminae. Fine grained laminae consisting of fine grained well oriented phyllosilicates and fine silt sized quartz grains. Coarser laminae consist of fine to medium silt sized quartz grains in a fine phyllosilicate groundmass. Well defined phyllosilicate orientation defines a cleavage parallel to bedding.

-Plate 7.28:- BSI analysis [x500mag]. Densly packed grains, with rare to occasional voids. Consists of subangular fine to medium silt sized quartz grains (Q), surrounded by fine grained groundmass of phyllosilicates with a general turbostratic arrangement. Occasional chlorite (Ch) and muscovite (M) grains present with orientation parallel and sub-perpendicular to bedding, some fracturing evident in these grains suggesting weathering. Crenulated cleavage traced by thin laminae of chlorite grains passing E-W in photomicrograph. Rare clastic contacts (Qc). Moderate recrystallization evident in phyllosilicate grains. Occasion acicular needles of $Ti0_2$ present. Slightly weathered Argillite.

Ranking: A = 3; B =2½; C=2; D=2 → 9½

C.1.B1 -Plate 7.29:- Petrographic description - [x100mag. XPL]. Consists of fine grained densly packed groundmass of clay minerals and organic material. Occasional fine to medium clasts of quartz and calcite present in the groundmass. No microlaminations evident.

-Plate 7.30:- BSI analysis [x500mag]. Very densly packed groundmass, with rare voids. Clay minerals, generally consisting of illite occur in pockets, (Cl) generally showing recrystallization. Angular clastic quartz grains present usually < 10µm in size, with not much dissolution effects (Q), generally surrounded by fine grained clay groundmass. Clay minerals with a general random to turbostratic low angle face-end arrangement. Rare clastic grain contact. Many large chlorite grains up to 40 µm in size present (Ch) consisting of compressed chlorite grains with inter layered or surrounding illite. Siderite present as a cementing agent (C). Much black organic debris present , and many acicular crystals of $Ti0_2$ (Ti). Claystone.

Ranking: A = 3; B =1½; C=1½; D=3 → 9

C.1.B2 -Plate 7.31:- Petrographic description - [x100mag. XPL]. Very densly compacted, fine groundmass of clay and clay to fine silt sized quartz grains. Microlamination evident consisting of clay rich horizons, locally cross bedding evident.

-Plate 7.32:- BSI analysis [x500mag]. Very densly compacted fine clay and quartz groundmass with traces of voids. Clay minerals with face-face laminar arrangement. Occasional fine silt sized quartz grains with clay wrap-around (Q). No evident clastic mineral contact. Clay mineral recrystallization evident in illite clusters (I). Occasional fragments of organic debris (O) compressed in laminate direction. Locally bound with carbonate cement (C). Feathery appearance of clay grains suggests possible authigenic constituents.

Ranking: A = 3; B =3; C=1; D=2 → 9

C.1.B4 -Plate 7.33:- Petrographic description - [x100mag. XPL]. Very densly compacted, fine groundmass of clay and fine silt sized quartz grains. Thin laminations evident of finer grained clay horizons and coarser silty horizons, trending NW-SE in photomicrograph. Well developed grain orientation.

-Plate 7.34:- BSI analysis [x500mag]. Very densly groundmass with traces of voids. Mainly composed of an illitic groundmass with a laminar to turbostratic face-face and low angle face-end arrangement, with larger mica grains (M) trending in the same orientation. Many subangular quartz grains (Q) up to 30μm in size. Traces of clastic grain contact (Qc). Occasional fragments of organic debris , and locally evident siderite cement binding clay grains (S). Silty Mudstone.

Ranking: A = 3; B =2½; C=2; D=2→ 9½

C.1.B5 -Plate 7.35:- Petrographic description - [x100mag. XPL]. Very densly compacted, fine clay and quartz groundmass. Preferred orientation of micas and quartz grains evident with a turbostratic face-face and low angle face-end arrangement. Occasional opaque pockets and partings possibly of organic material.

-Plate 7.36:- BSI analysis [x400mag]. Densly compacted clay and mica groundmass with occasional voids. Clay minerals with a general turbostratic face-face and low angle face-end arrangement (EF). Micas generally parallel and occasionally perpendicular to bedding (M). Occasional fine to medium silt sized quartz grains with clay wrap-around (Q). No evident clay mineral recrystallization. No evident clastic point contacts. Organic material present in pockets as a binding material or as partings (O) parallel to grain orientation. Occasional pyrite fromboids present (Py), as a result of early diagenetic growth, as evident by the surrounding clay distortion caused by compression. Mudstone

Ranking: A = 2½; B =2; C=1; D=2→ 7½

C.2.1 -Plate 7.37:- Petrographic description - [x100mag. XPL]. Dense fine clay and fine to medium silt sized quartz groundmass. Clay and clastic constituents are generally well oriented, with microlaminations defined by organic rich horizons, trending in a NE-SW direction.

-Plate 7.38:- BSI analysis [x1000mag]. Moderately densly compacted groundmass of clay minerals separated by partings of organic material. Clay minerals oriented in a wavy nature in the direction of lamination, in a turbostratic face-face and low angle face-end (T) arrangement and locally arranged as clay pockets (Ro). Much organic material present in thin partings (O) or pockets. Occasional clastic grains consist of subangular quartz grains (Q) and rare plagioclase feldspar grains showing clay and organic material wrap around (F). No clastic grain contact evident. Presence of many euhedral pyrite crystals (Py) generally within pockets of organic material and siderite crystal rhombs (S). No evident recrystallization of clay minerals, feathery nature possibly due to some authentic clay growth, and high magnification. Voids are evident in

[Plate 7.39:- SEI x500mag.] (V) parallel to lamination, suggesting microfractures caused by stress relief. Mudstone.

Ranking: A = 2; B =1½; C=1; D= 1½;→ 6

C.3.1 -Plate 7.40:- Petrographic description - [x100mag. XPL]. Densly packed fine to medium silt sized quartz grains in a clay matrix. Evident carbonate grains cementing clasts. Micas with turbostratic face-face and face-end orientation. Evident thick microlaminations consisting of coarser siltstone laminae, and finer mudstone laminae. Many opaque grains of organic material. Interlaminated.

-Plate 7.41:- BSI analysis - [x500mag.]. Very densly packed groundmass consisting of clay and silt sized material with rare voids. Consists of many subangular up to 20µm size quartz grains (Q) occasionally touching, with occasional clay mineral wrap around. Fine groundmass of clay minerals with a turbostratic face-face and low angle face-end to localy random arrangement. Evident laminations with grains coarsening to the base of the photomicrograph. Occasional large (<50µm) pods of intergrown muscovite/chlorite, locally bent due to consolidation (M/Ch). Some organic matter present acting as binding material (O). Much siderite cement present (S) and occasional pyrite fromboids (Py) grown in late stages of diagenesis as no compression displacement of clay minerals evident. Siltstone/Mudstone.

Ranking: A = 3; B =1½; C=2; D=3 → 9½

C.4.1 -Plate 7.42:- Petrographic description - [x100mag. XPL]. Densly packed fine matrix composed of clay minerals, fine to medium silt sized quartz and dolomite clasts. No evident mineral orientation weak lamination evident, material passing from coarser to finer grain size from W to E on the photomicrograph. Many dark opaque pockets possibly fragments of organic matter or pyrite.

-Plate 7.43:- BSI analysis - [x600mag]. Moderately densly compacted grains and matrix with occasional voids. Matrix composed of clay material randomly oriented or in pockets, (Cl). Quartz grains evident (Q) generally subangular to subrounded, with no evident clay wrap around. Occasional pockets of organic matter binding clay grains (O), and locally in-filled voids containing pyrite fromboids (Py). Scattered pockets of dolomite cement (D). Claystone/Mudstone.

Ranking: A = 2; B =1½; C=1; D= 1½;→ 6

C.5.1 -Plate 7.44:- Petrographic description - [x200mag XPL]. Moderately densly packed fine groundmass clay and opaque material. Lamination evident with laminae of mica grains passing NE-SW in the photomicrographs. General turbostratic low angle face-end mica arrangement. Occasional spherosiderites present indicative of a paleosol.

-Plate 7.45: BSI analysis - [x500mag]. Moderately densly packed groundmass with occasional voids. Consisting of a fine matrix of clay minerals with a general randomly oriented arrangement. Many mica (M) and chlorite (Ch) grains present, up to 10-15µm in size, randomly oriented. Sample containing occasional non touching quartz grains (Q), some siderite cement (S), and occasional pyrite fromboids (Py) within organic matter pockets. [Plate 7.46:- BSI - x150mag.]. Many spherosiderites grains present up to 100µm in diameter (S), quartz grains evident with dissolution and recrystallization rims (Q) up to 80µm in size. Clays and micas randomly oriented. Many microfractures evident (MF), possibly due to stress relief and slight weathering effects. Slightly weathered clayey Mudstone.

Ranking: A = 2; B =1; C=1; D= 2→ 6

C.5.2 -Plate 7.47:- Petrographic description - [x100mag. XPL]. Densly packed, consisting of silt sized subangular quartz grains, occasionally touching, in a groundmass of clay minerals. Occasional muscovite grains present with a general turbostratic low angle face-end orientation.

-Plate 7.48:- BSI analysis - [x200mag.]. Densly packed sample consisting of a silt sized quartz and mica fraction in a clay groundmass with occasional voids. Clay groundmass is generally randomly oriented or in pockets. Many larger (<70µm) muscovite (M) and chlorite (Ch) grains present, with evident leaching zones, split ends, and bent grains due to transportation and slight weathering. Quartz grains generally subangular, generally <40µm in size and rarely <80µm, generally touching (Q). Locally containing pyrite fromboids infilling voids (Py) and some organic matter present locally dispersed, Slightly weathered Siltstone/Mudstone.

Ranking: A = 2½; B =1; C=2½; D= 2;→ 8

C.6.1 -Plate 7.49:- Petrographic description - [x100mag. XPL]. Densly compacted, consisting of a clay and clay to fine silt sized quartz groundmass, supporting angular fine to medium silt sized quartz fragments. No evident lamination visible.

-Plate 7.50:- BSI analysis - [x500mag.]. Moderately densly compacted with occasional voids surrounding grains. Consisting of subangular silt sized quartz grains, (<45µm) locally touching showing evidence of dissolution (Q). Clay matrix with a random to turbostratic low angle face-end arrangement. Locally illite-chlorite recrystallization evident (I-Ch). Occasional discrete organic clasts (O), disseminated pyrite fromboids (Py) and locally carbonate cementation (C). Very silty Mudstone.

Ranking: A = 2; B =1½; C=2; D= 1½;→ 7

C.7.1 -Plate 7.51:- Petrographic description - [x100 mag. XPL]. Moderately densly compacted, consisting of an subangular fine to coarse silt sized fraction composed of quartz and micas in a fine clay groundmass. Many pockets of opaque matter possible organic material. Quartz and mica grains with a generally random orientation.

-Plate 7.52:- BSI analysis - [x500mag.] Moderately densly compacted , with occasional voids. Consisting of fine to coarse silt sized (<60µm) subangular quartz grains (Q), occasionally touching. Surrounded by a clay matrix consisting of illitic (I) and chloritic material (Ch), with a generally random to low angle turbostratic face-end arrangement. Occasionally large pockets of recrystallized illite/chlorite are evident together with disseminated carbonate cement (M-Ch). Large micas present showing fractures and bending possibly due to transportation (BM). Many pyrite fromboids and crystals (Py) present, generally within or near pockets of organic (O) matter, showing early growth with compression of clay minerals around the crystals [Plate 7.53-SEI -x1000mag.]. Pockets of pyrite crystals are evident within organic layers, and possibly replacing calcareous shell debris (Py). Locally surrounded by many voids (V), up to 15μm in size. Very silty <u>Mudstone</u>.

Ranking: A = 2; B =1; C=2; D= 2 → 7

C.8.2 -Plate 7.54:- Petrographic description - [100mag. XPL]. Densly packed coarse silt sized quartz grains. Many disseminated black opaque pockets, possibly of organic matter, lamination evident with clay rich horizon to the bottom SE section of the photomocrograph.

-Plate 7.55:- BSI analysis - [x500 mag.] Moderately densly packed fine clay groundmass, generally with a turbostratic face-face and low angle face-end arrangement, occasional fine voids and microfractures seen (Mf) parallel to the lamination. Occasional fine quartz grains (<8μm) present (Q), with clay wrap around. Much siderite cement present (S) intermixed with disseminated pyrite fromboids (Py), siderite containing traces of phosphorous possibly derived from bone material. With occasional pockets of organic debris (O). <u>Claystone</u>.

Ranking: A = 2; B =1½; C=1; D= 2;→ 6½

C.8.3 -Plate 7.56:- Petrographic description - [x100mag. XPL] Densly packed coarse silt sized quartz, mica and rock fragments (Rf) in a fine clay groundmass. Occasional plagioclase feldspar grains evident (Kf). Much opaque material present, defining lamination in a NW-SE trend on the photomicrograph.

-Plate 7.57:- BSI analysis [x500 mag.]. Densly packed with occasional voids (V) composed mainly of angular silt sized (<30μm) quartz grains (Q) with point contact. Matrix of clay minerals generally randomly oriented to turbostratic low angle face-end arrangement and wrapped around quartz grains. Locally cemented with siderite (S). Locally some quartz overgrowths seen (G) and some organic material present (O). <u>Siltstone</u>.

Ranking: A = 2; B =1½; C=3; D= 2½; → 9

C.9.2 -Plate 7.58:- Petrographic description - [x100mag. XPL]. Dense organic groundmass with pockets of clay material, and carbonates, and rare clay to fine silt sized quartz grains.

-Plate 7.59:- BSI analysis - [x500 mag.]. Densly compacted, well laminated organic groundmass with voids (V) less than 4μm in size. Organic material separating clay minerals with a turbostratic face-face and low angle face-end arrangement and rare quartz (Q) and feldspar (F) grains. Much siderite cement (S) and occasional pyrite (Py) crystals seen in an organic wrap-around. <u>Canneloid Claystone.</u>

Ranking: A = 2; B =2; C=1; D= 3 → 8

C.10.1 -Plate 7.60:- Petrographic description - [x100mag. XPL]. Densly compacted clay and fine silt sized quartz groundmass. With much medium coarse silt sized quartz grains, and mica grains generally randomly oriented.

-Plate 61:- BSI analysis - [x500 mag.] Moderately densly compacted, with some voids (V) around quartz and clay grains. Much angular silt sized quartz (<45μm) locally showing point contact (Q), within a matrix of clay minerals including fine micas (M) with a general random to turbostratic grain arrangement. Clays occasionally occur in pockets (Cl), locally anhedral pyrite cementing voids evident (Py), and carbonate cement (C).

Occasional fragments of organic matter (O). Silty Mudstone.

Ranking: A = 2; B =1½; C=2; D= 2; → 7½

C.11.1 -Plate 7.62:- Petrographic description - [x100mag. XPL]. Dense, laminated clay and clay to silt sized quartz matrix. With occasional medium silt sized quartz fragments. Pockets of opaque material, possibly organic matter and iron stained horizons defining lamination.

-Plate 7.63:- BSI analysis - [x500mag.]. Moderately dense to loose clay groundmass with many small voids, locally up to 30μm in size (V). Clay minerals well oriented in a laminar to turbostratic face-face and low angle face-end arrangement. Occasional quartz grains present, generally 5-15μm in size (Q). No clay recrystallization evident, locally carbonate grains are present, weakly cementing the clay minerals (C). Locally organic debris present defining lamination planes. Rare pyrite crystal grown in a void (Py). Claystone.

Ranking: A = 1½; B =2½; C=1; D= 1½; →6½

C.11.2 -Plate 7.64:- Petrographic description - [x100mag. XPL]. Densly packed, laminated fine to coarse silt size quartz generally touching. Plagioclase feldspar and mica grains, interlaminated between clay rich horizons containing occasional fine silt sized quartz grains, and oriented mica grains.

-Plate 7.65:- BSI analysis - [x500mag.]. Finer laminae, consisting of clay groundmass, generally in pockets (Cl) or turbostratic arrangement, wrapping around occasional fine silt sized (<10μm) quartz grains. Generally moderately densly compacted with some voids (V). Many large chlorite (Ch) and muscovite mica (M) grains present, generally split, probably due to transportation, and generally in a turbostratic orientation. Siderite cement present (S) and many disseminated pockets of pyrite fromboids (Py). Large organic clast present (O). Claystone.

-Plate 7.66:- BSI analysis - [x500mag.] Coarser laminae, moderately densly compacted with occasional microfractures present (MF). Consists largely of fine to medium silt sized (<30μm) quartz grains with much point contact (Q). Clay minerals generally in a turbostratic face-face and low angle face-end arrangement (Cl). Much siderite cement (S) locally disseminated with pyrite fromboids, and occasional pyrite crystals (Py) and disseminated pyrite. Pockets of organic debris present (O). Siltstone.

Sample - Interlaminated. Claystone/Siltstone.

Ranking: [Finer laminae] A = 2; B =1½; C=2; D= 2;→ 7½

Ranking: [Coarser laminae] A = 1½; B =2; C=3; D=2½;→ 9

Combined→8½

C.12.1 -Plate 7.67:- Petrographic description - [x100mag. XPL]. Densly compacted fine groundmass of clay minerals and clay to fine silt sized quartz fragments. Laminated in an NE-SW orientation on the photomicrograph, and generally bound by opaque organic material.

-Plate 7.68:- BSI analysis - [x1000mag.]. Loose to moderately densly packed, consisting of an organic groundmass, generally laminated. Occasional quartz grains present (<5μm) (Q) with mica (M) and clay grains, generally appearing in a turbostratic arrangement. Occasional pyrite crystals present (Py). Soft material therefore difficult to polish, although voids present within organic mass and around detail components (V). Canneloid Claystone.

Ranking: A = 1½; B =2; C=1; D= 2; → 6½

C.12.2 -Plate 7.69:- Petrographic description - [x100mag. XPL]. Moderately densly compacted fine to coarse silt sized quartz, muscovite and biotite mica grains, within a clay matrix. Many opaque pockets of organic material. Many quartz grains showing point contact, micas including quartz grains with a generally random orientation.

-Plate 7.70:- BSI analysis - [x300mag.]. Loose to moderately dense. Consisting of many subangular silt sized (<50μm) quartz grains, showing evidence of dissolution, (Q), and occasionally point contact. Clay matrix supporting the clastic grains in a general turbostratic face-face and low angle face-end arrangement, and wrap-around the quartz grains (W). Occasional voids evident around the clastic grains, and occasional microfractures (MF) parallel to the laminations. Containing occasional carbonate grains (C), loosely binding the clay minerals, and occasional late stage pyrite fromboids (Py). Chlorite (Ch), present, generally oriented in the lamination direction, generally appears broken, probably due to weathering or transportation. Rare K-feldspar grains present (F) with evident dissolution along twinning planes. Much organic material present (O), acting as a binding agent. Slightly weathered organic very silty Mudstone.

Ranking: A = 1½; B =2; C=2; D= 2 → 7½

C.13.1 -Plate 7.71:- Petrographic description - [x100mag. XPL]. Moderately densly compacted, well oriented fine groundmass of clay minerals. Occasional fine to medium silt sized quartz and carbonate grains present in the clay matrix. Occasional pockets of opaque material, possibly organic matter. Well defined lamination.

-Plate 7.72:- BSI analysis - [x750mag.]. Moderately densly compacted, with many small voids. Consisting of turbostratically arranged clay grains. Much siderite cement, appearing as discrete grains (S), occasionally wrapping around clay pockets, early grown as clay minerals compressed around the grains. Occasional silt sized quartz grains present (<15μm) (Q) generally wrapped by clay minerals. Pyrite crystals present within partings of organic material (Py), occasional partings of organic material (O) parallel to lamination. Organic Claystone.

Ranking: A = 1½; B =2; C=1; D= 2 → 6½

C.13.2 -Plate 7.73:- Petrographic description - [x100mag. XPL]. Moderately densly compacted, laminated. Laminae composed of angular fine to coarse silt sized quartz grains in a fine clay matrix generally touching, and organic rich clay groundmass with fine to medium silt sized quartz and mica grains. Micas generally oriented in a turbostratic arrangement. Rare sandstone rock fragment present (Rf).

-Plate 7.74:- BSI analysis - [x500mag.]. Moderately densly compacted with occasional voids. Many subangular fine to coarse silt sized (5-40μm) quartz grains, (Q) occasionally touching, set in a groundmass of turbostratic arranged to locally poorly oriented clay grains (R). With clay wrap around quartz grains locally evident. Many large broken micas grains (M), locally bent due to compression. Some siderite cementation (S) present, and pockets of organic material (O). Laminated Siltstone.

Ranking: A = 2½; B 1½; =; C=2; D= 2 → 8

C.13.3 -Plate 7.75:- Petrographic description - [x20mag. XPL]. Moderately densly packed fine to medium silt sized quartz in a clay matrix. Lamination evident, defined by opaque, possibly organic material. Occasional micas present with a random orientation.

-Plate 7.76:- BSI analysis - [x500mag.]. Moderately densly compacted, with occasional up to 8μm size voids (V). Consisting of a clay groundmass of clay aggregate pockets, mainly kaolinite (K). Occasional silt sized (<25μm) sized quartz grains present (Q) surrounded by clay, with rare euhedral authigenic quartz growth (aQ) within a void. Some organic material present (O), and pyrite fromboids within clay pockets (Py). Slight traces of siderite cement (S). Clayey Mudstone.

Ranking: A = 2; B = 1; C=1; D = 1½ → 5½

C.14.1 -Plate 7.77:- Petrographic description - [x100mag. XPL]. Moderately densly compacted clay and fine silt sized quartz grains, with occasional thin laminae running E-W on the photomicrograph, containing opaque grains, possibly organic material. Micas evident with a moderately random orientation.

-Plate 7.78:- BSI analysis - [x500mag.]. Moderately compacted with many small voids. Consisting mainly of a clay groundmass with a general turbostratic low angle face-end arrangement, trending N-S in the photomicrograph. Occasional quartz grains evident (Q), without well developed clay mineral wrap around. Siderite cement present in small pockets (S), much disseminated pyrite crystals and fromboids (Py). Some grains of organic material present (O). Clayey Mudstone.

Ranking: A = 2; B = 1½; C=1; D= 2 → 6½

C.15.1 -Plate 7.79:- Petrographic description - [x20mag. XPL]. Fine grained clay and fine silt sized quartz matrix. Generally contorted laminations present. With many discrete pockets of organic material.

-Plate 7.80:- BSI analysis - [x400mag.] Moderately dense with some small voids present. Groundmass consisting of undulose laminar to turbostratic low angle face-end arranged clay grains. Occasional small (<15μm) quartz grains present (Q) generally discrete with clay wrap around. Occasional large mica grains present (<40μm) interlaminated with chlorite (M-Ch), occasionally broken, possibly due to compression or transportation defects, as also seen in the smaller chlorite grains (Ch). Much disseminated pyrite fromboids present (Py). Organic material present (O) in large pockets (<200μm) with clay and quartz grains penetrating the rim due to compression, and pyrite (Py) also present within the pocket. Clayey Mudstone.

Ranking: A = 2; B = 1½; C=1; D= 1½; → 6

C.16.1 -Plate 7.81:- Petrographic description - [x100mag. XPL]. Moderately densly cemented material, occurring as laminated spherical calcareous clay pods, separated by laminae of organic material containing quartz grains and carbonate grains with occasional mica grains. Carbonate cement occasionally occurs in partings cementing together the clay pods as seen in [Plate 7.82 - x200mag. XPL].

-Plate 7.83:- BSI analysis - [x500mag.]. Very dense due to cementation, with occasional microfractures developing along partings of organic material (O). Clay occurring in pockets (Cl) and occasional quartz grains (Q), all cemented with disseminated siderite (S). occasional small pyrite fromboids present (Py). Calcareous, carbonaceous, clayey Mudstone.

Ranking: A = 2½; B = 1; C=1; D= 3 → 7½

C.17.1 -Plate 7.84:- Petrographic description - [x100mag. XPL]. Moderately densly packed groundmass of clay and fine to medium silt sized quartz grains. Lamination trending in a NE-SW direction on the photomicrograph. Many possible mudrock fragments (Rf), and opaque pockets becoming partings trending in the lamination direction, possibly consisting of organic matter.

-Plate 7.85:- BSI analysis - [x350mag.]. Densly packed with occasional small voids present. Groundmass of clay oriented in a turbostratic low angle face-end to randomly oriented arrangement. With much angular silt sized (<40µm) quartz grains showing evidence of dissolution (Q), and commonly showing point contact (cQ). Clay minerals tend to be wrapped around the quartz grains. Many pockets of disseminated pyrite fromboids (Py) occasionally binding clay minerals. Large pockets of organic matter present, acting as a binder (O). Very silty Mudstone.

Ranking: A = 2½; B = 1½; C=3; D= 2 → 9

C.17.2 -Plate 7.86:- Petrographic description - [x100mag. XPL]. Moderately dense, poorly developed lamination with grading becoming finer to the E of the photomicrograph. Consists of a clay and fine silt sized quartz matrix. With much matrix bound fine to coarse silt sized grains of quartz and mica. Many opaque pockets of organic matter, and occasional mudrock fragments (Rf).

-Plate 7.87:- BSI analysis - [x500mag.]. Densly packed with occasional voids between quartz grains. Groundmass of turbostratic to randomly oriented clays minerals, occasionally occuring as pockets. Many quartz grains (Q) generally <30µm in size with common point contact. Locally disseminated pockets of siderite cement (S), and occasional pyrite fromboids (Py). Rare organic matter inclusions present (O). Very silty Mudstone/Siltstone.

Ranking: A = 2½; B = 1½; C=3; D= 2½ → 9½

C.18.1 -Plate 7.88:- Petrographic description - [x100mag. XPL]. Moderately dense with poorly developed NE-SW lamination. Consisting of angular fine to medium silt sized quartz, and mica grains and clay pockets, in a clay matrix. Micas present generally in a turbostratic to random orientation. Many opaque pockets of possible organic material.

-Plate 7.89:- BSI analysis - [x350mag.]. Moderately dense with many voids

(V). Consisting of randomly oriented granular possibly kaolinitic clay, surrounding angular quartz (Q) grains, generally <30μm in size. Many mica (M) and chlorite (Ch) grains, generally fractured, and broken possibly due to transportation effects. Moderate amount of disseminated pyrite present (Py) and some grains of organic material (O). Silty Mudstone.

Ranking: A = 2; B = 1; C = 1; D = 2 → 6

### 7.5.2 Discussion of results and methods.

According to the BGS basin maturity chart presented in Figure 2.3 (chapter 2), the illite 'crystallinity' and vitrinite reflectance measurements show that the samples analysed range from early to late diagenetic and are of epizonal rank with no anchizone rank material being present within the data set. The majority of samples are "diagenetic" in rank and can be divided into early- mid- and late- diagenetic types as presented in Table 7.5 along with a classification based on vitrinite reflectance data. The data show that for 12 of the 41 samples analysed the results for illite 'crystallinity' and vitrinite reflectance place them within different rank groups. These discrepancies can be accounted for on the basis of lithological, mineralogical or tectonic constraints, except for sample C1B5 for which no explanation can be found. Where the discrepancies occur

| Diagenetic rank catagory. | Ilite 'crystallinity' | Vitrinite reflectance. |
|---|---|---|
| Early diagenesis:<br>Ic = >1.0°2θ<br>Ro% = <0.06. | O11, O12, S11, C1B1, C1B5, C21, C31, C41, C71, C131, C132, C133, C151, C181. | O11, O12, C21, C131, C132, C133, C141, C161, C181. |
| Mid diagenesis:<br>Ic = ~1.0 - 0.65°2θ<br>Ro% = 0.60 - 1.35. | S31, C1B4, C51, C61, C82, C92, C101, C111, C112, C121, C122, C141, C161, C172. | S31, S32, C41, C51, C52, C61, C71, C82, C83, C92, C101, C111, C112, C121, C122, C151, C171, C172. |
| Late diagenesis:<br>Ic = 0.65 - 0.42°2θ<br>Ro% = 1.35 - 1.90. | S32, C1B2, C52, C83, C171. | C1B1, C1B2, C1B4, C1B5, C31. |
| Epizone:<br>Ic = <0.25°2θ<br>Ro% = >4.00% | Ca11,Ca12, Ca13, O21, O31, D11, D12, D21. | O31, D21. |

Table 7.5 Rank catagorization of the samples based on illite 'crystallinity' and vitrinite reflectance.

of more than one grade. In two cases borderline determinations are included in with these results. The explanation for the discrepancies for the samples with anomolous correlations are as follows:-

- S11- Ic = early diagenetic: %Ro = mid diagenetic. The sample is moderately weathered and from a wet site , therefore the illite in the sample may have undergone regressive changes.
- S32- Ic = late diagenetic: %Ro = mid diagenetic. The sample is a siltstone which probably contains precipitated authigenic illite.
- C1B1- Ic = early diagenetic: %Ro = late diagenetic. This sample has a high organic content which would retard illite crystallization.
- C1B4- Ic = mid diagenetic: %Ro = late diagenetic. This sample is a siltstone with insufficient illite.
- C1B5- Ic = early diagenetitc %Ro = late diagenetic, this sample is a seatearth with insufficient illite and organic matter
- C31- Ic = early diagenetic: %Ro = late diagenetic. High calcareous content which would retard illite crystallization.
- C41- Ic = early diagenetic: %Ro = mid diagenetic. High calcareous content which would retard illite crystallization.
- C71- Ic = early diagenetic: %Ro = mid diagenetic. This sample is moderately weathered and from a wet, exposed site, therefore the illite in the sample may have undergone regressive changes.
- C141- Ic = mid diagenetic: %Ro = borderline early to mid diagenetic. The borderline result may have been due to difficulties obtaining vitrinite measurements.
- C151- Ic = early diagenetic: %Ro = mid diagenetic. This sample is from a site which has been affected by severe small scale tectonic movements which may have increased the rank of the organic matter by inducing loss of volatiles.
- C161- Ic = mid diagenetic: %Ro = borderline early to mid diagenetic. The borderline result may have been due to difficulties obtaining vitrinite measurements.
- C171- Ic = late diagenetic: %Ro = mid diagenetic. This sample is a siltstone which probably contains well developed authigenic illite

It is evident from the data that good agreement exists between the results for the diagenetic rank parameters for the samples. The few discrepencies are due to natural limitations as previously discussed and possible unavoidable machine and operator error.

The analysis of the optical photomicrographs did not provide much information, apart from indicating the form of the general clastic content, and the presence of laminations and grain orientation, all of which were also observed using back-scatter imagery (BSI). It must be remembered that due to the unavoidable problems encountered in sample preparation of mudrocks, it is not feasible to classify them using petrographic analysis, as an area of only a few hundred microns in diameter and up to thirty microns in thickness can be observed. Furthermore due to the difficulties in preparing specimens, it is the most competent materials and mineral constituents which tend to survive the preparation procedures. Using backscatter imagery, detailed textural information can be obtained for each specimen in both the BSI and secondary electron (SE) modes, the SE mode is most useful in confirming the presence of voids which are indistinguishable from organic material in BSI mode.

The process of illite 'crystallinity' maturation is generally regarded as an irreversible process, although exposure to weathering over a long period of time can result in illite degradation due to leaching of interstitial $K^+$ and replacement by $OH^-$. This change in illite 'crystallinity' is a relatively slow process in comparison with the physical changes which accompany exhumation. Such stress relief and weathering effects are not adequately detected using Ic measurements. On the other hand a ranking which takes into account textural data, the rock fabric and actual durability is more likely to correlate with relevant engineering parameters. Combining textural data in the form of ranking or brief key descriptions with crystallinity values will give a better indication of the maturity and level of physical soundness of mudrocks. The results for the ranking values for each of the four descriptive categories are presented in Table 7.6, and the terms are defined as follows:

(A) Density and degree of mineral packing.

(B) Clay mineral orientation.

(C) Degree of clastic constituent contact.

(D) Degree of cementation.

The illite 'crystallinity' and textural ranking data are compared in Table 7.7 and the relationship is further evaluated in Chapter 9. It is evident that a general relationship exists between the data sets although there is some overlap between the textural rank values for diagenetic zones. Illite 'crystallinity' values tend to be higher for samples with higher rank values  and low for samples with a low textural rank classification. These results are related since diagenetic changes affecting 'crystallinity' values also implement the textural changes in the mudrock. Discrepencies between textural data and crystallinity values will result due to mineralogical differences, such as carbonate and clastic content between samples. As such, cement and the amount of clastic material are important parameters controlling the engineering properties of the mudrocks.

Therefore it is considered that textural evaluation of mudrocks using the scheme described together with illite 'crystallinity' data are essential when evaluating physical behaviour of mudrocks, since these methods of analysis are relatively rapid and easy to perform. Further discussion of these data in terms of mineralogy and effects on engineering properties are included in Chapter 9.

| Sample. | A | B | C | D | Textural rank. |
|---|---|---|---|---|---|
| Ca11 | 3 | 3 | 2 | 3 | 11 |
| Ca12 | 3 | 3 | 3 | 3 | 12 |
| Ca13 | 3 | 3 | 3 | 3 | 12 |
| O11 | 2 | 1 ½ | 1 | 2 | 6 ½ |
| O12 | 1 ½ | 1 ½ | 1 | 2 | 6 |
| O21 | 3 | 3 | 2 ½ | 3 | 11 ½ |
| O31 | 3 | 3 | 2 | 3 | 11 |
| S11 | 2 | 2 | 1 | 2 | 7 |
| S31 | 2 | 2 | 3 | 3 | 10 |
| S32 | 2 | 2 | 3 | 3 | 10 |
| D11 | 2 ½ | 3 | 1 | 3 | 9 ½ |
| D12 | 3 | 2 ½ | 2 | 2 | 9 ½ |
| D21 | 3 | 2 ½ | 2 | 2 | 9 ½ |
| C1B1 | 3 | 1 ½ | 1 ½ | 3 | 9 |
| C1B2 | 3 | 3 | 1 | 2 | 9 |
| C1B4 | 3 | 2 ½ | 2 | 2 | 9 ½ |
| C1B5 | 2 ½ | 2 | 1 | 2 | 7 ½ |
| C21 | 2 | 1 ½ | 1 | 1 ½ | 6 |
| C31 | 3 | 2 | 2 | 3 | 10 |
| C41 | 2 | 1 ½ | 1 | 1 ½ | 6 |
| C51 | 2 | 1 | 1 | 2 | 6 |
| C52 | 2 ½ | 1 | 2 ½ | 2 | 8 |
| C61 | 2 | 1 ½ | 2 | 1 ½ | 7 |
| C71 | 2 | 1 | 2 | 2 | 7 |
| C82 | 2 | 1 ½ | 1 | 2 | 6 ½ |
| C83 | 2 | 1 ½ | 3 | 2 ½ | 9 |
| C92 | 2 | 2 | 1 | 3 | 8 |
| C101 | 2 | 1 ½ | 2 | 2 | 7 ½ |
| C111 | 1 ½ | 2 ½ | 1 | 1 ½ | 6 ½ |
| C112 | 2 | 1 ½ | 2 | 2 | 7 ½ |
| C121 | 1 ½ | 2 | 1 | 2 | 6 ½ |
| C122 | 1 ½ | 2 | 2 | 2 | 7 ½ |
| C131 | 1 ½ | 2 | 1 | 2 | 6 ½ |
| C132 | 2 ½ | 1 ½ | 2 | 2 | 8 |
| C133 | 2 | 1 | 1 | 1 ½ | 5 ½ |
| C141 | 2 | 1 ½ | 1 | 2 | 6 ½ |
| C151 | 2 | 1 ½ | 1 | 1 ½ | 6 |
| C161 | 2 ½ | 1 | 1 | 3 | 7 ½ |
| C171 | 2 ½ | 1 ½ | 3 | 2 | 9 |
| C172 | 2 ½ | 1 ½ | 3 | 2 ½ | 9 ½ |
| C181 | 2 | 1 | 1 | 2 | 6 |

A = Density and degree of mineral packing. B = Clay mineral orientation. C = Clastic contact. D = Degree of cementation.

Table 7.6 Values for textural rank classification of the samples.

| Diagenetic classification based on illite 'crystallinity'. | Samples (Ic: Texturalrank) | Range of the group textural rank classification. |
|---|---|---|
| Early diagenetic:<br>Ic = >1.0 °2θ | O11(2.98:6½), O12(2.90:6), S11(2.30:7), C1B1(1.11:9), C1B5(1.80:7½), C21(1.17:6), C31(1.06:10), C41(2.35:6), C71(2.90:7), C131(2.82:6½), C132(2.69:8), C133(2.69:5½), C151(2.78:6), C181(3.20:6). | 6 - 7½<br>(MEDIAN = 6) |
| Mid diagenetic:<br>Ic = 1.0 - 0.65 °2θ | C1B4(0.96:9½), C51(0.70:6), C61(0.89:7), C82(0.89:6½), C92(0.93:8) C101(0.91:7½), C111(0.66:6½), C112(0.70:7½), C121(0.75:6½), C122(0.86:7½), C141(0.72:6½), C161(0.93:7½), C172(0.69:9½). | 6 - 9½<br>(MEDIAN = 7.5) |
| Late diagenetic:<br>Ic = 0.65 - 0.42 °2θ | S31(0.62:10), S32(0.55:10), C1B2(0.48:9), C52(0.64:8), C83(0.56:9) C171(0.64:9). | 8-10<br>(MEDIAN = 9) |
| Epizone:<br>Ic = <0.25 °2θ | Ca11(0.22:11), Ca12(0.20:12), Ca13(0.19:12), O21(0.22:11½), O31(0.20:11), D11(0.22:9½), D12(0.22:9½), D21(0.21:9½). | 9½ - 12<br>(MEDIAN = 11.5) |

Table 7.7 Comparison of illite 'crystallinity' and textural rank data.

Plate 7.1 Sample Ca.1.1. Standard petrographic photomicrograph. [x100mag. XPL]

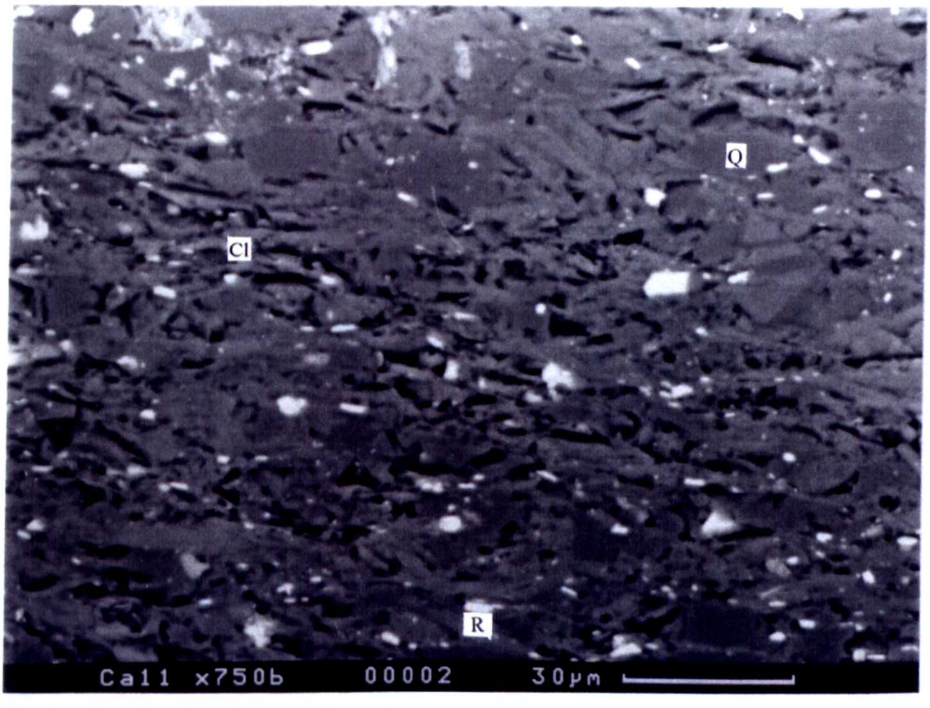


Plate 7.2 Sample Ca.1.1. BSI photomicrograph. [x750mag.]

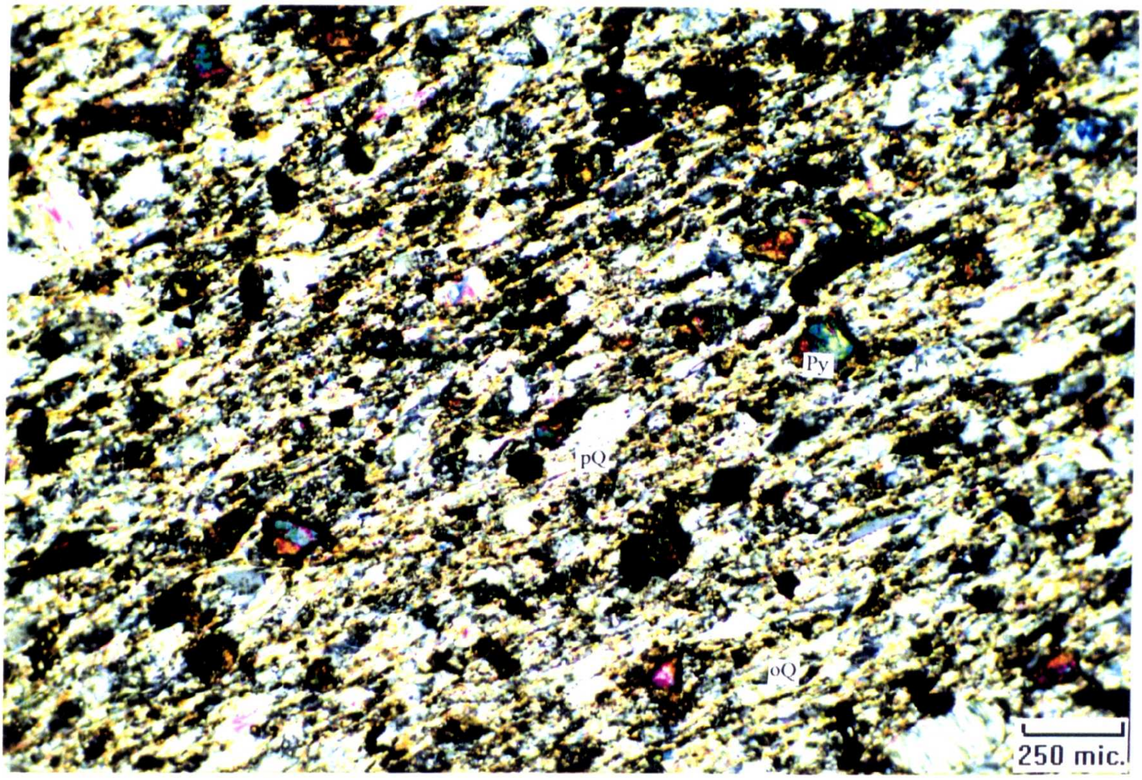


Plate 7.3 Sample Ca.1.2. Standard petrographic photomicrograph. [x100mag. XPL]

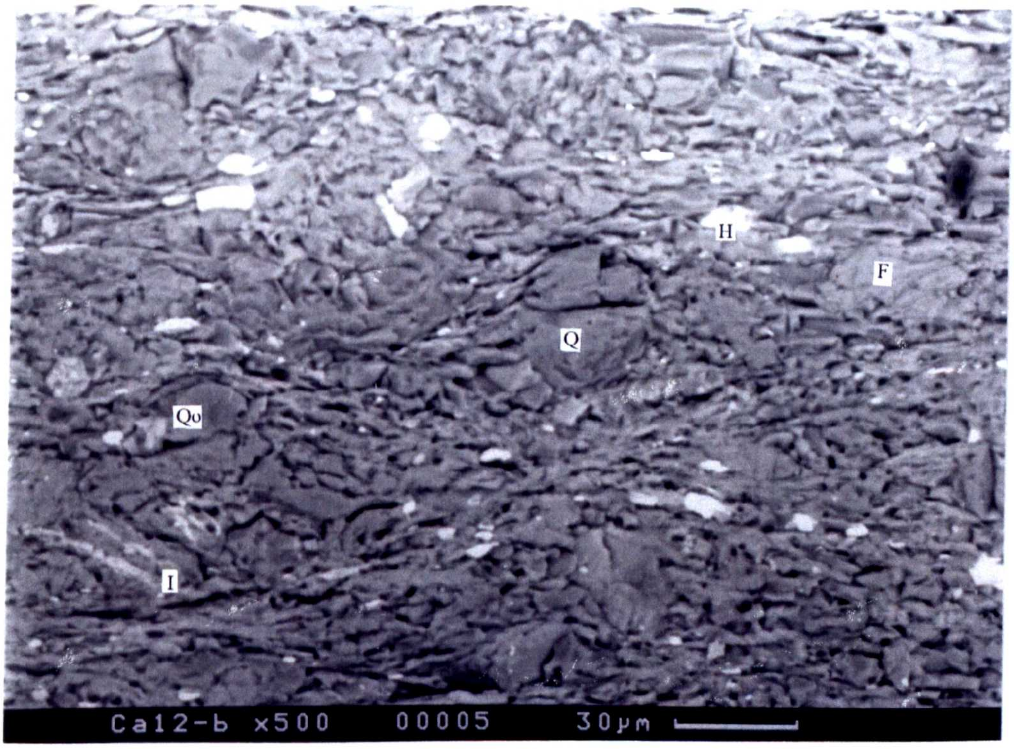


Plate 7.4 Sample Ca.1.2. BSI photomicrograph. [x500mag.]

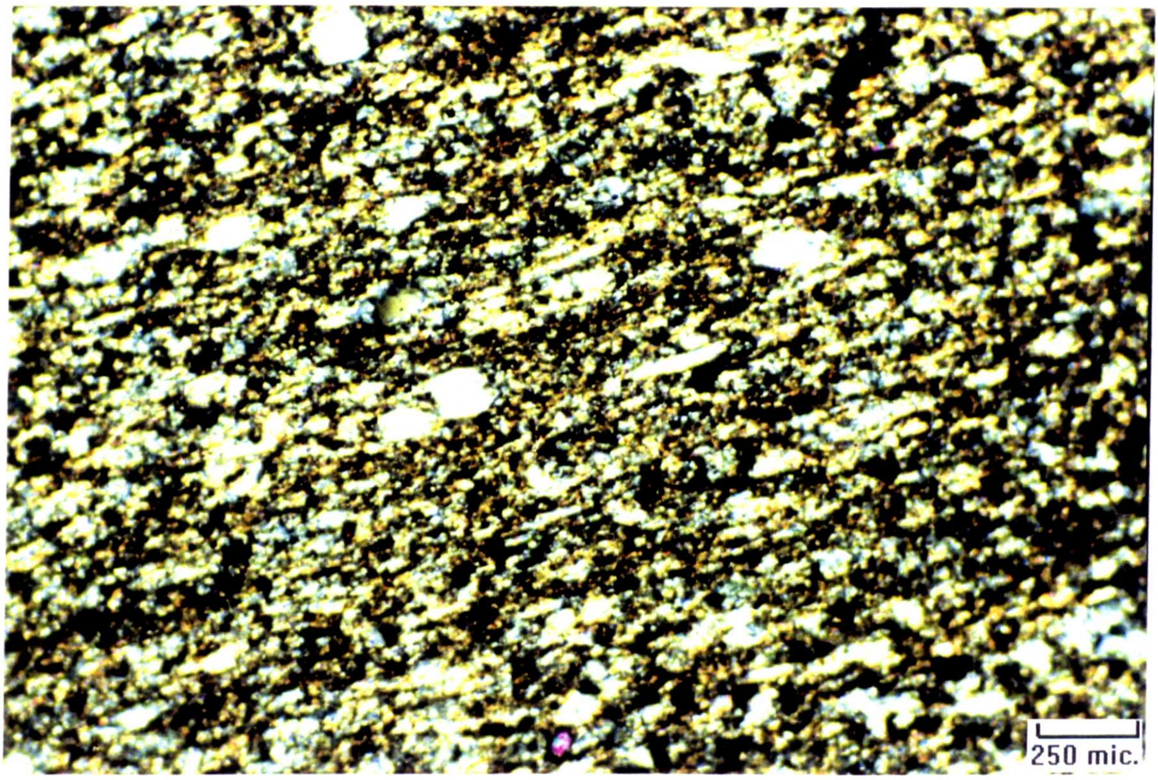


Plate 7.5 Sample Ca.1.3. Standard petrographic photomicrograph. [x100mag. XPL]

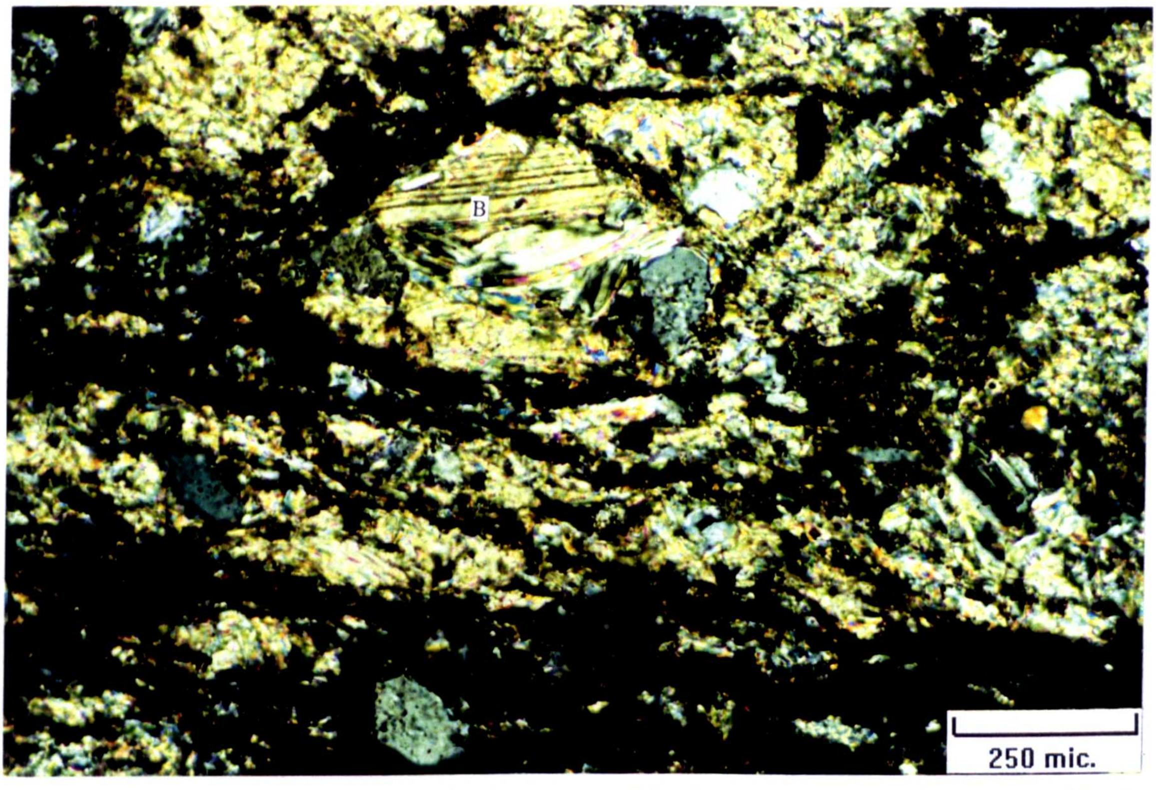


Plate 7.6 Sample Ca.1.3. Standard petrographic photomicrograph. [x200mag. XPL]

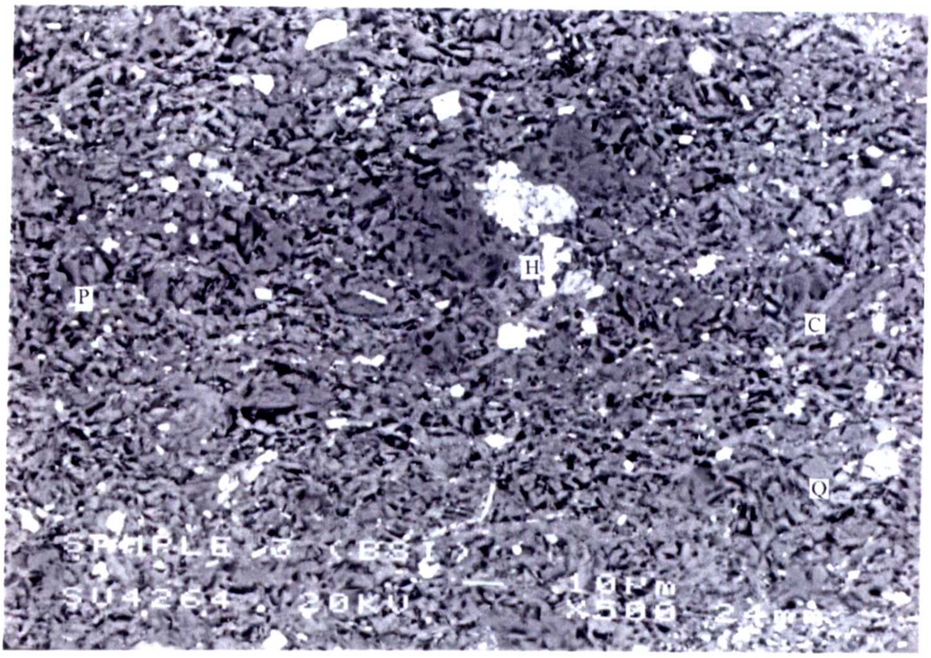


Plate 7.7 Sample Ca.1.3. BSI photomicrograph. [x500mag.]

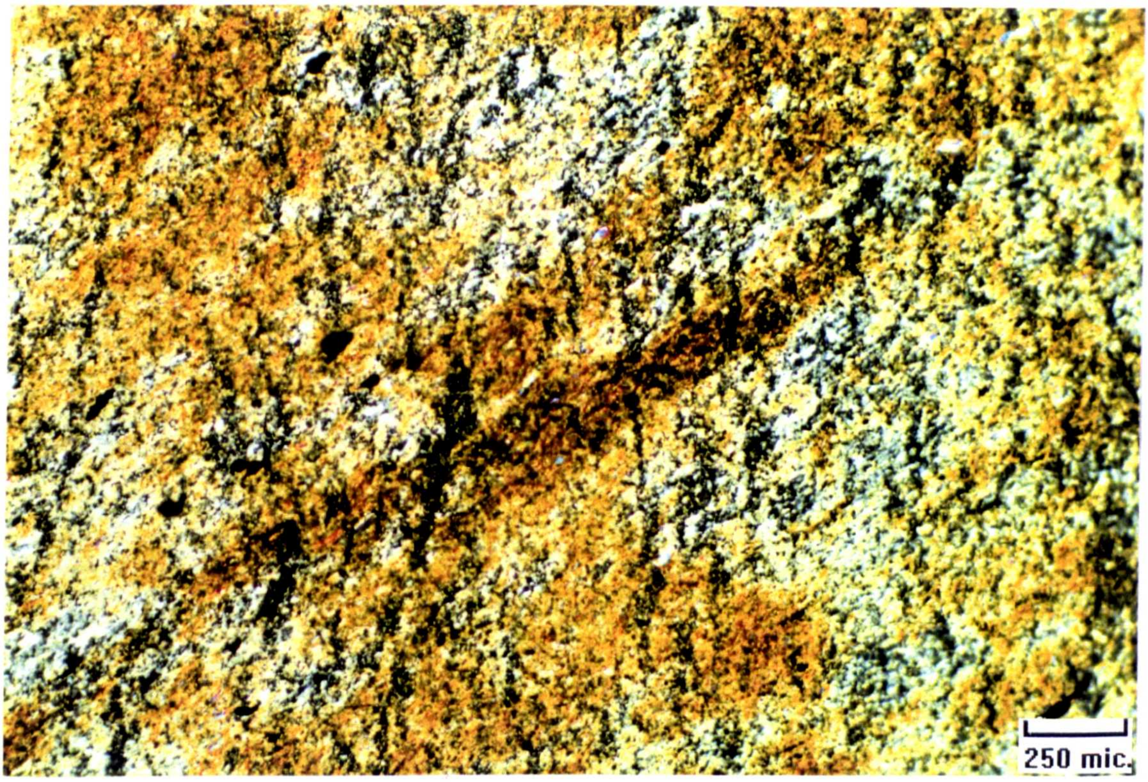


Plate 7.8 Sample O.1.1. Standard petrographic photomicrograph. [x100mag. XPL]

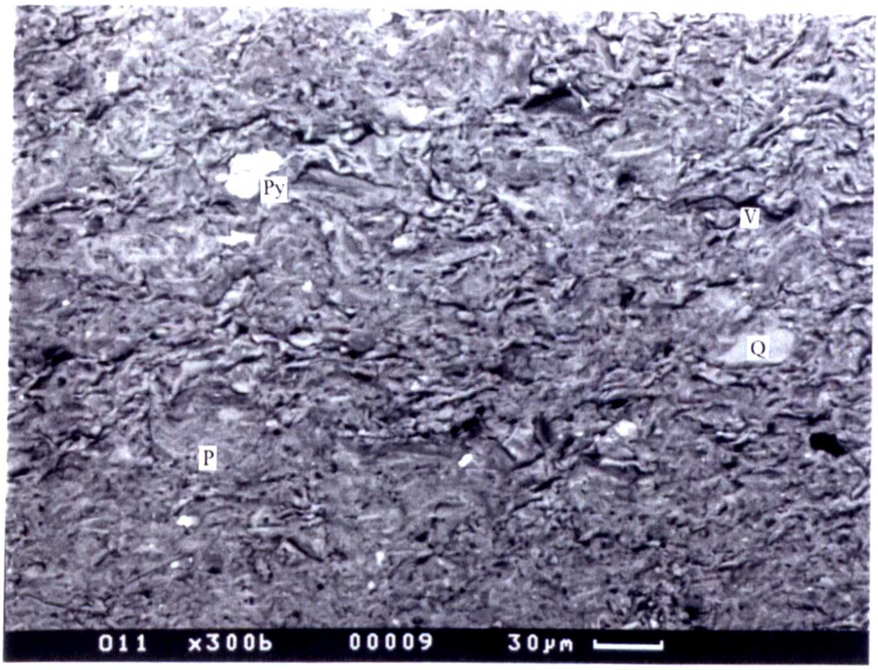


Plate 7.9 Sample O.1.1. BSI photomicrograph. [x300mag.]

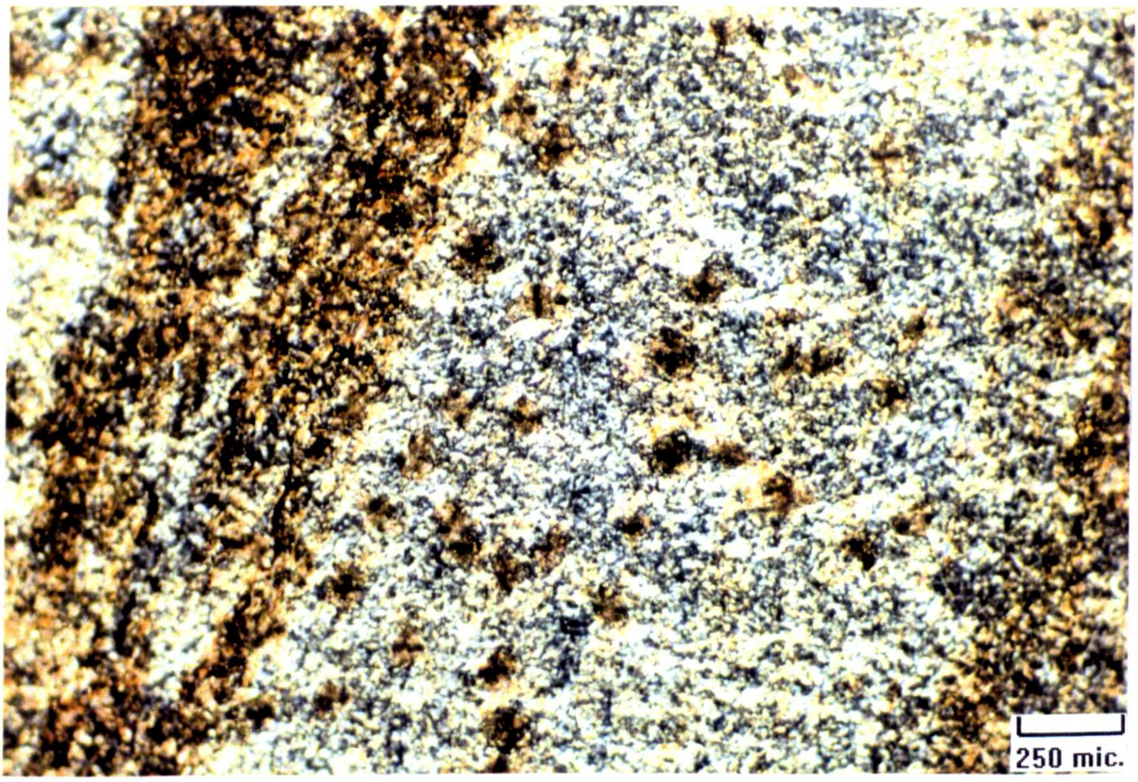


Plate 7.10 Sample O.1.2. Standard petrographic photomicrograph. [x100mag. XPL]

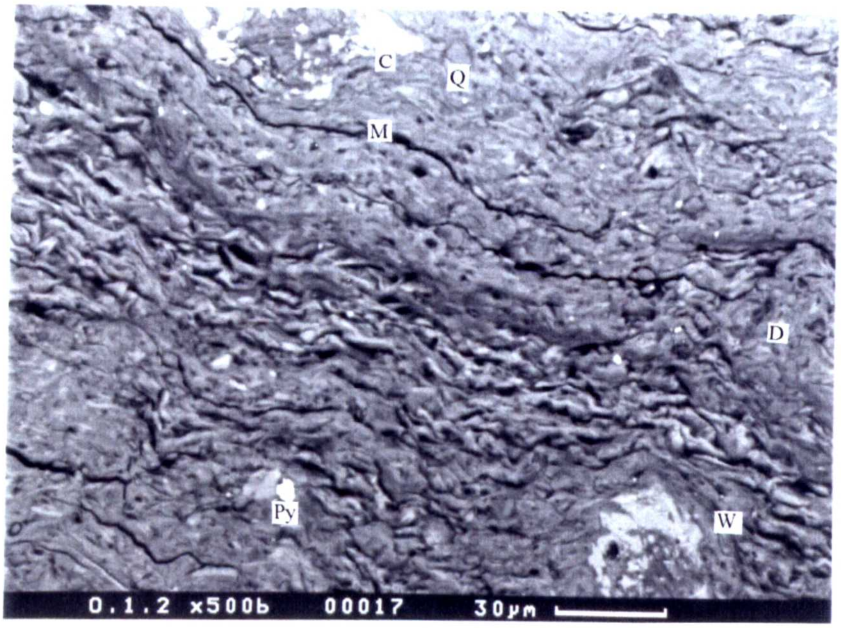


Plate 7.11 Sample O.1.2. BSI photomicrograph. [x500mag.]

Plate 7.12 sample O.2.1. Standard petrographic photomicrograph. [x100mag. XPL]

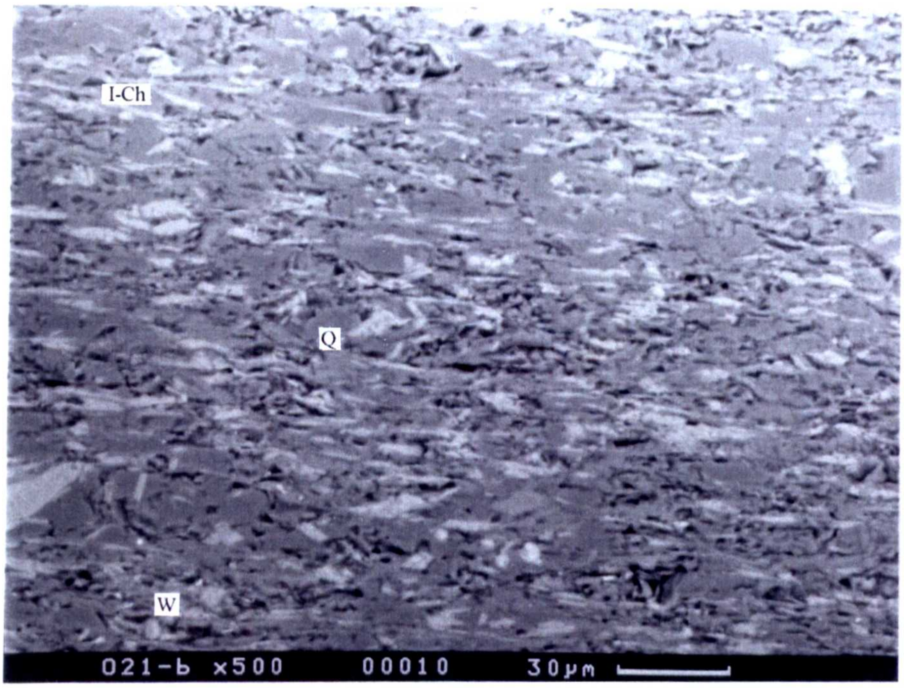


Plate 7.13 Sample O.2.1. BSI photomicrograph. [x500mag.]

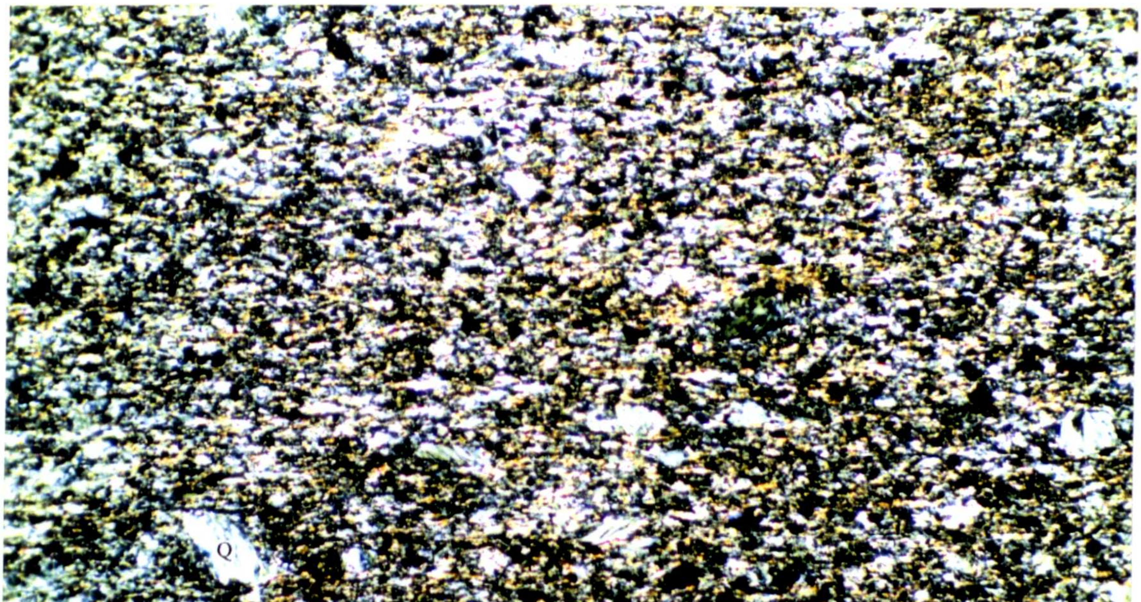


Plate 7.14 Sample O.3.1. Standard petrographic photomicrograph. [x100mag. XPL]

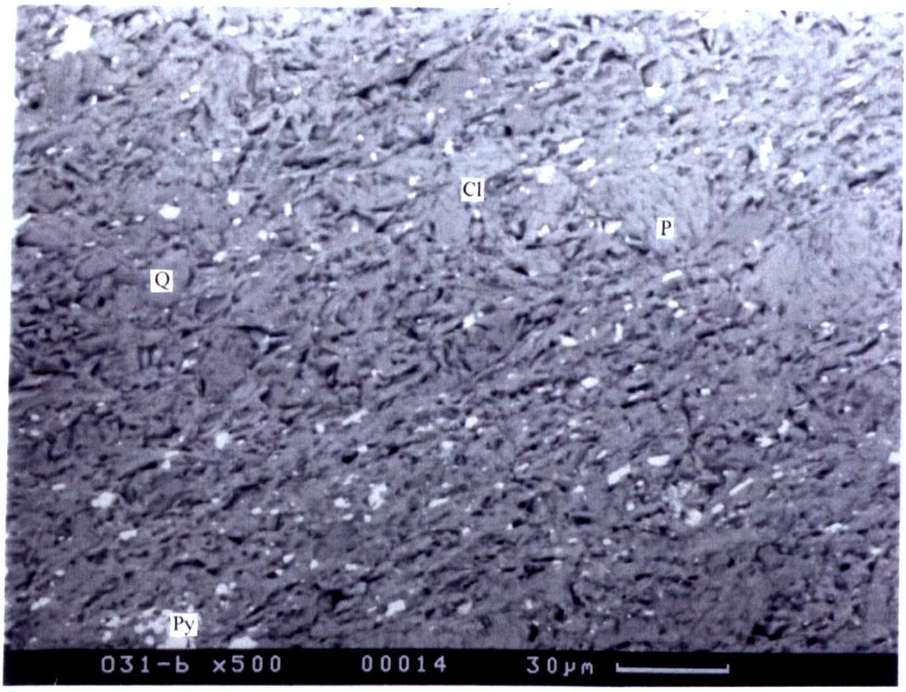


Plate 7.15 Sample O.3.1. BSI photomicrograph. [x500mag.]

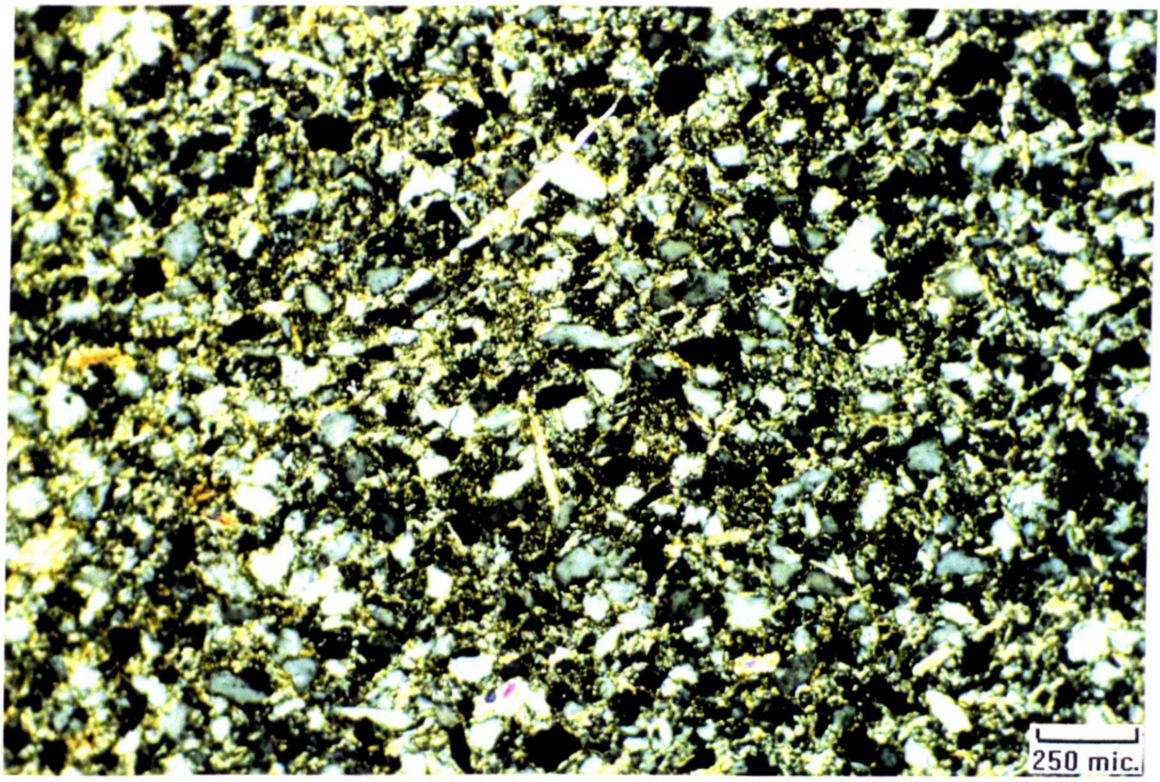


Plate 7.16 Sample S.1.1. Standard petrographic photomicrograph. [x100mag. XPL]

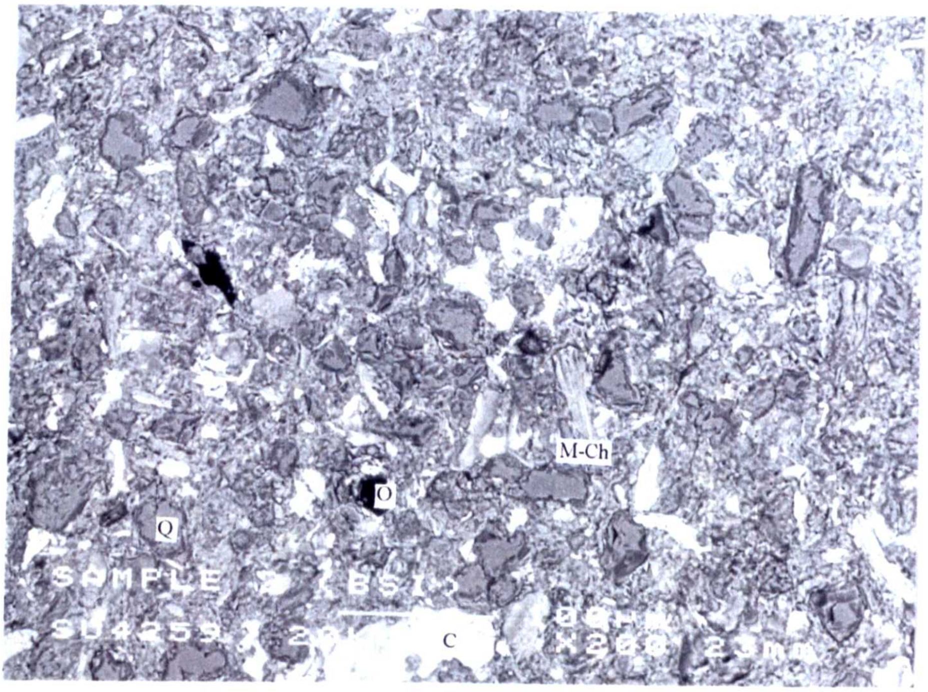


Plate 7.17 Sample S.1.1. BSI photomicrograph. [x200mag.]

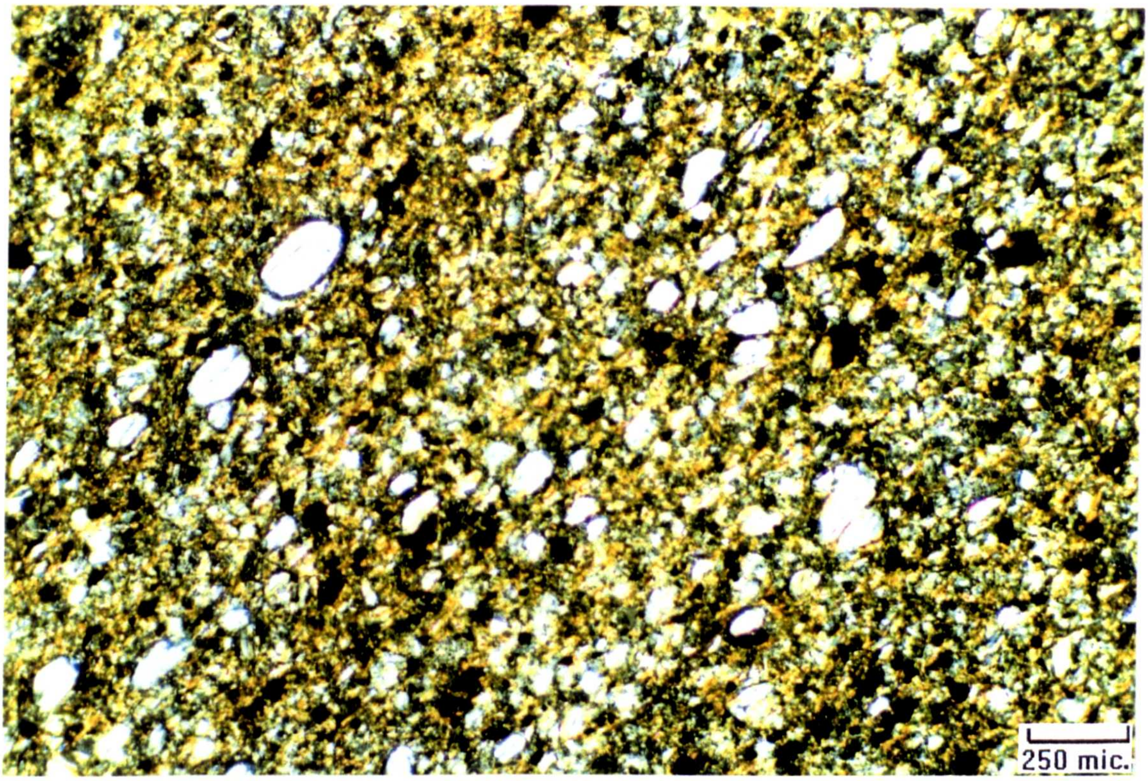


Plate 7.18 Sample S.3.1. Standard petrographic photomicrograph. [x100mag.]

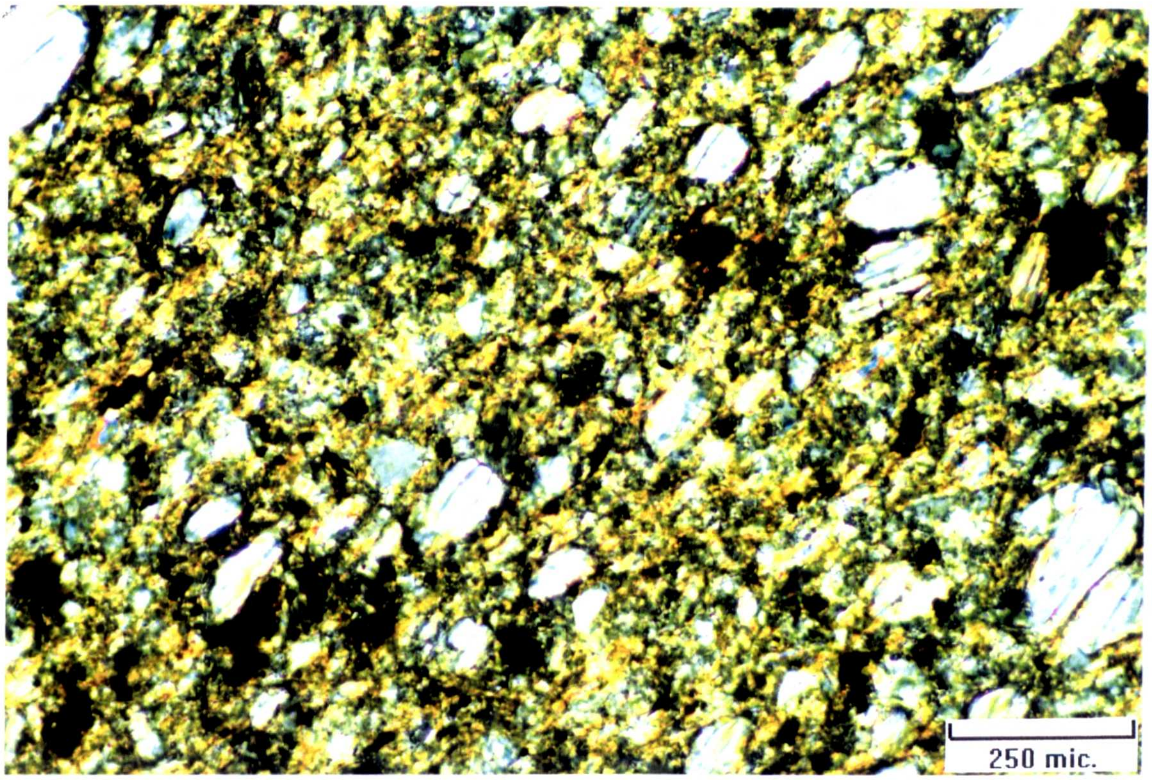


Plate 7.19 Sample S.3.1. Standard petrographic photomicrograph. [x200mag. XPL]

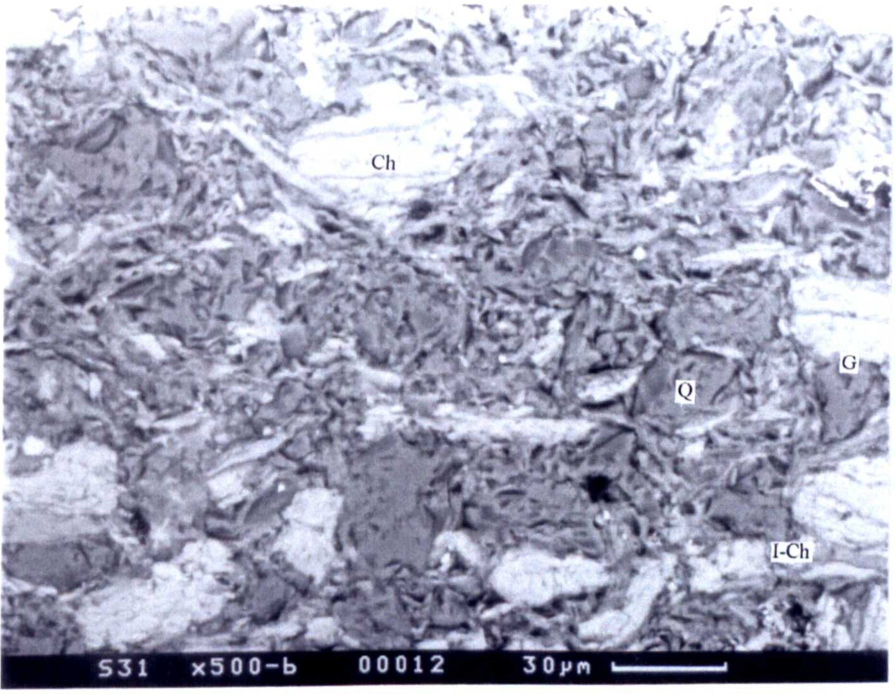


Plate 7.20 Sample S.3.1. BSI photomicrograph. [x500mag.]

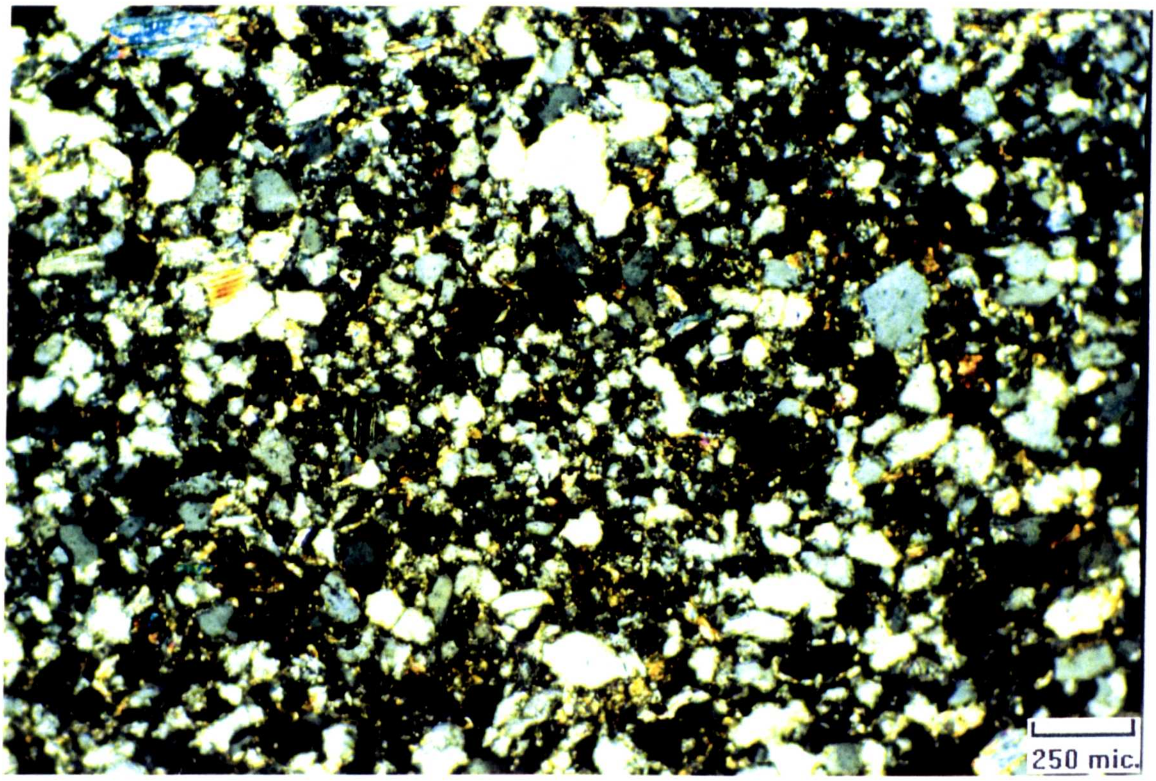


Plate 7.21 Sample S.3.2. Standard petrographic photomicrograph. [x100mag. XPL]

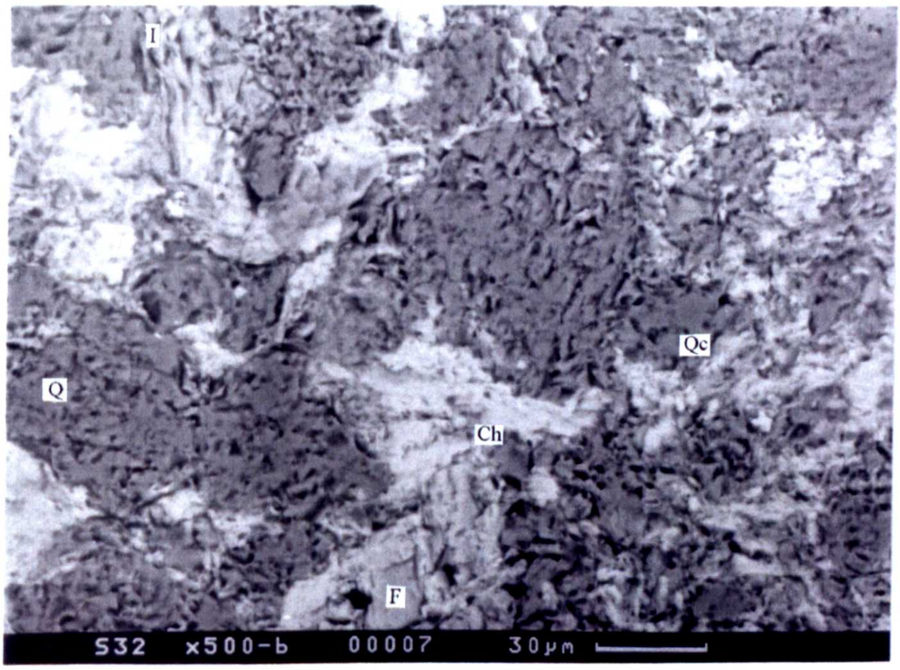


Plate 7.22 Sample S.3.2. BSI photomicrograph. [x500mag.]

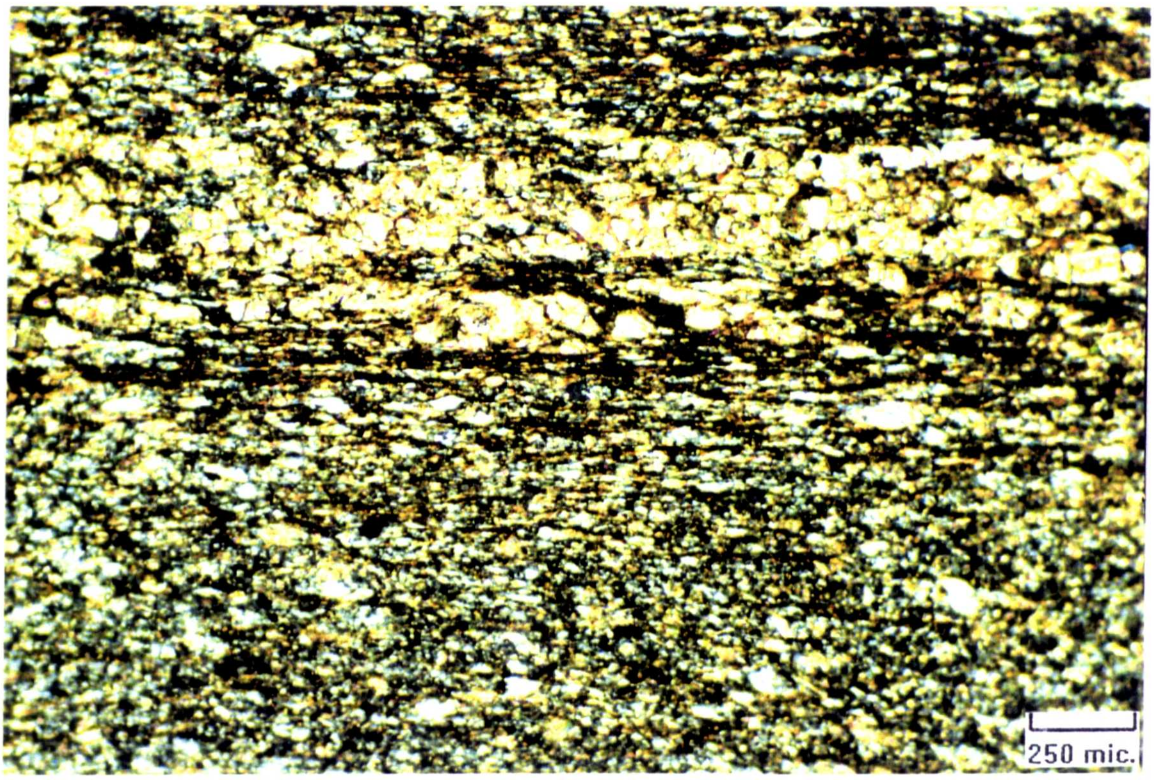


Plate 7.23 Sample D.1.1. Standard petrographic photomicrograph. [x100mag. XPL]

Plate 7.24 Sample D.1.1. BSI photomicrograph. [X500mag.]

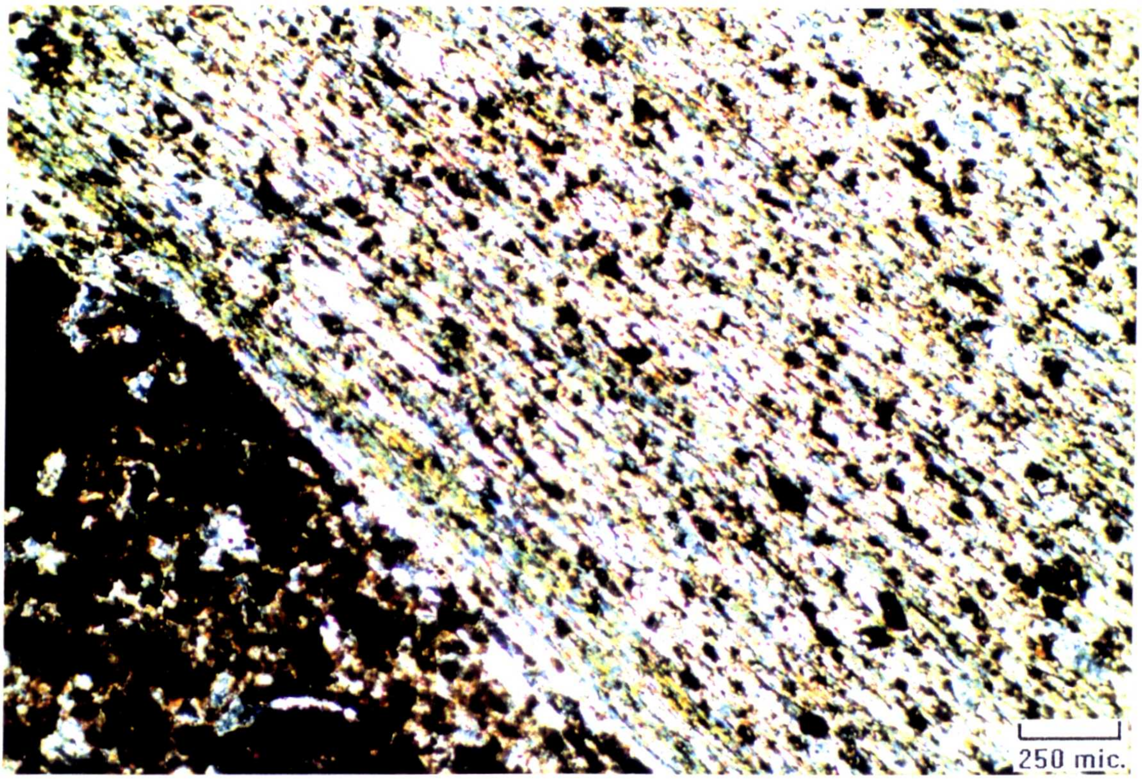


Plate 7.25 Sample D.1.2. Standard petrographic photomicrograph. [x100mag. XPL]

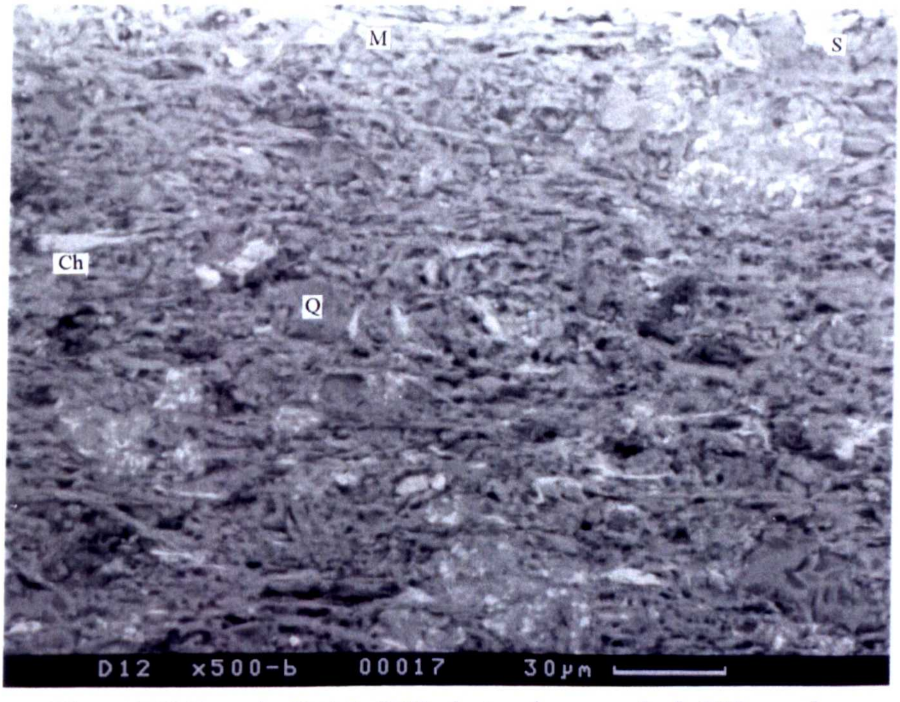


Plate 7.26 Sample D.1.2. BSI photomicrograph. [x500mag.]

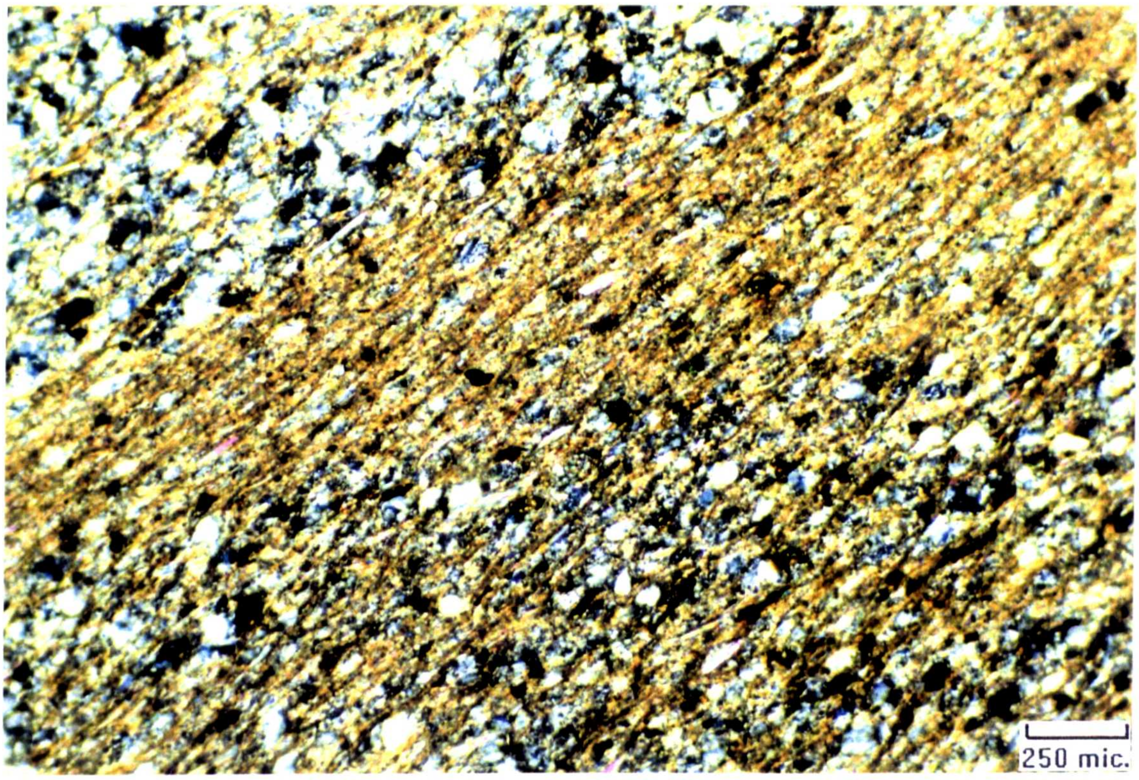


Plate 7.27 Sample D.2.1. Standard petrographic photomicrograph. [x100mag.]

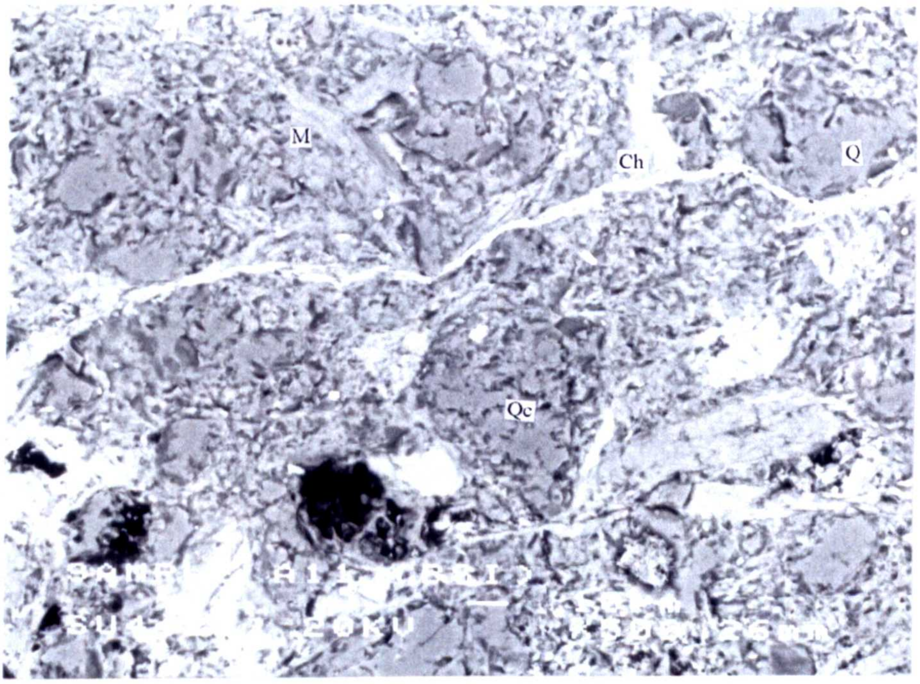


Plate 7.28 Sample D.2.1.BSI photomicrograph. [x500mag.]

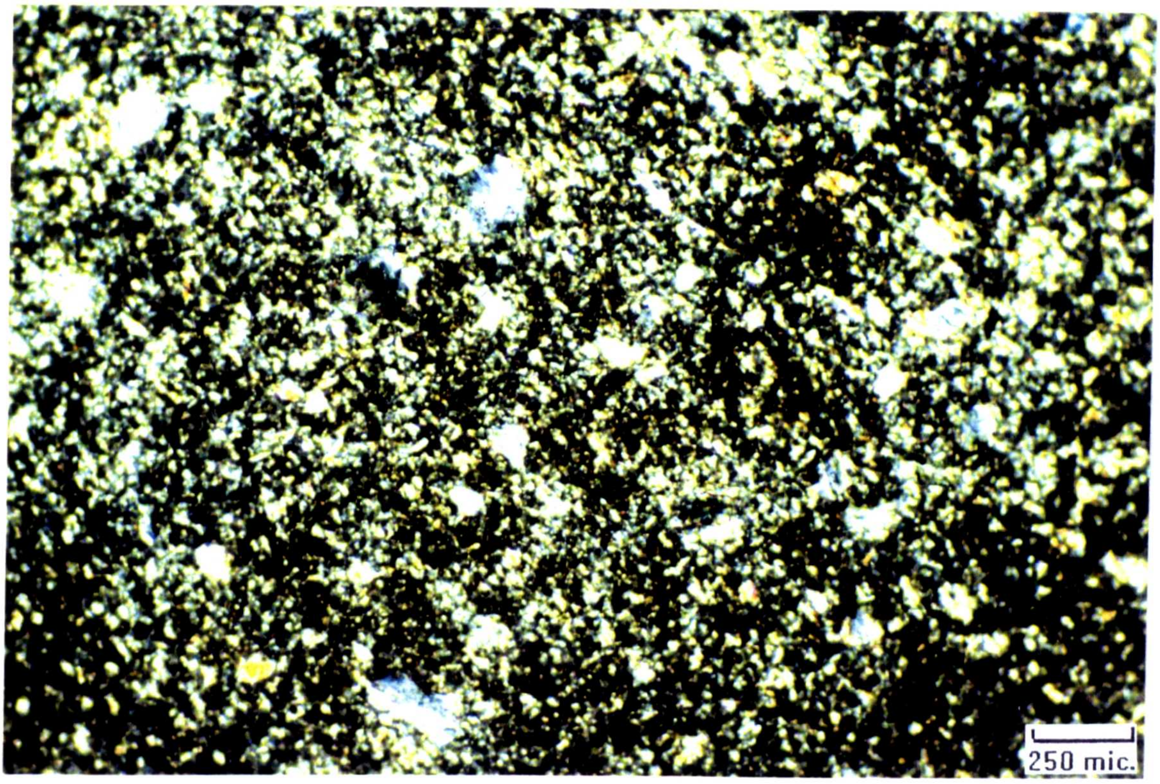


Plate7.29 Sample C.1.B1. Standard petrographic photomicrograph. [x100mag. XPL]

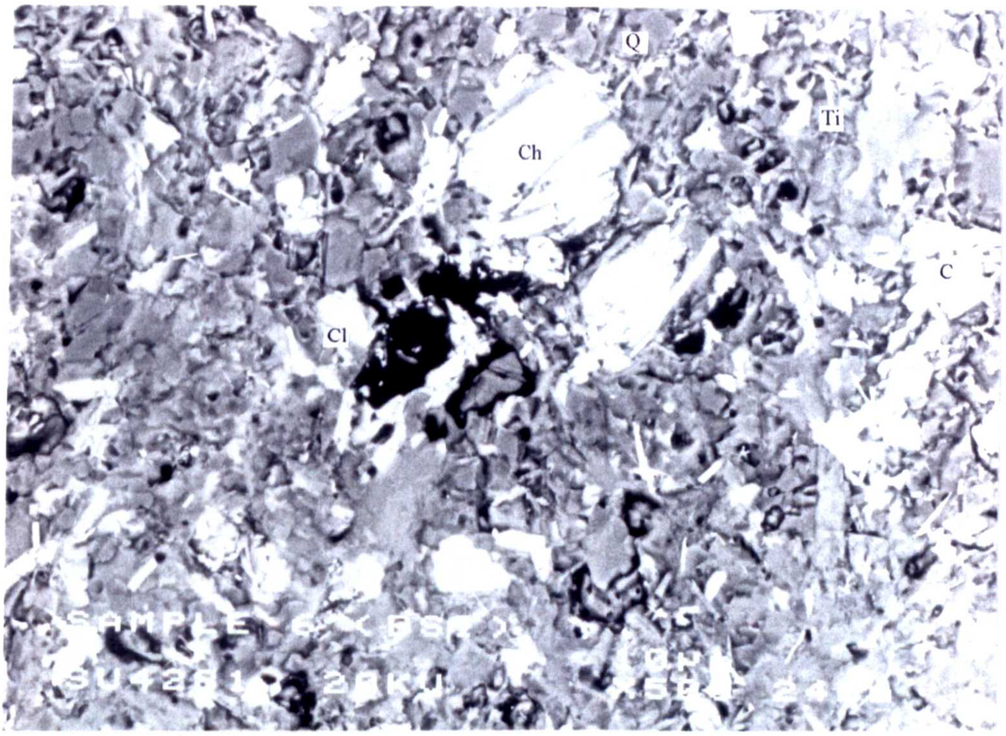


Plate 7.30 Sample C.1.B1. BSI photomicrograph. [x500mag.]

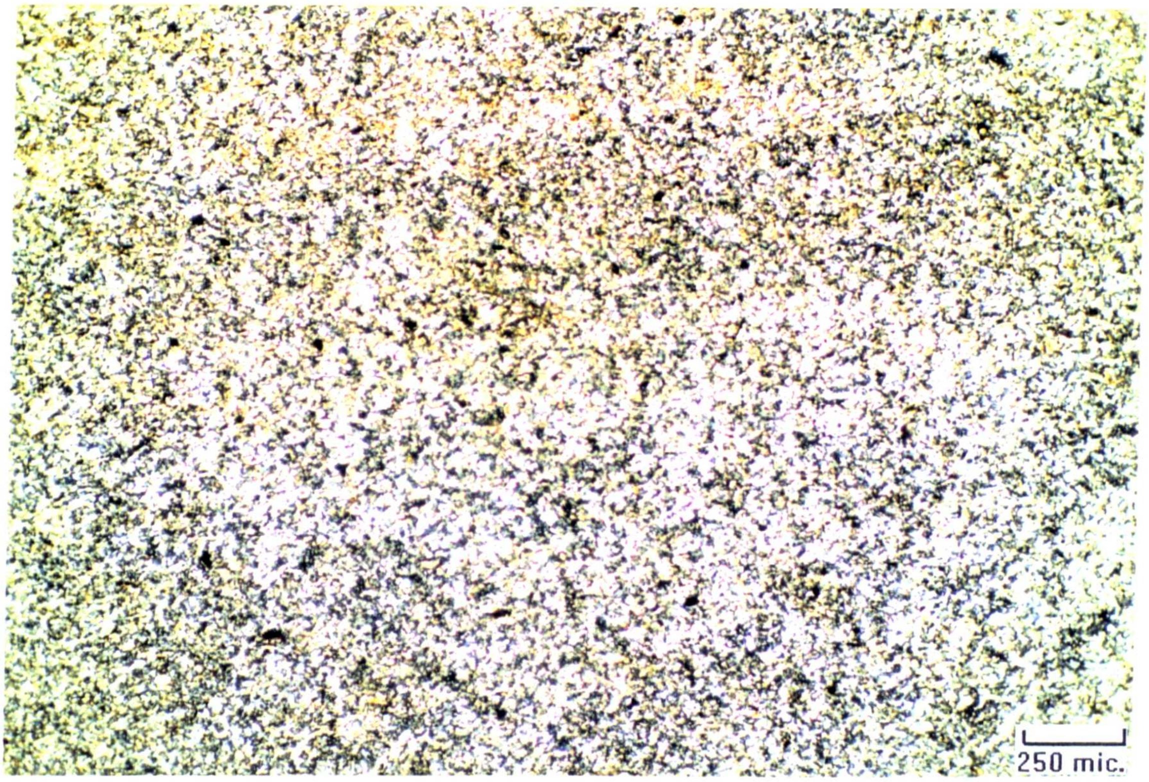


Plate 7.31 Sample C.1.B2. Standard petrographic photomicrograph. [x100mag. XPL]

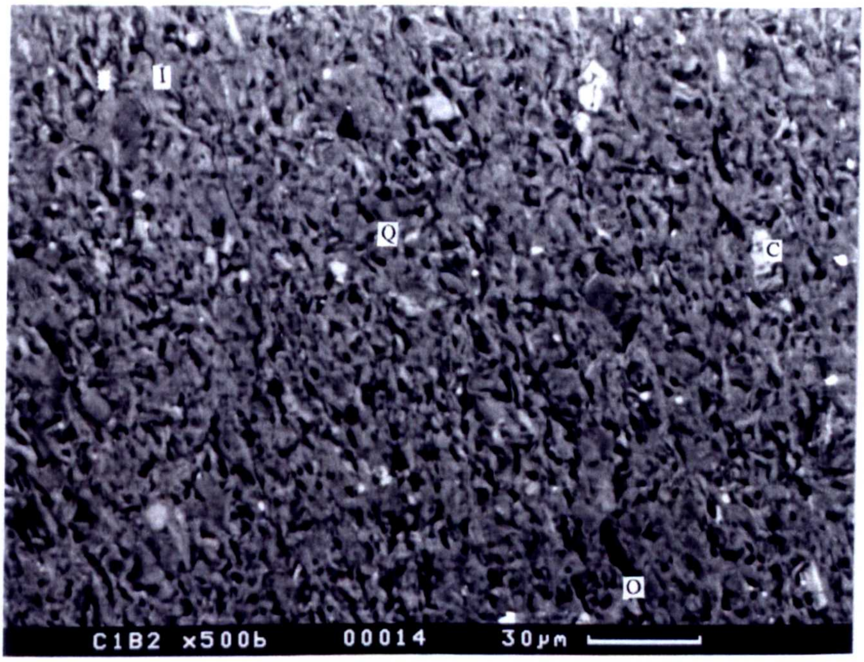


Plate 7.32 Sample C.1.B2. BSI photomicrograph. [x500mag.]

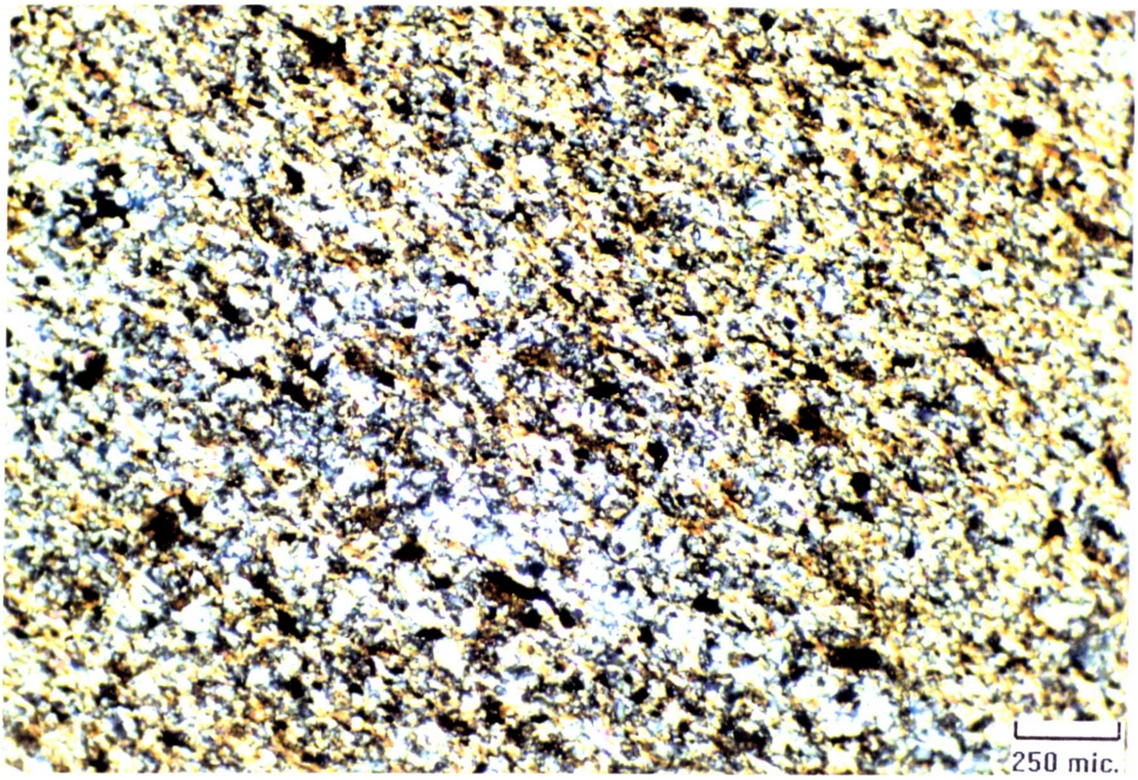


Plate 7.33 Sample C.1.B4. Standard petrographic photomicrograph. [x100mag.XPL]

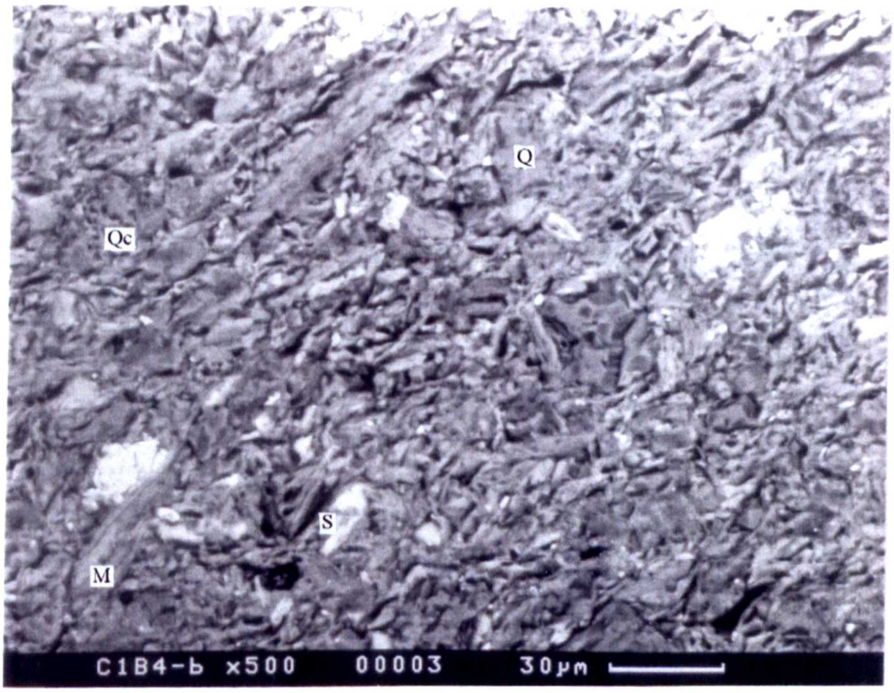


Plate 7.34 Sample C.1.B4. BSI photomicrograph. [x500mag.]

Plate 7.35 Sample C.1.B5. Standard petrographic photomicrograph. [x100mag. XPL]

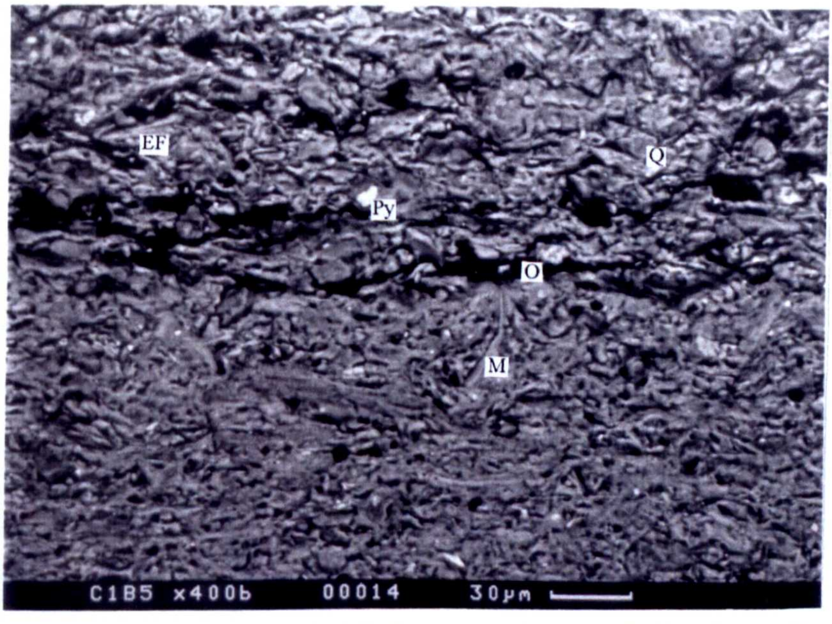


Plate 7.36 Sample C.1.B5. BSI photomicrograph. [x400mag.]

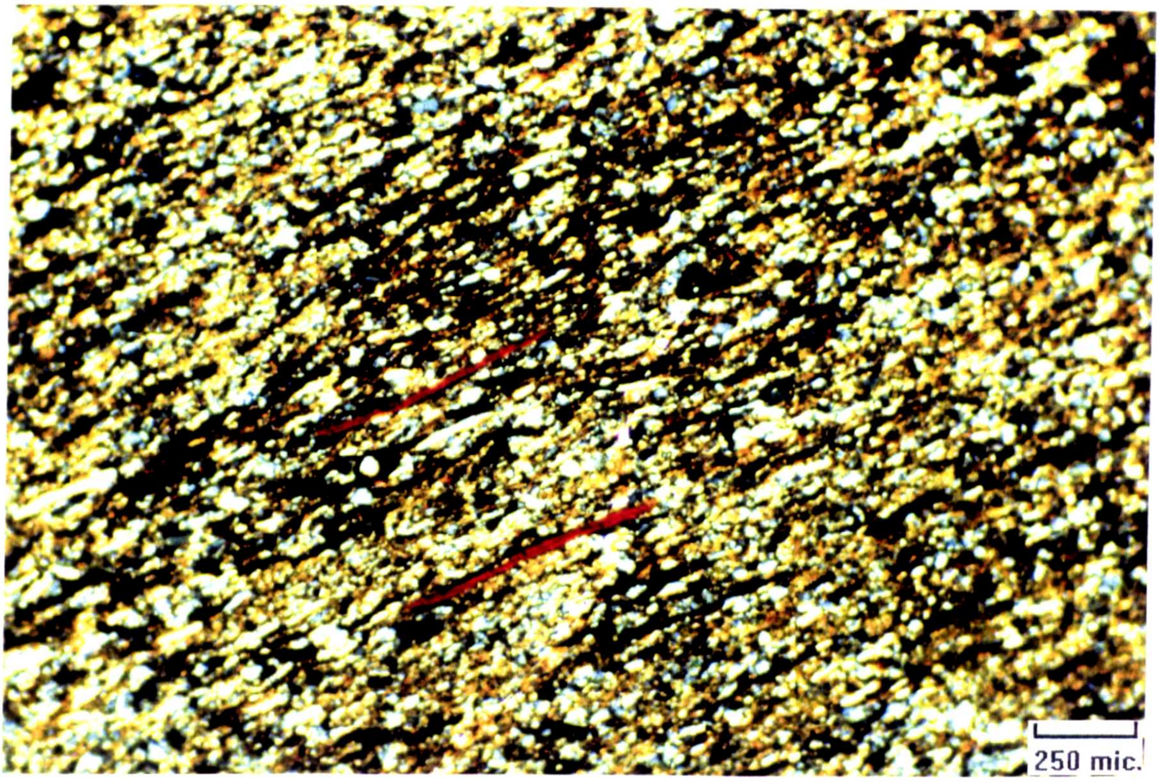


Plate 7.37 Sample C.2.1. Standard petrographic photomicrograph. [x100mag. XPL]

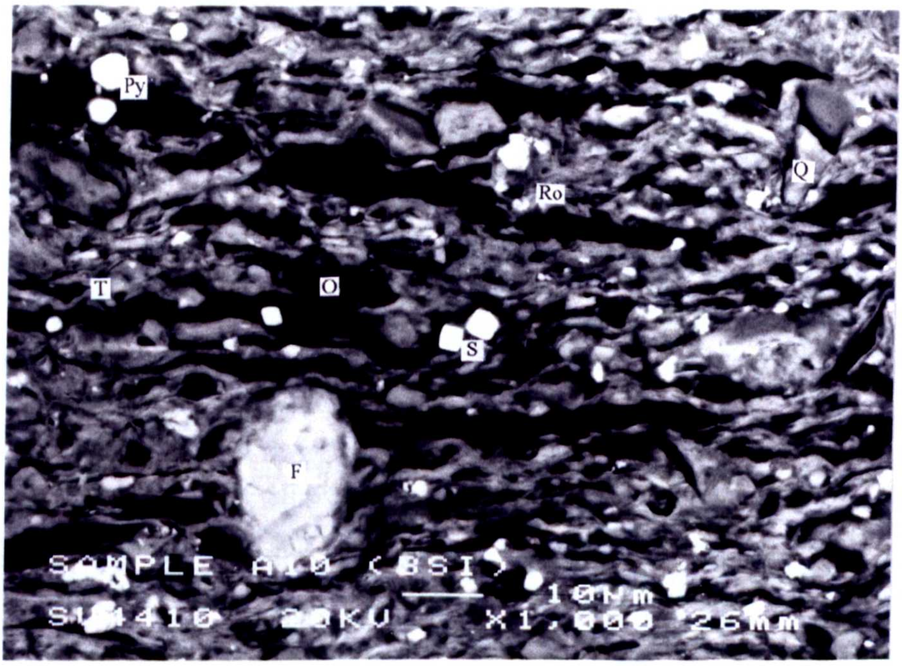


Plate 7.38 Sample C.2.1. BSI photomicrograph. [x1000mag.]

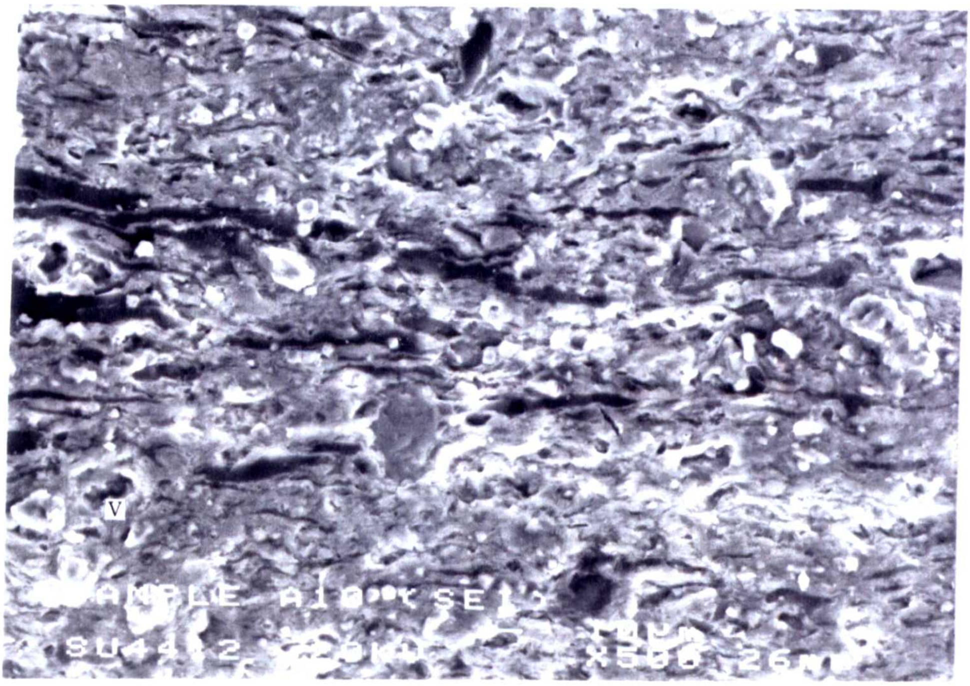


Plate 7.39 Sample C.2.1. SEI photomicrograph. [x500mag.]

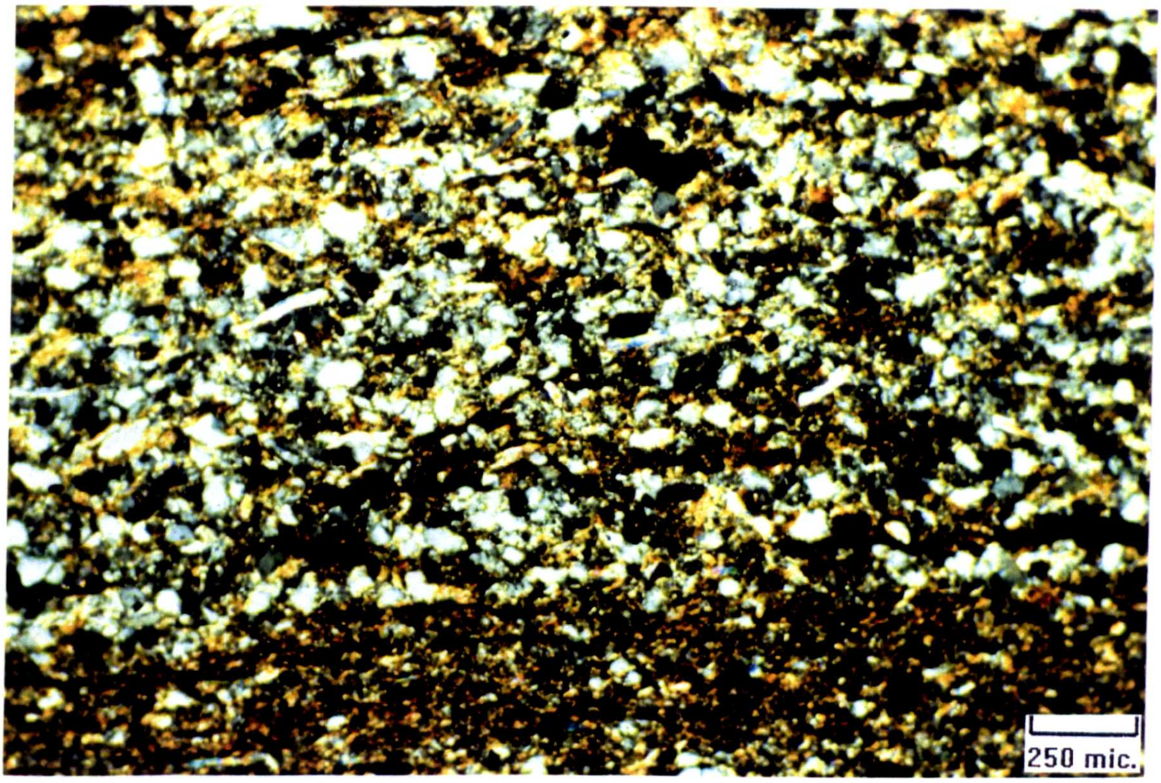


Plate 7.40 Sample C.3.1. Standard petrographic photomicrograph. [x100mag. XPL]

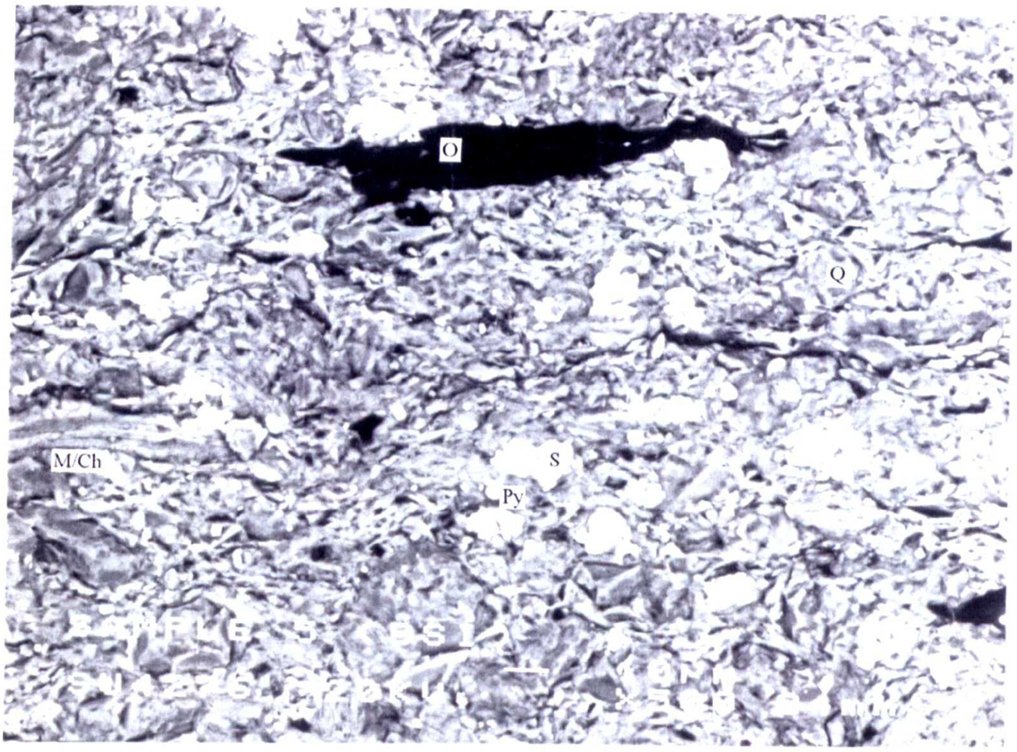


Plate 7.41 Sample C.3.1. BSI photomicrograph. [x500mag.]

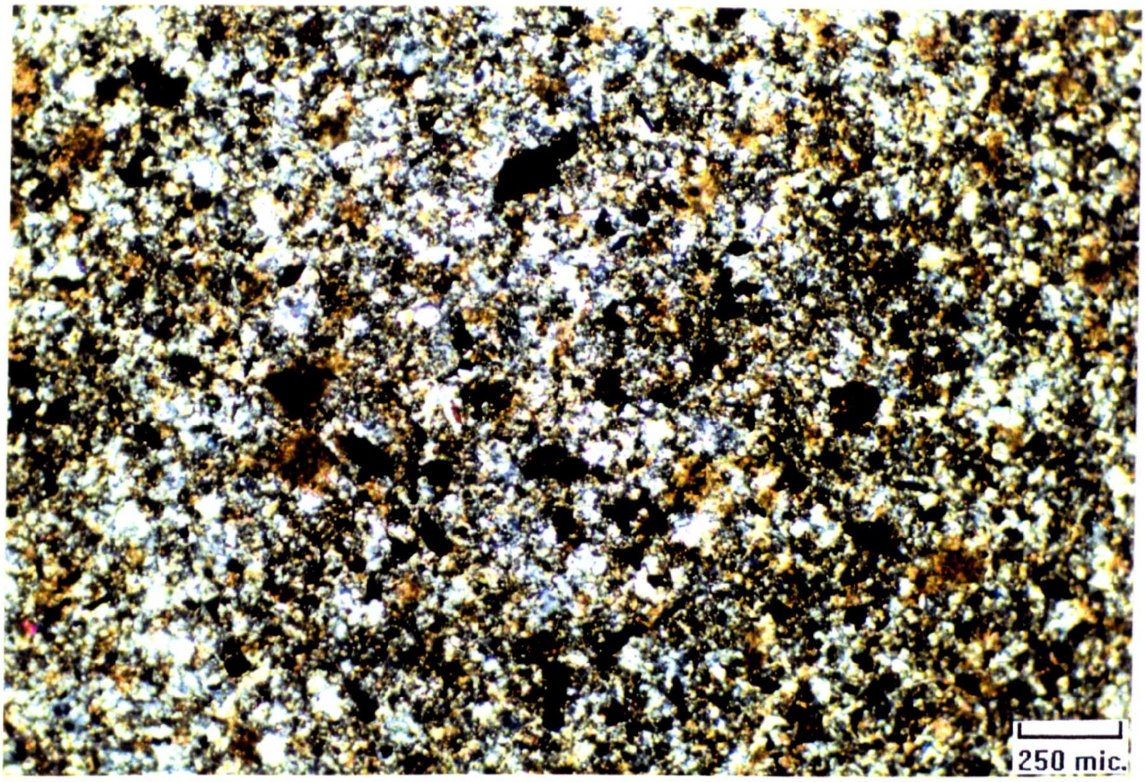


Plate 7.42 Sample C.4.1. Standard petrographic photomicrograph. [x100mag. XPL]

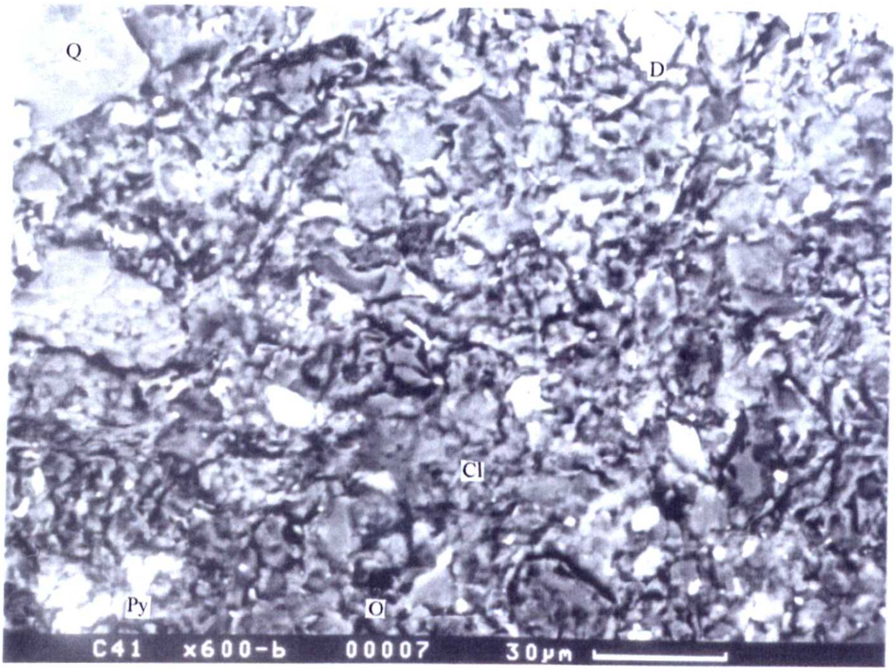


Plate 7.43 Sample C.4.1. BSI photomicrograph. [x600mag.]

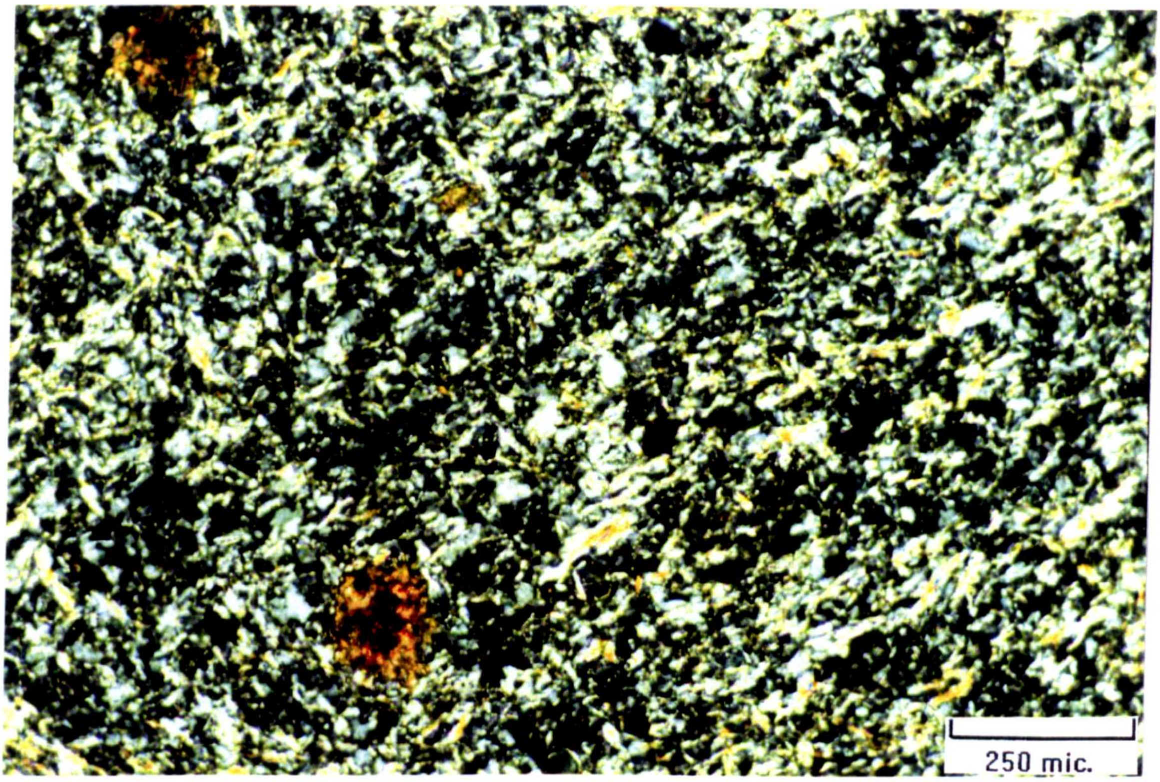


Plate 7.44 Sample C.5.1. Standard petrographic photomicrograph. [x200mag. XPL]

Plate 7.45 Sample C.5.1. BSI photomicrograph. [x500mag.]

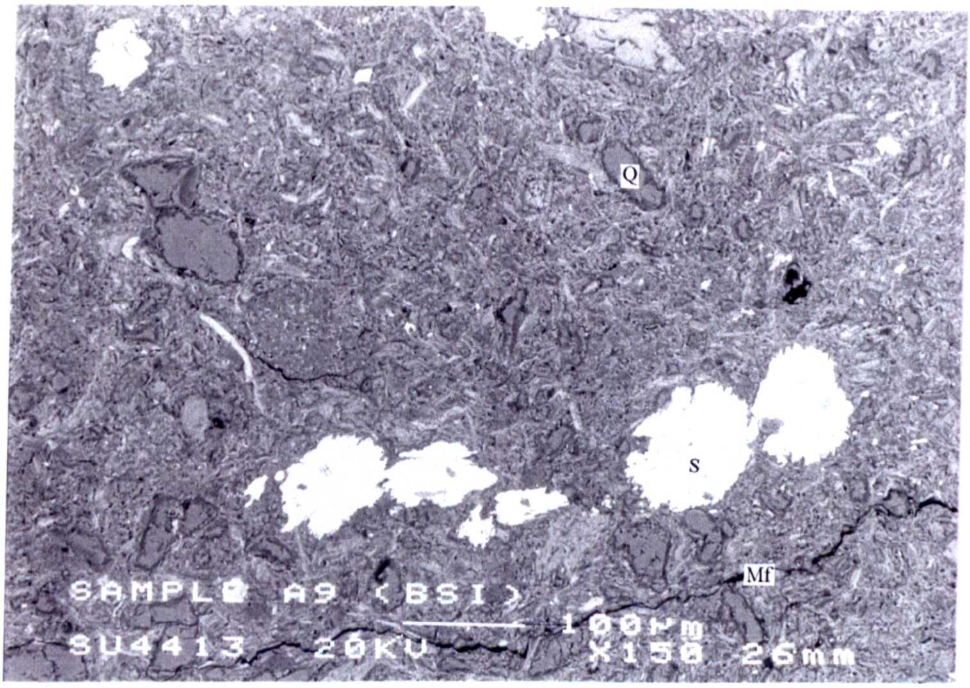


Plate 7.46 Sample C.5.1. BSI photomicrograph. [x150mag.]

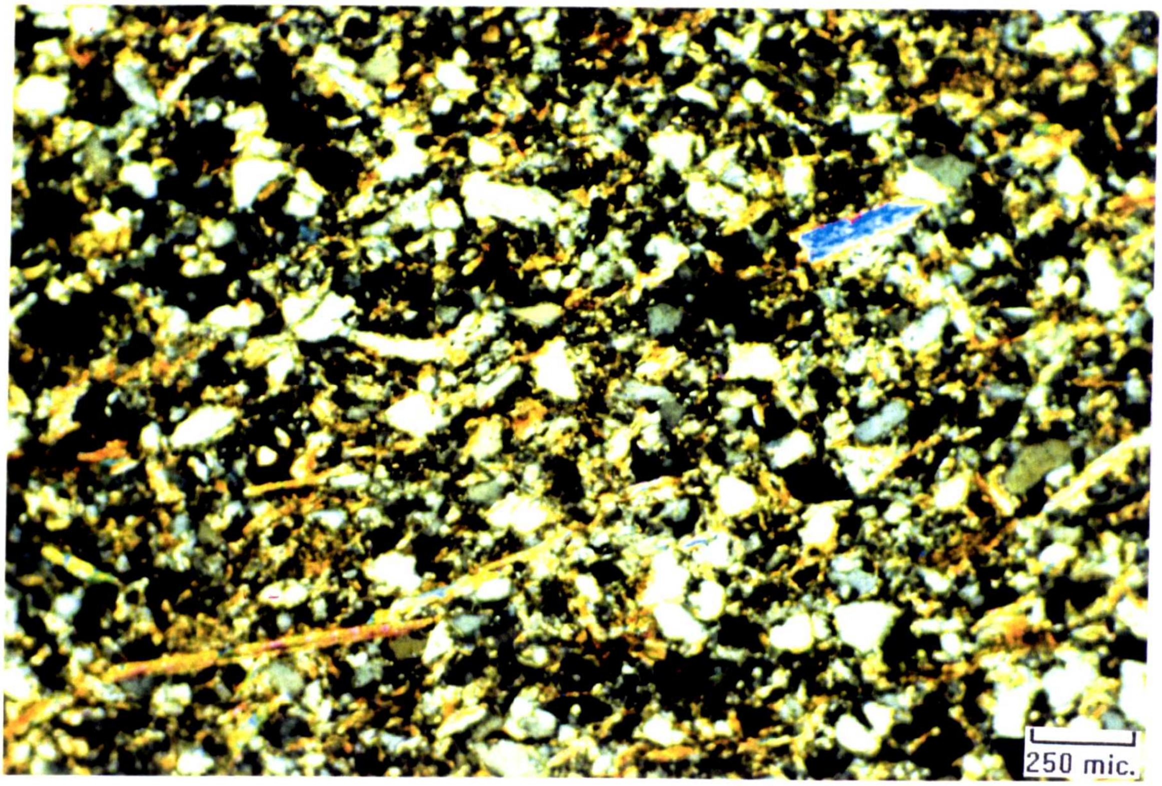


Plate 7.47 Sample C.5.2. Standard petrographic photomicrograph. [x100mag. XPL]

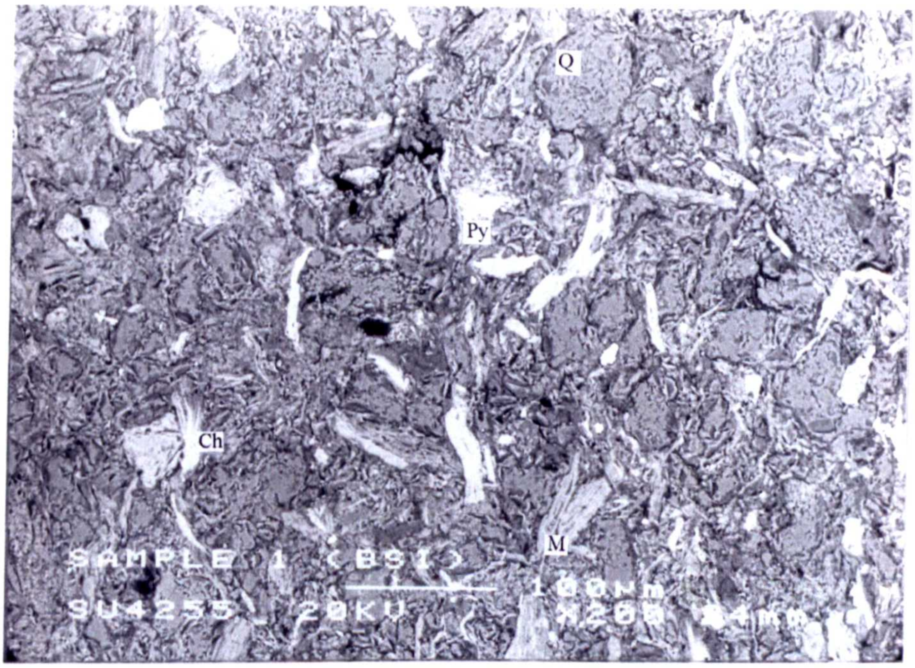


Plate 7.48 Sample C.5.2. BSI photomicrograph. [x200mag.]

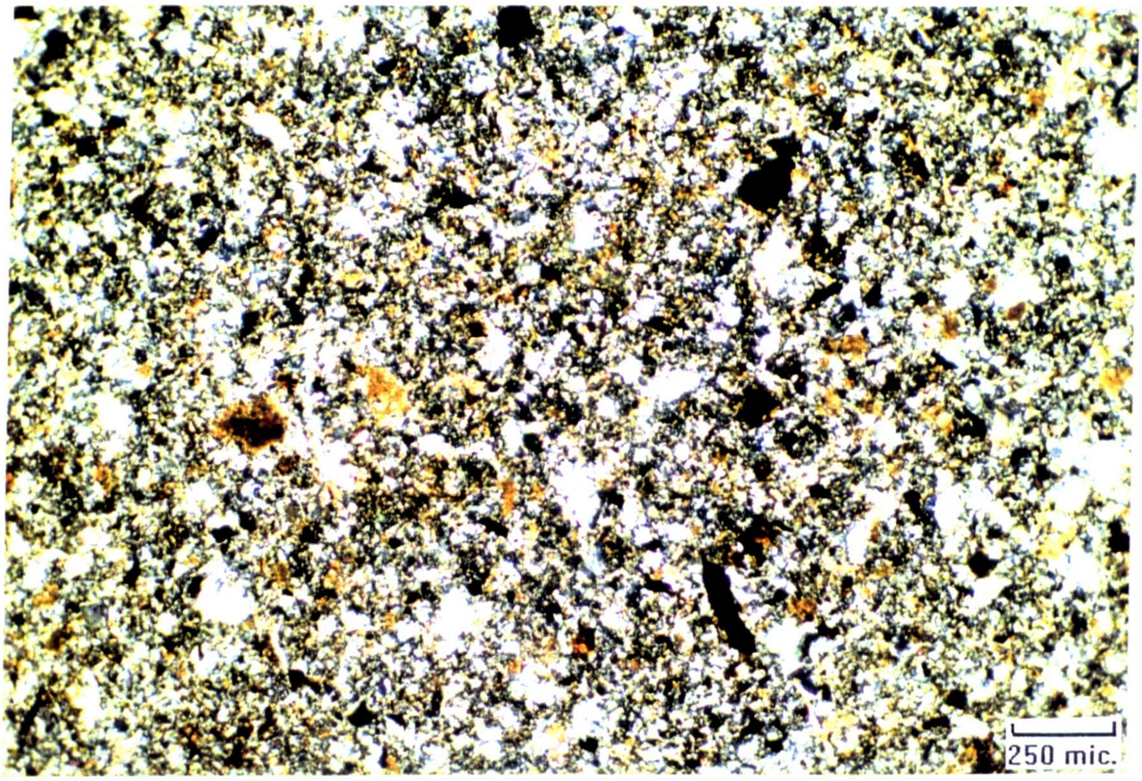


Plate 7.49 Sample C.6.1. Standard petrographic photomicrograph. [x100mag. XPL]

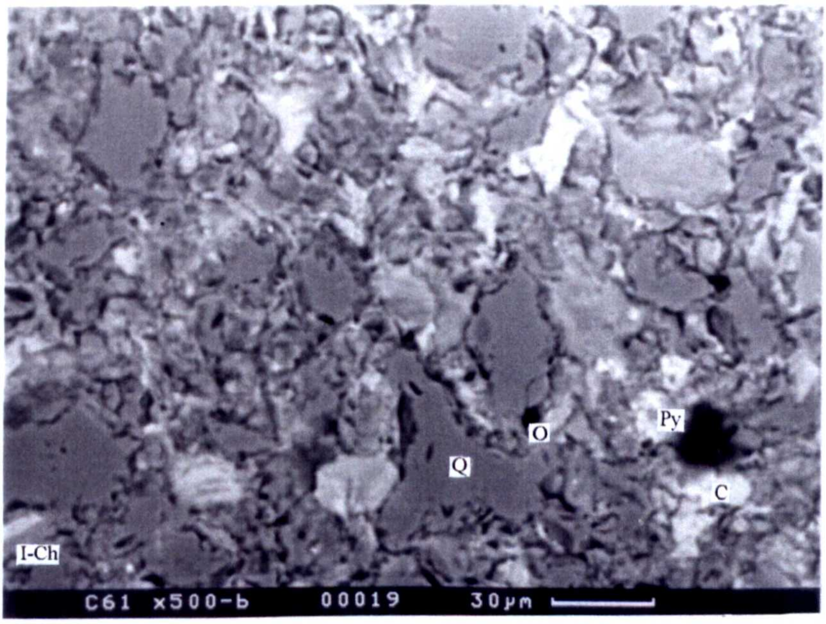


Plate 7.50 Sample C.6.1. BSI photomicrograph. [x500mag.]

Plate 7.51 Sample C.7.1. Standard petrographic photomicrograph. [x100mag. XPL]

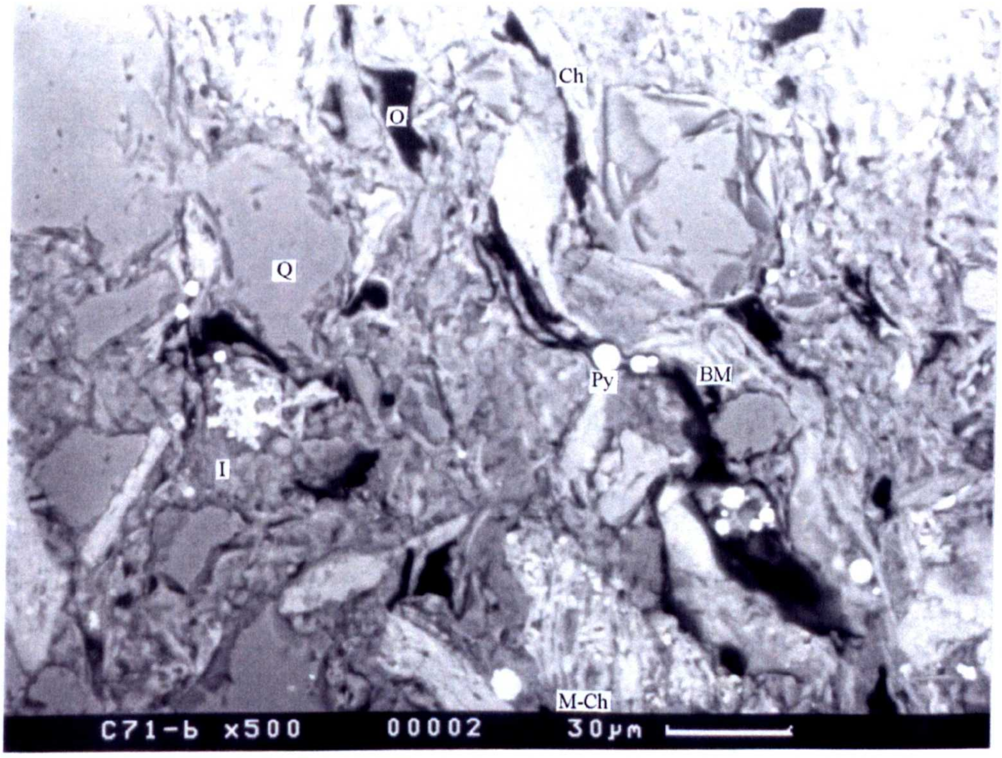


Plate 7.52 Sample C.7.1. BSI photomicrograph. [x500mag.]

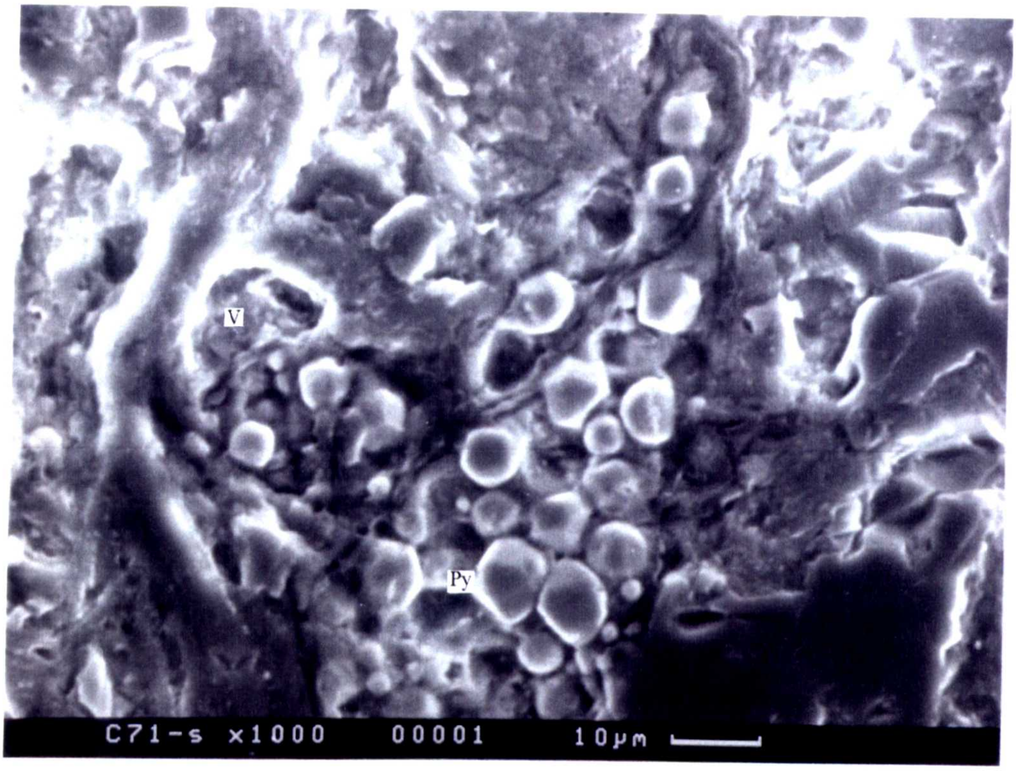


Plate 7.53 Sample C.7.1. SEI photomicrograph. [x1000mag.]

Plate 7.54 Sample C.8.2. Standard petrographic photomicrograph. [x100mag. XPL]

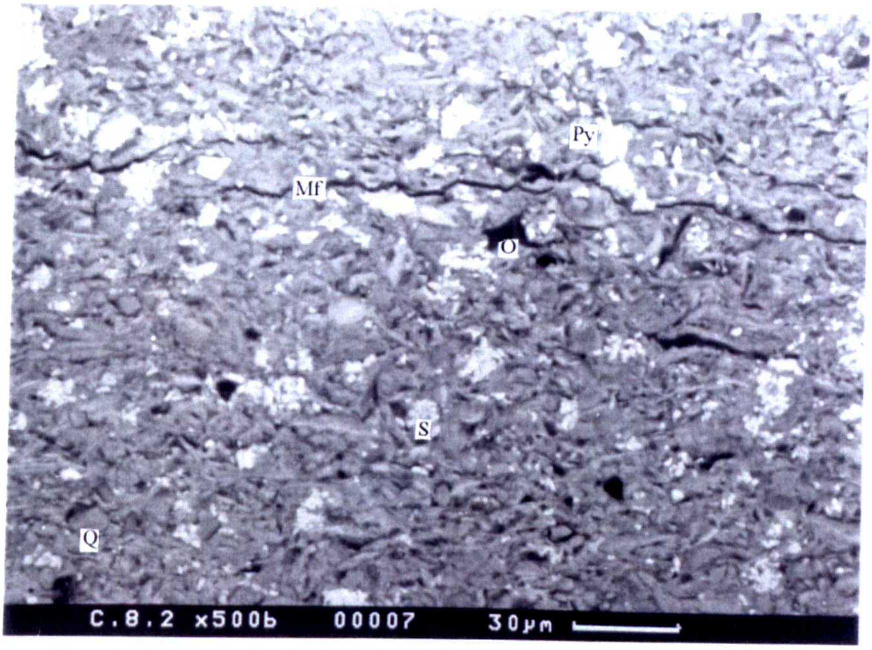


Plate 7.55 Sample C.8.2. BSI photomicrograph. [x500mag.]

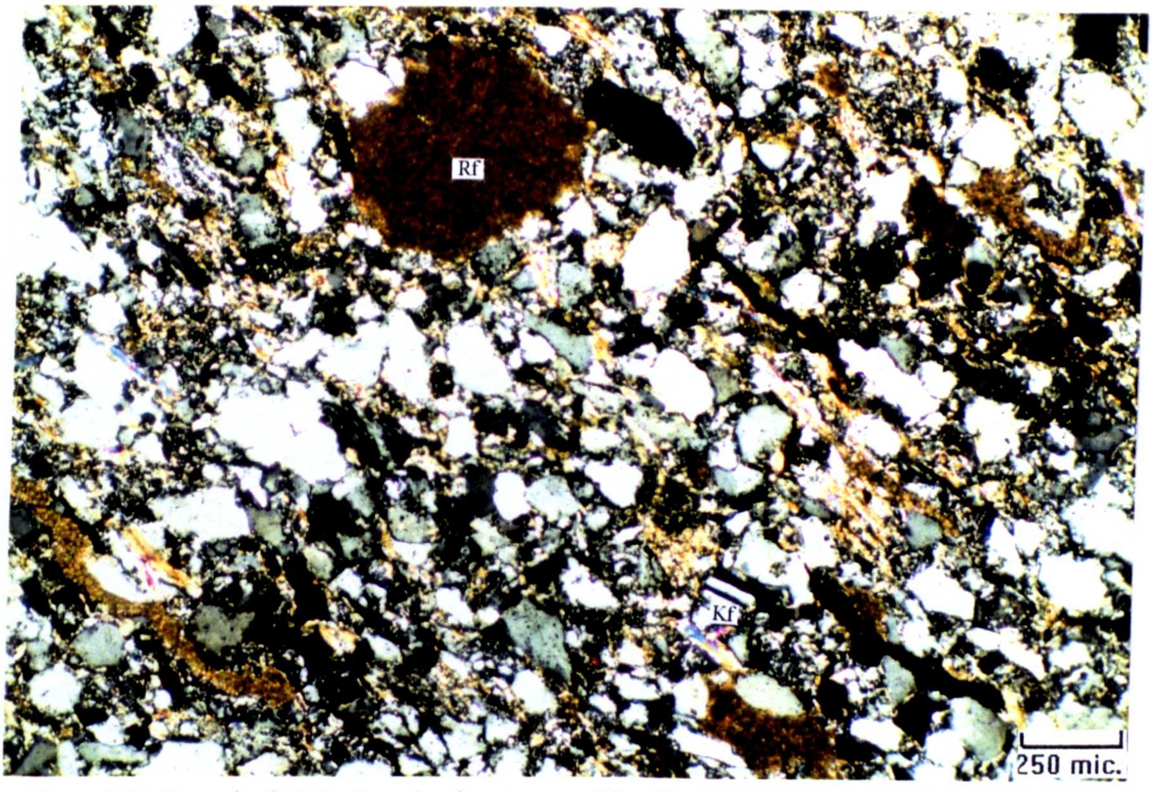


Plate 7.56 Sample C.8.3. Standard petrographic photomicrograph. [x100mag. XPL]

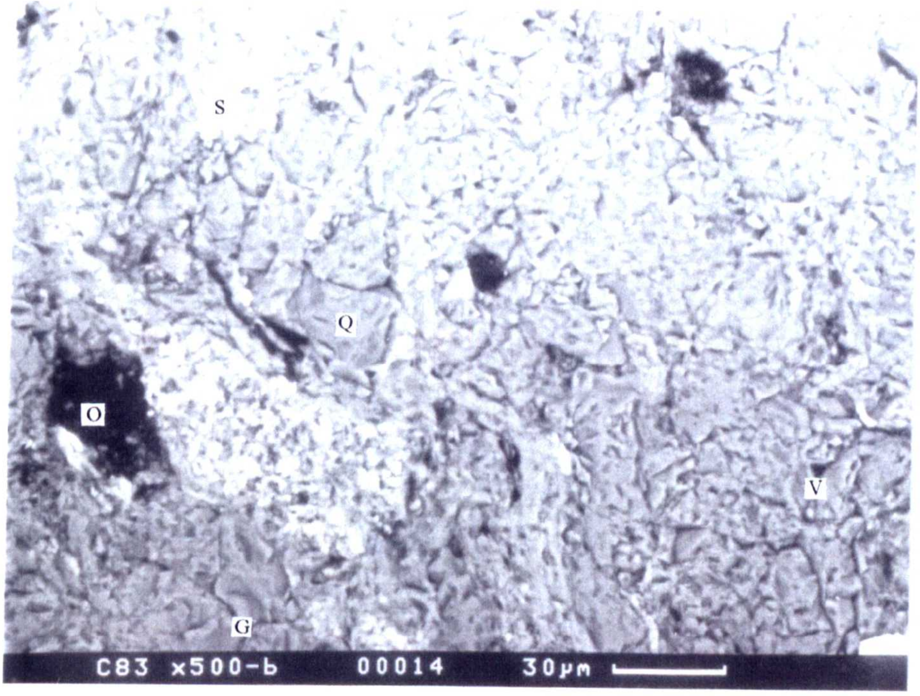


Plate 7.57 Sample C.8.3. BSI photomicrograph. [x500mag.]

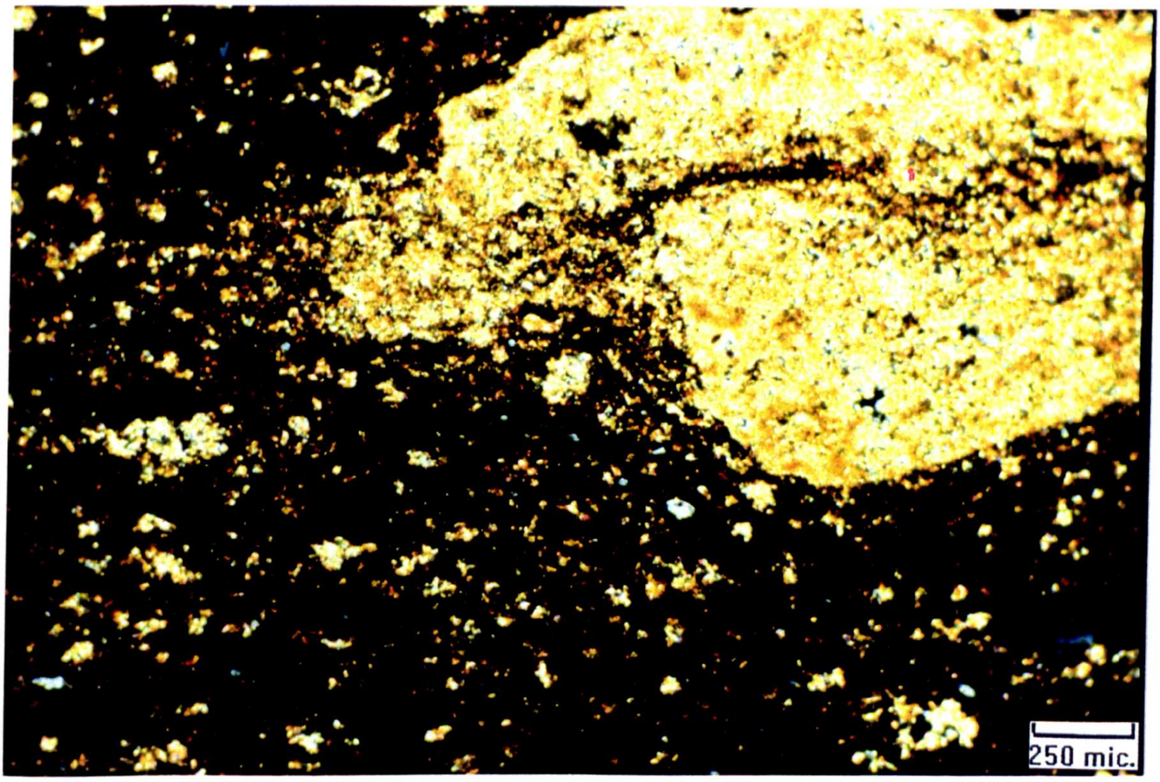


Plate 7.58 Sample C.9.2. Standard petrographic photomicrograph. [x100mag. XPL]

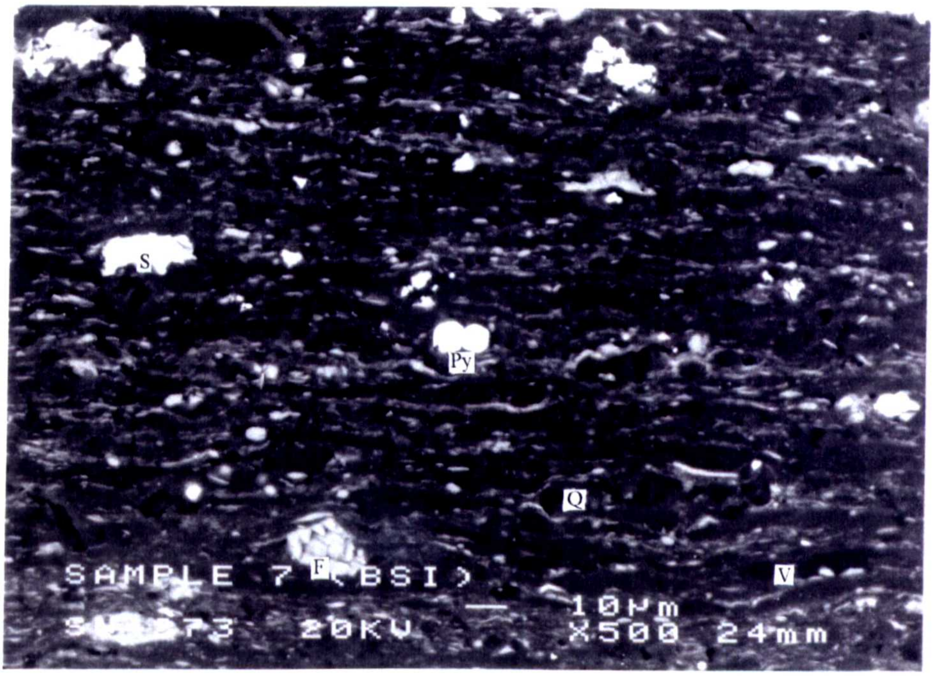


Plate 7.59 Sample C.9.2. BSI photomicrograph. [x500mag.]

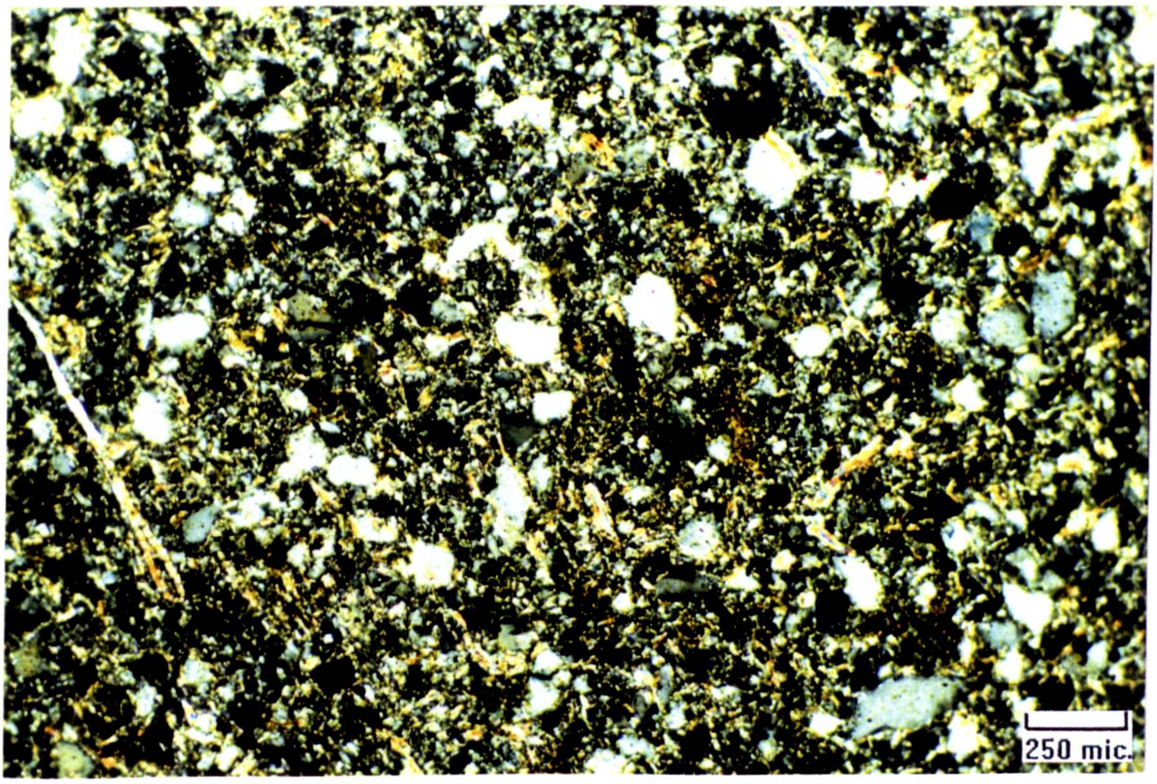


Plate 7.60 Sample C.10.1. Standard petrographic photomicrograph. [x100mag. XPL]

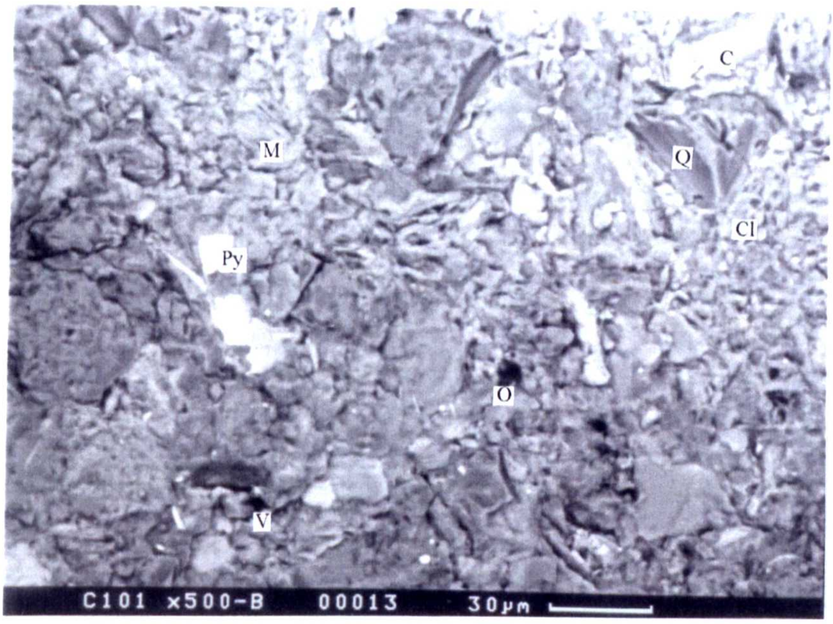


Plate 7.61 Sample C.10.1. BSI photomicrograph. [x500mag.]

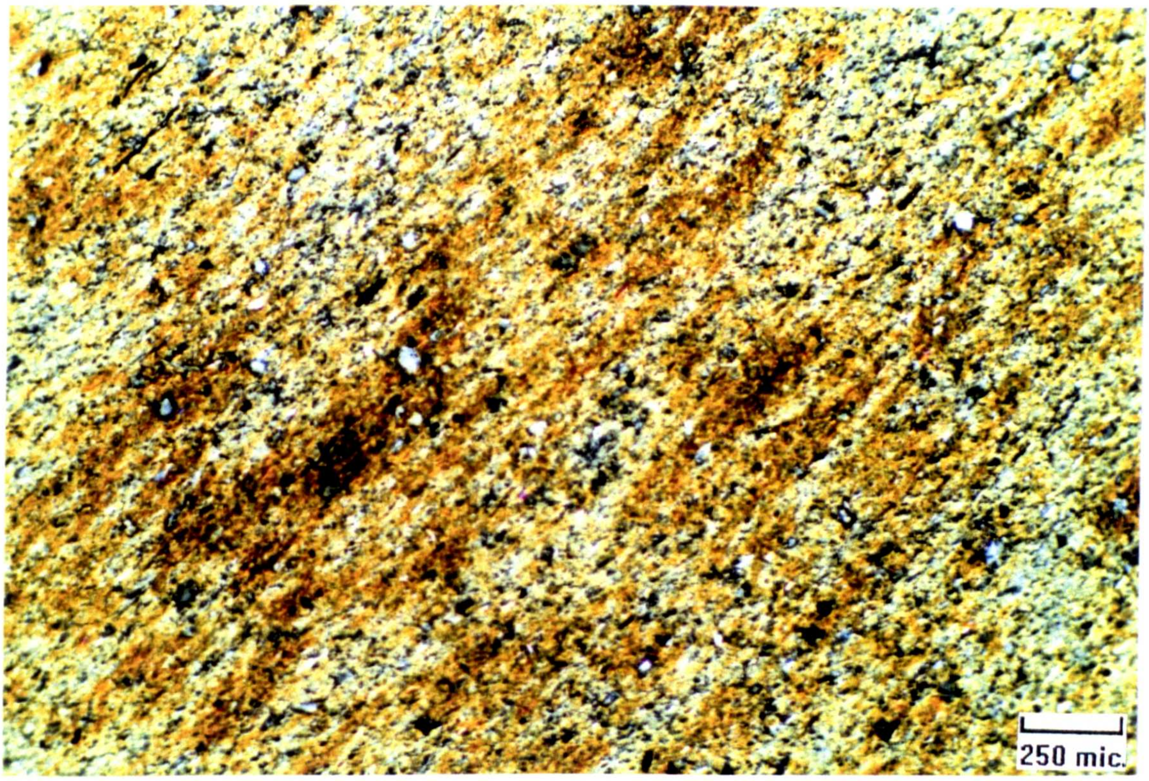


Plate 7.62 Sample C.11.1. Standard petrographic photomicrograph. [x100mag. XPL]

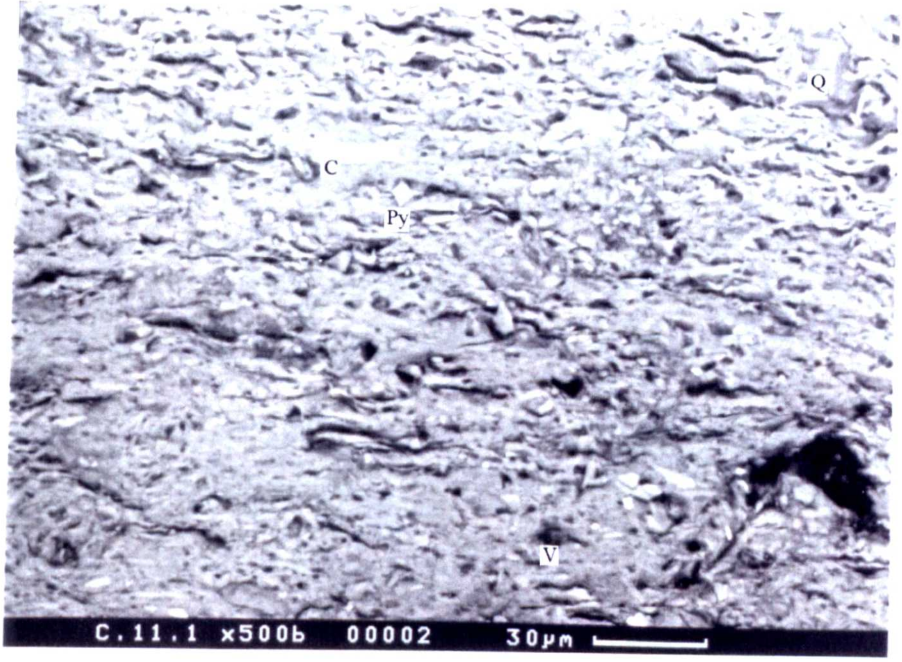


Plate 7.63 Sample C.11.1. BSI photomicrograph. [x500mag.]

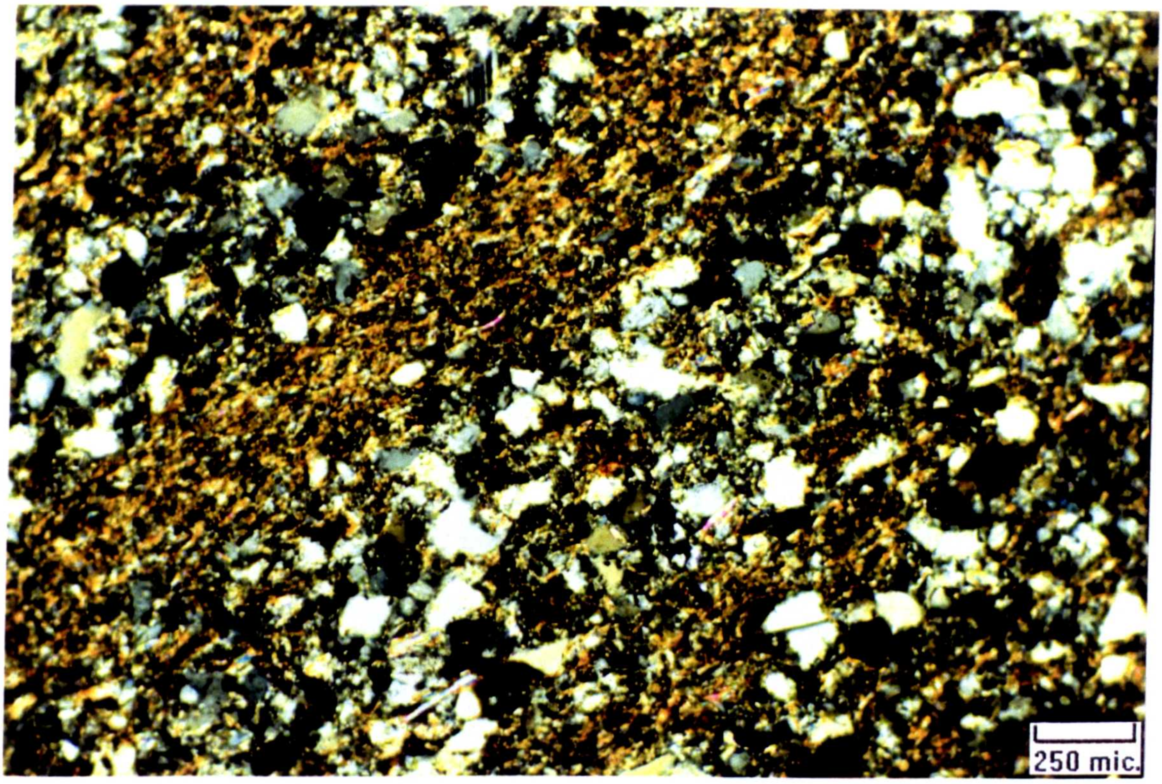


Plate 7.64 Sample C.11.2. Standard petrographic photomicrograph. [x100mag. XPL]

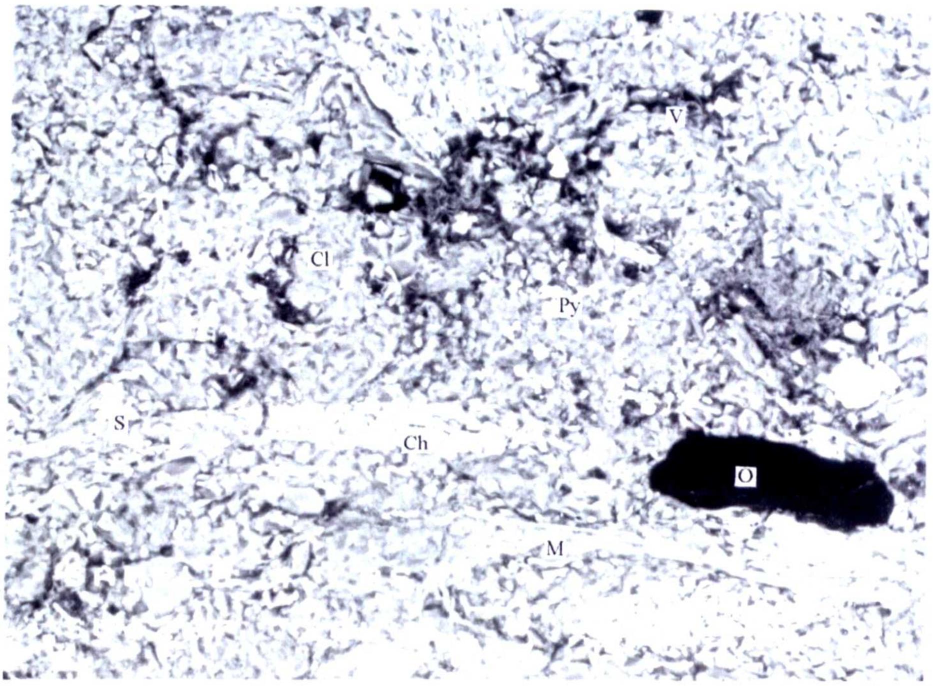


Plate 7.65 Sample C.11.2. BSI photomicrograph. [x500mag.]. Clay rich laminae.

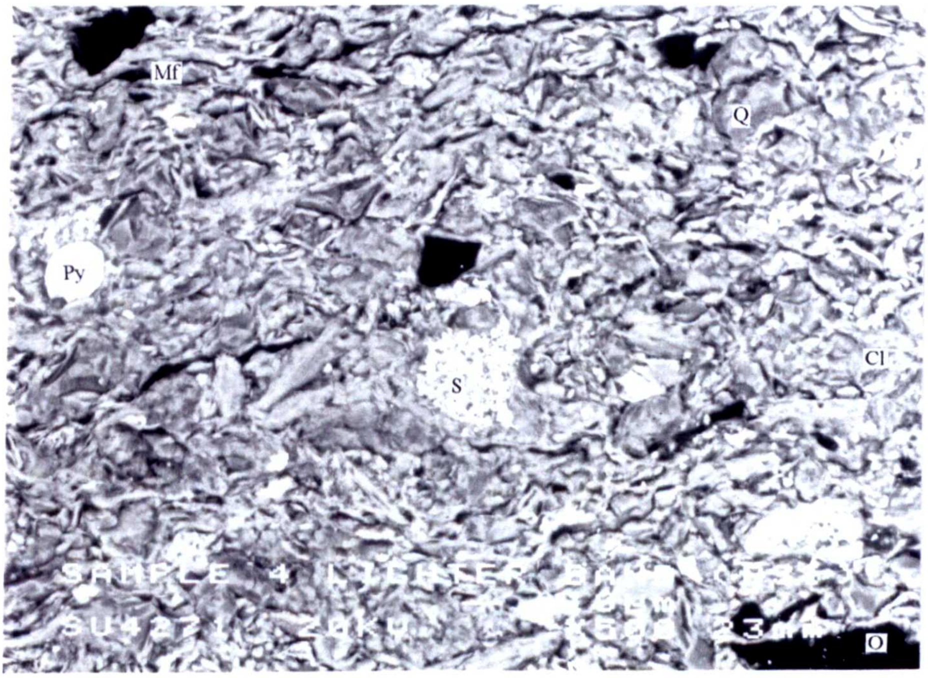


Plate 7.66 Sample C.11.2. BSI photomicrograph. [x500mag.]. Silt rich laminae.

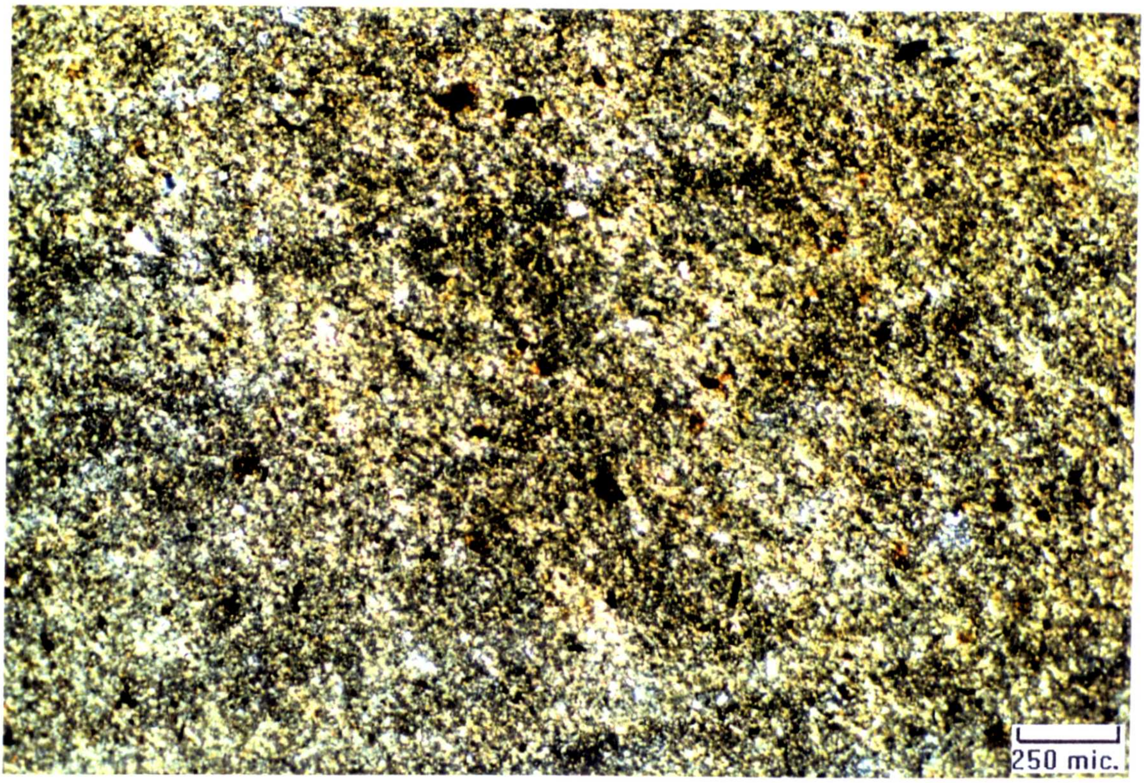


Plate 7.67 Sample C.12.1. Standard petrographic photomicrograph. [x100mag. XPL]

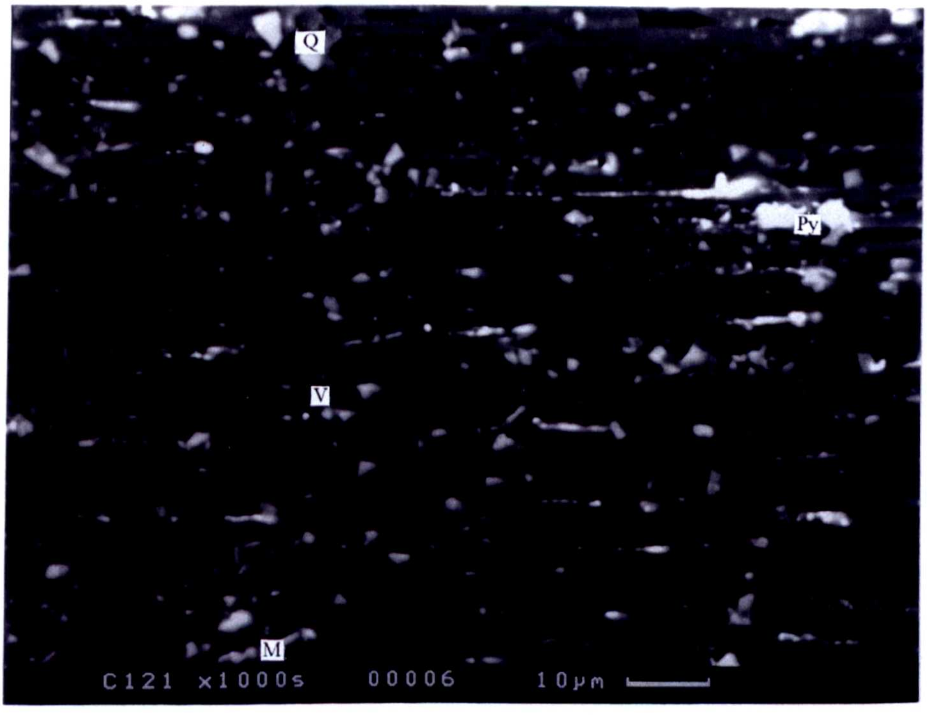


Plate 7.68 Sample C.12.1. BSI photomicrograph. [x1000mag.]

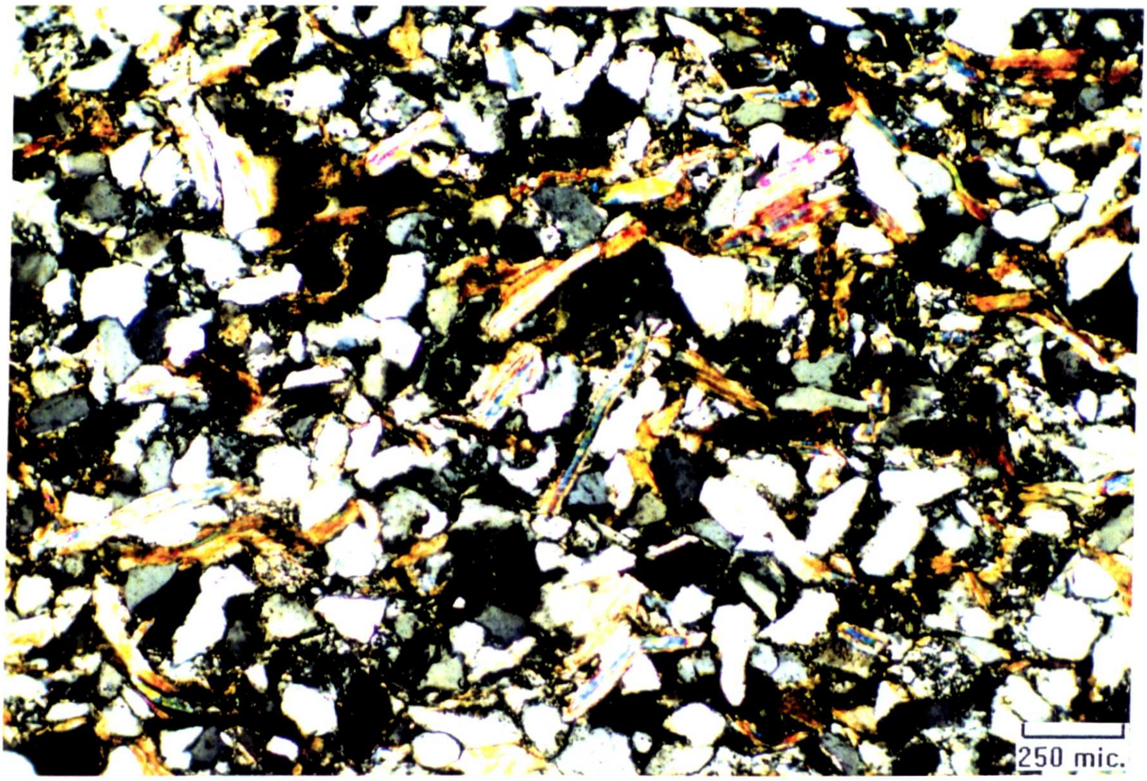


Plate 7.69 Sample C.12.2. Standard petrographic photomicrograph. [x100mag. XPL]

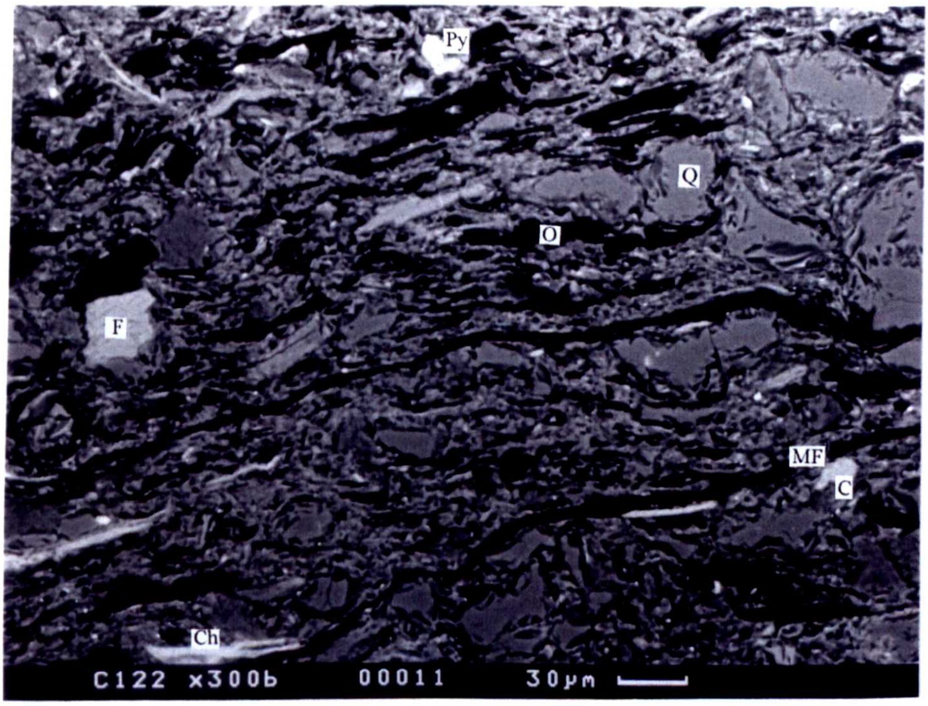


Plate 7.70 Sample C.12.2. BSI photomicrograph. [x300mag.]

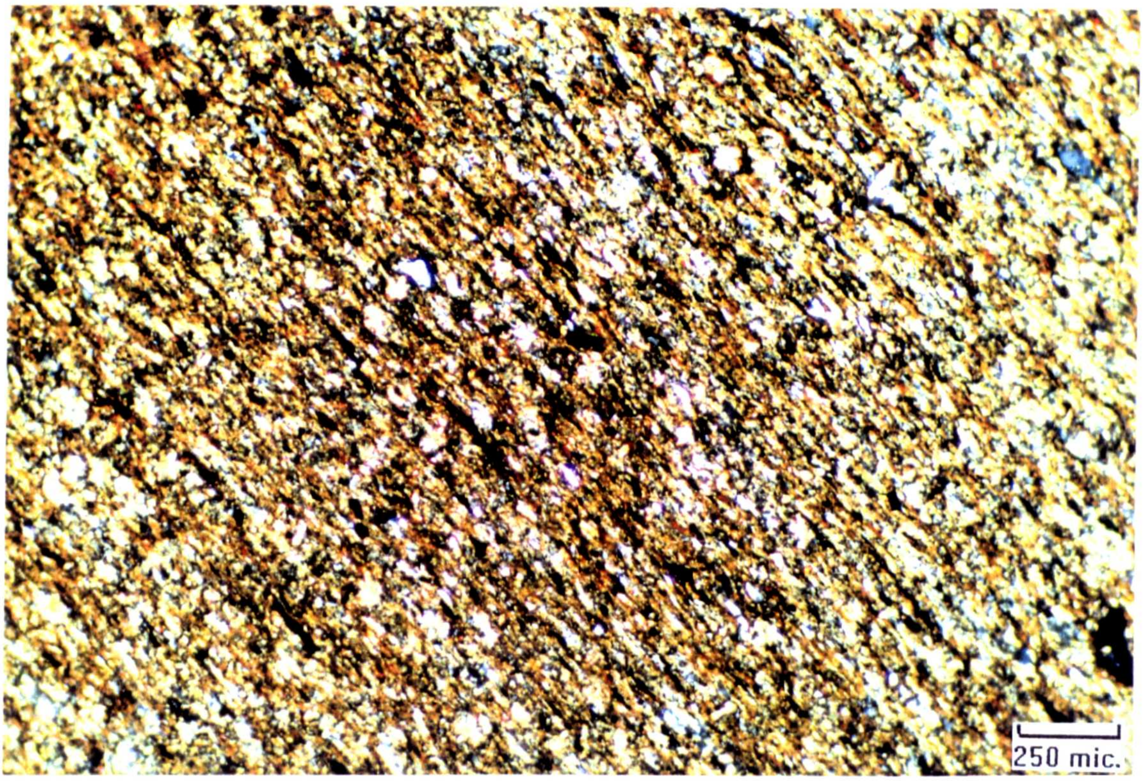


Plate 7.71 Sample C.13.1. Standard petrographic photomicrograph. [x100mag. XPL]

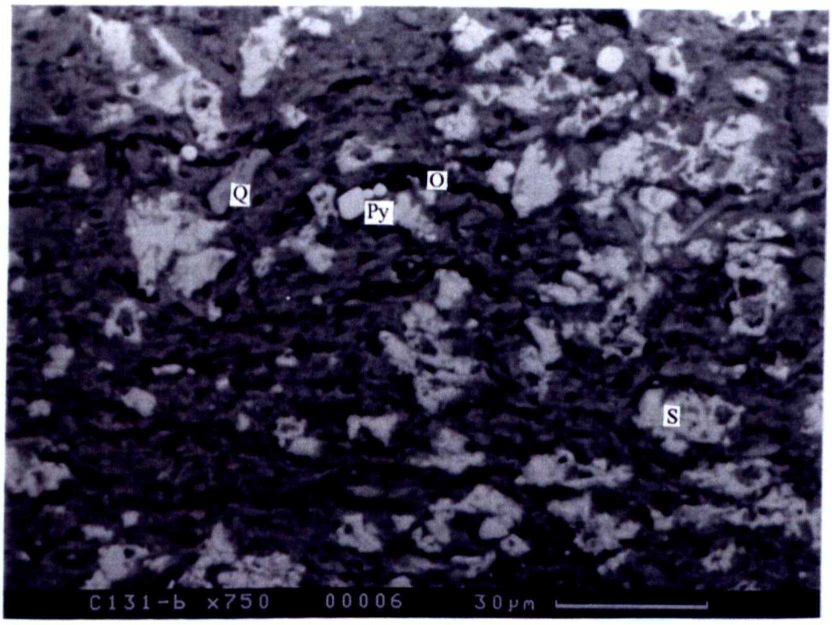


Plate 7.72 Sample C.13.1. BSI photomicrograph. [x750mag.]

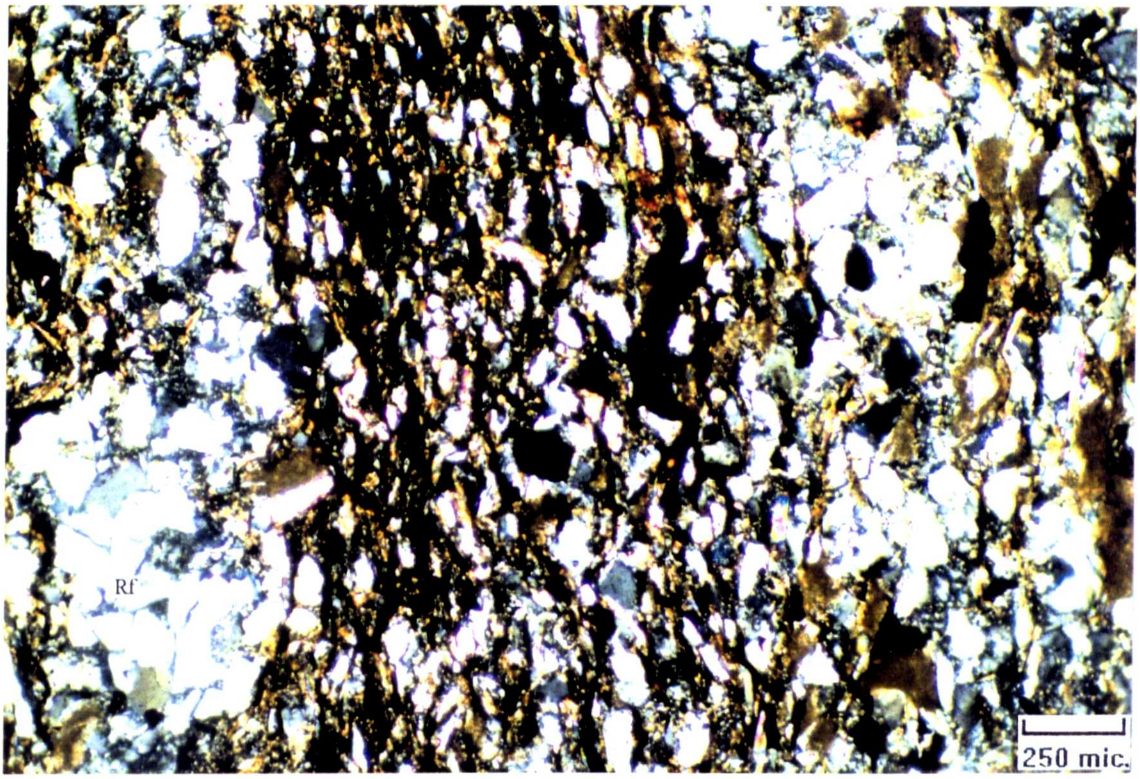


Plate 7.73 Sample C.13.2. Standard petrographic photomicrograph. [x100mag. XPL]

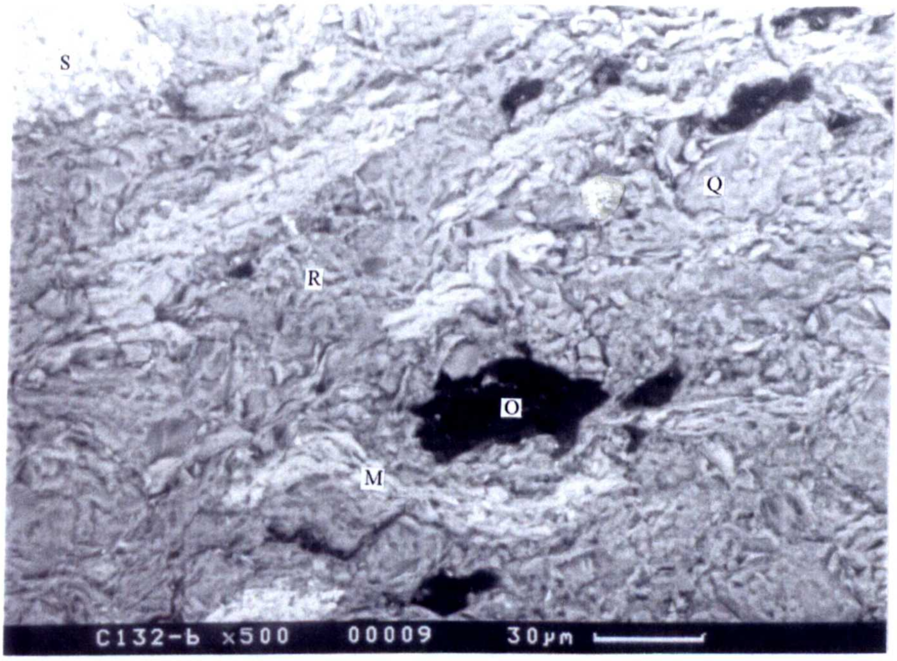


Plate 7.74 Sample C.13.2. BSI photomicrograph. [x500mag.]

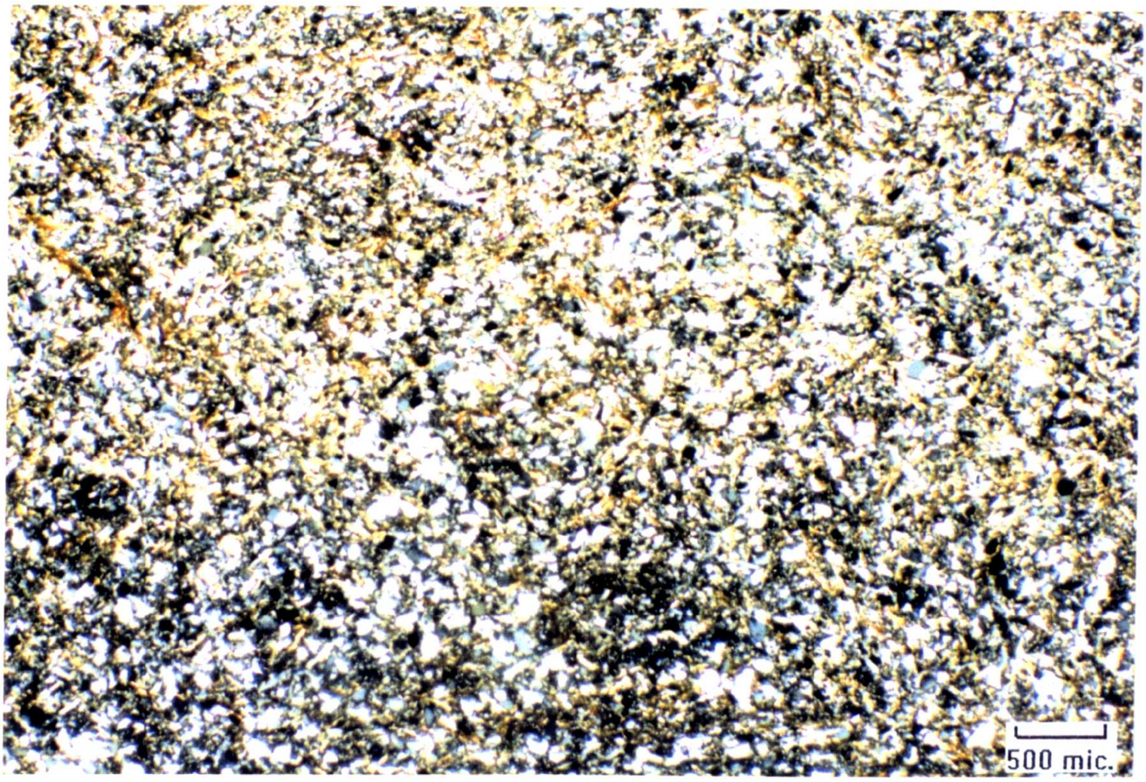


Plate 7.75 Sample C.13.3. Standard petrographic photomicrograph. [x20mag. XPL]

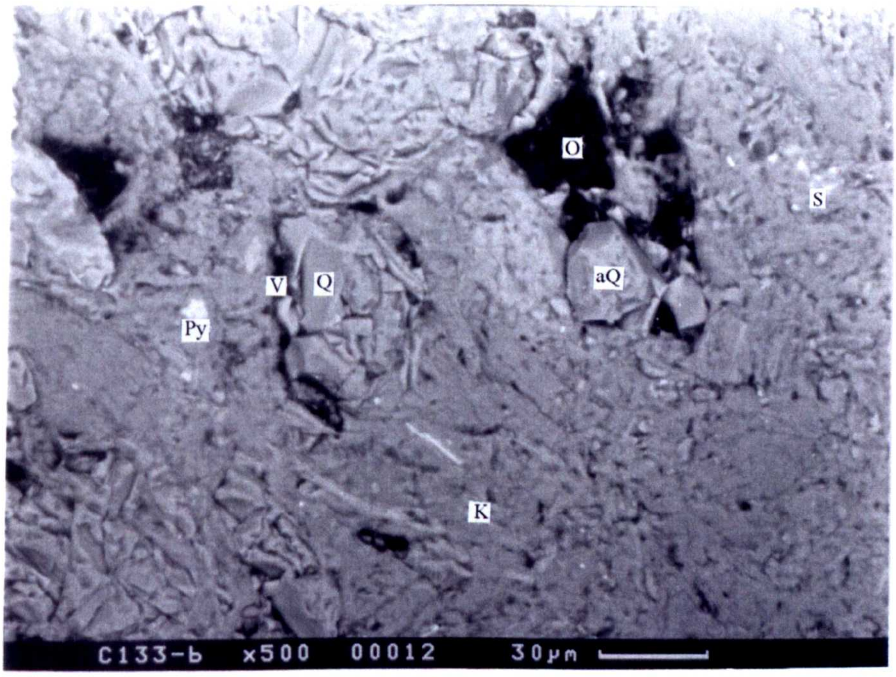


Plate 7.76 Sample C.13.3. BSI photomicrograph. [x500mag.]

Plate 7.77 Sample C.14.1. Standard petrographic photomicrograph. [x100mag. XPL]

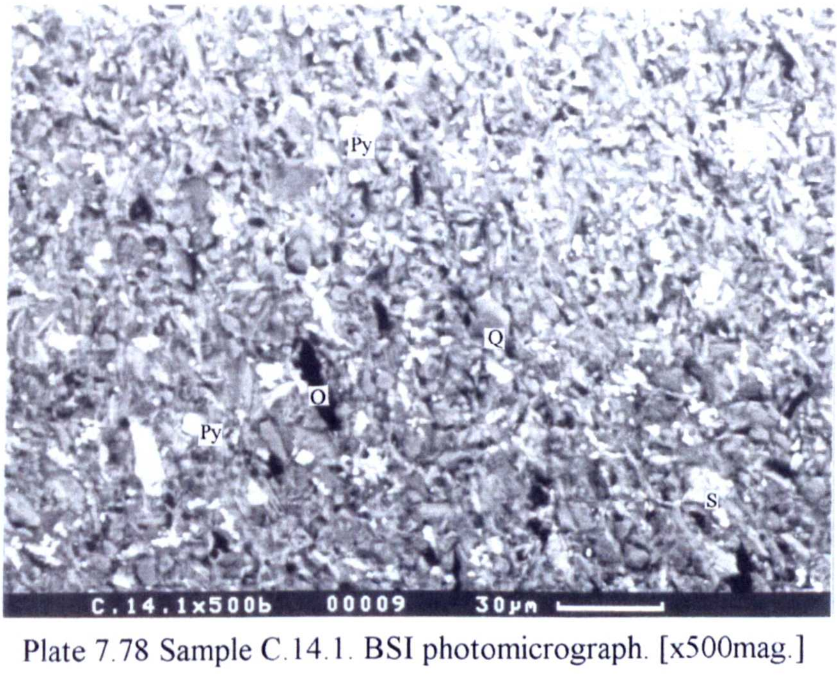


Plate 7.78 Sample C.14.1. BSI photomicrograph. [x500mag.]

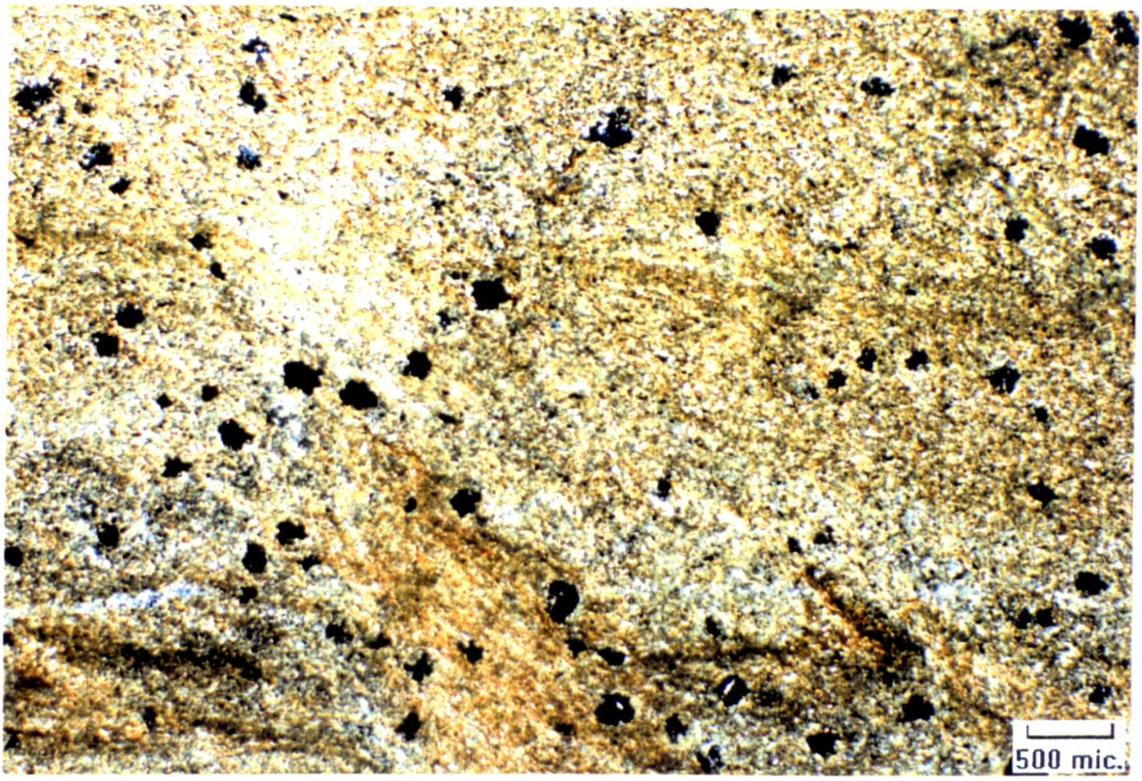


Plate 7.79 Sample C.15.1. Standard petrographic photomicrograph. [x20mag. XPL]

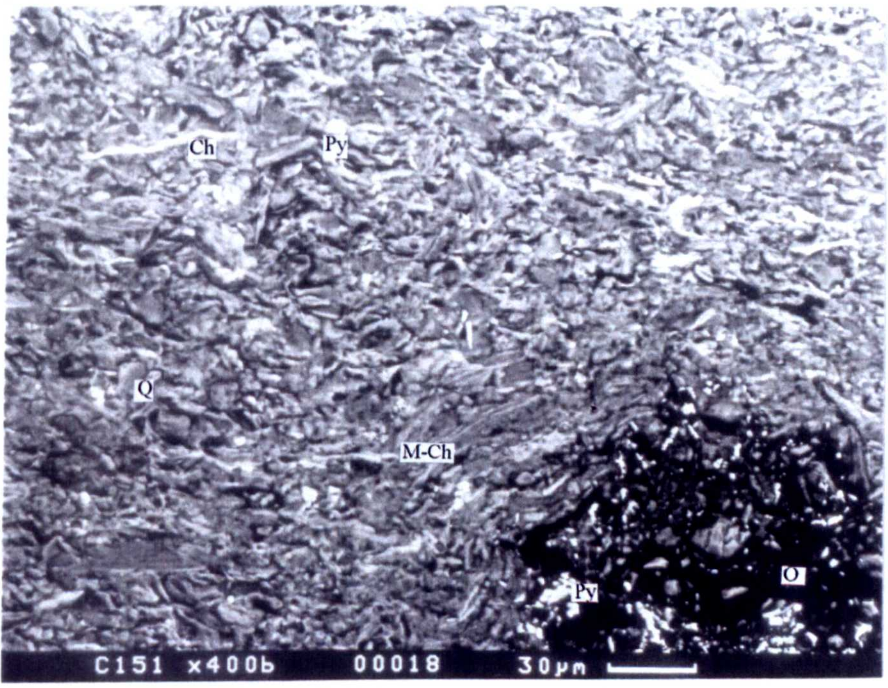


Plate 7.80 Sample C.15.1. BSI photomicrograph. [x400mag.]

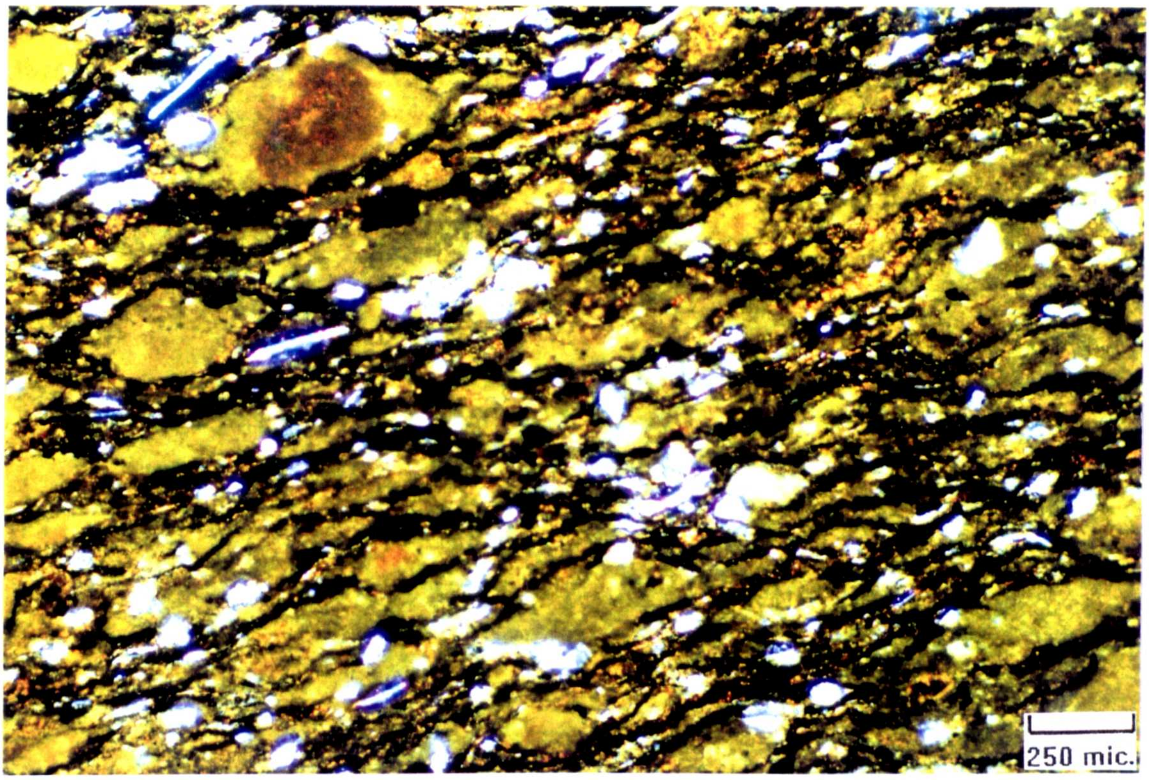


Plate 7.81 Sample C.16.1. Standard petrographic photomicrograph. [x100mag. XPL]

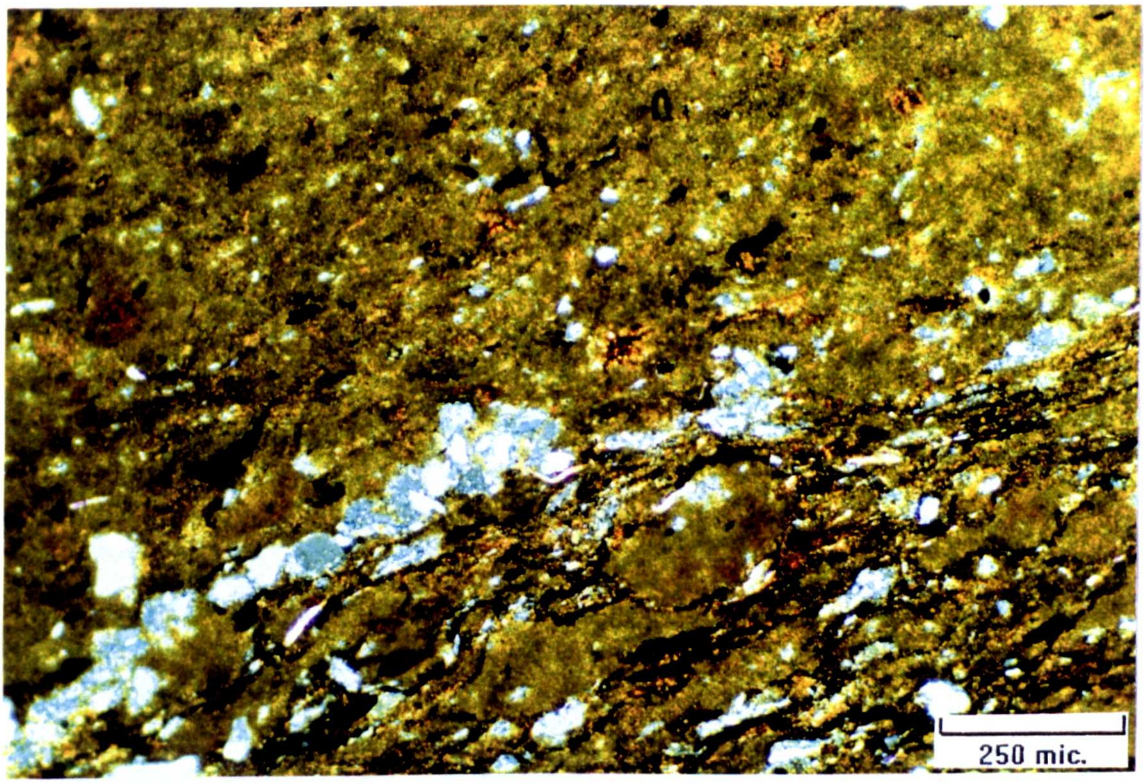


Plate 7.82 Sample C.16.1. Standard petrographic photomicrograph. [x200mg. XPL]

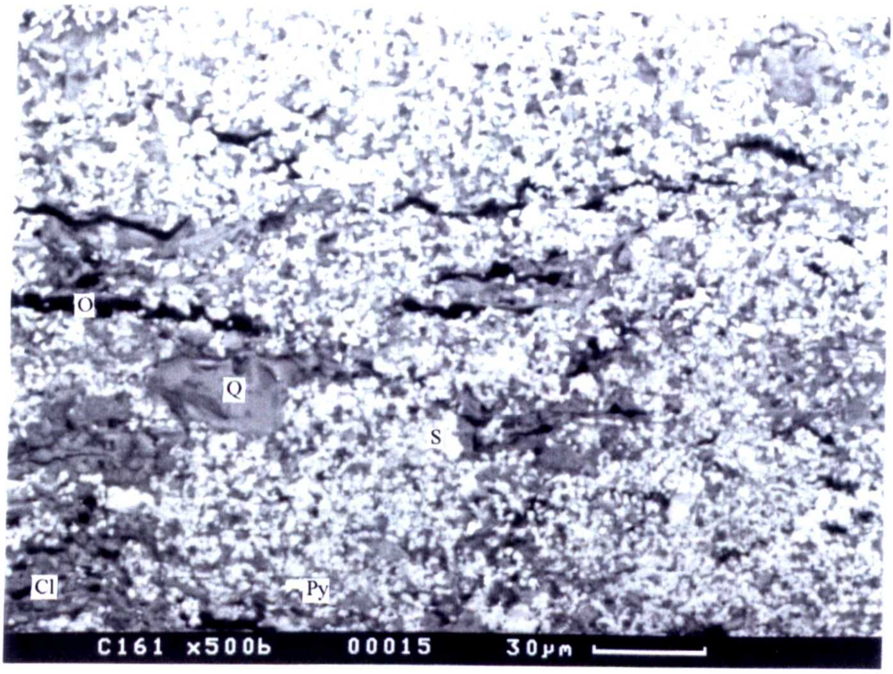


Plate 7.83 Sample C.16.1. BSI photomicrograph. [x500mag.]

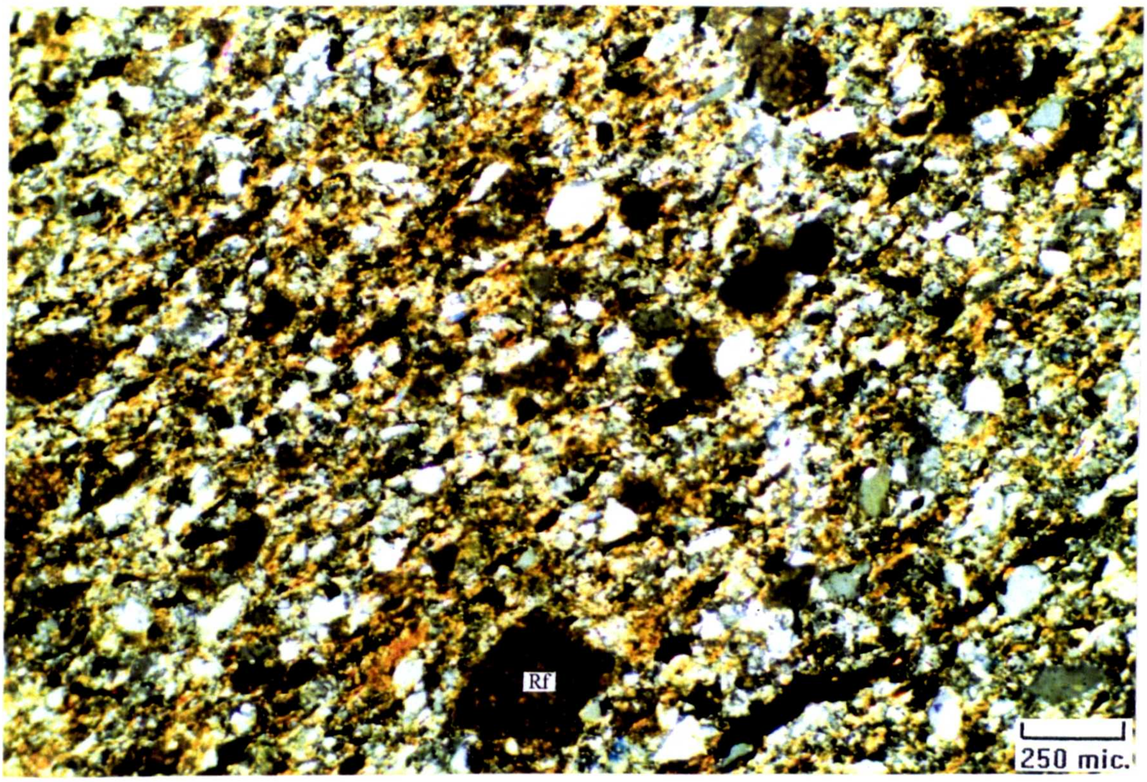


Plate 7.84 Sample C.17.1. Standard petrographic photomicrograph. [x100mag. XPL]

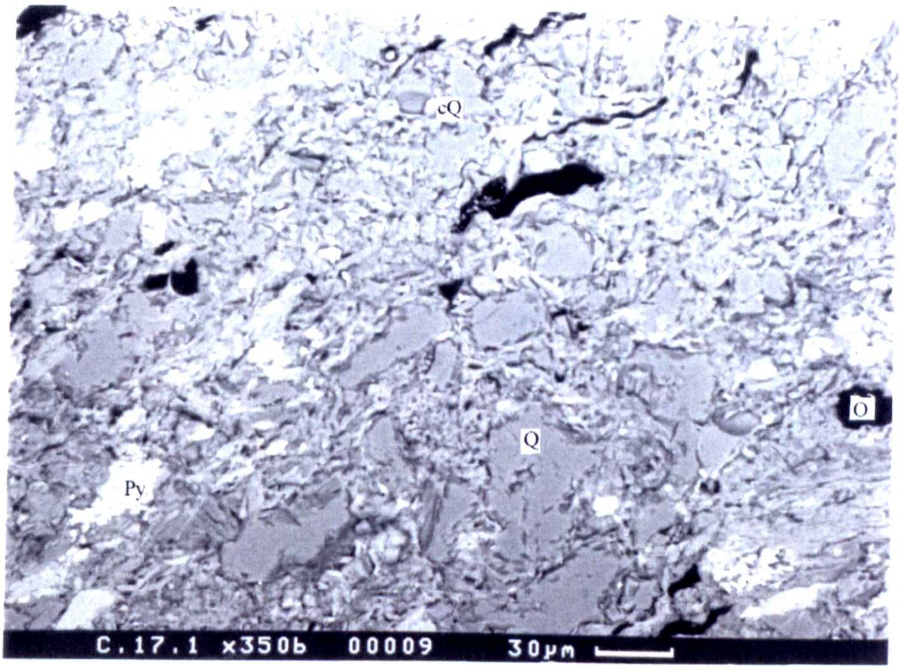


Plate 7.85 Sample C.17.1. BSI photomicrograph. [x350mag.]

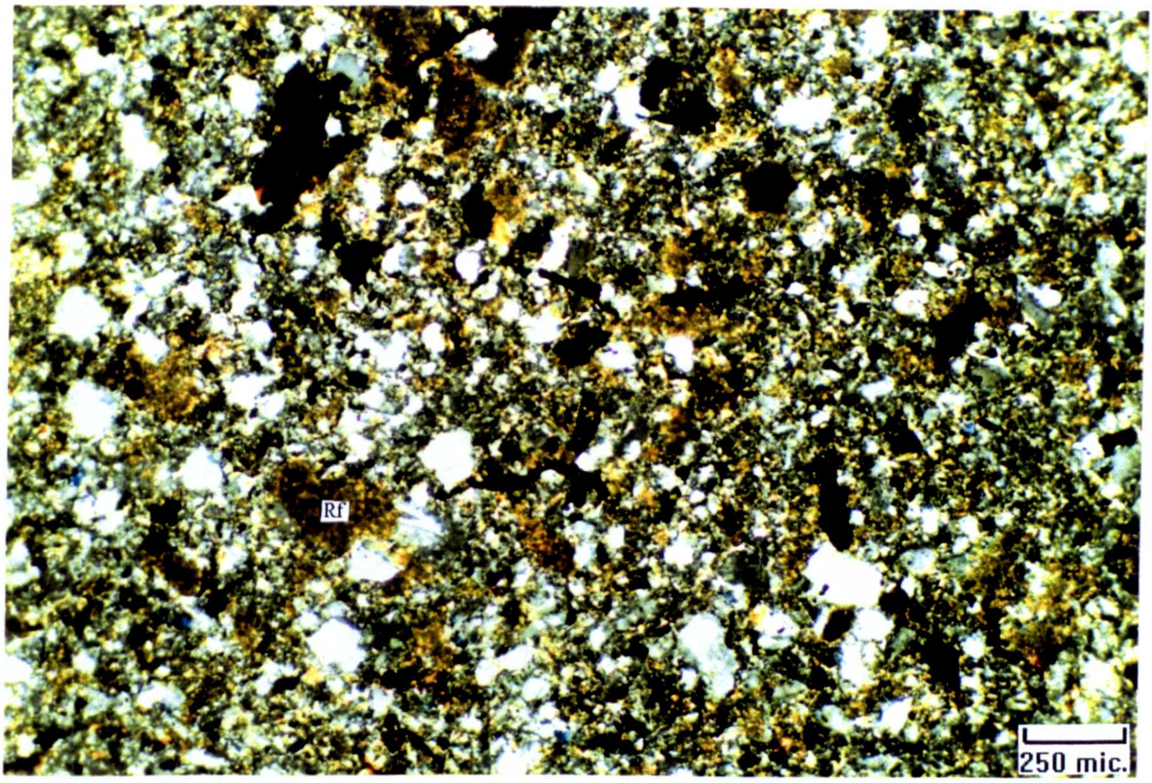


Plate 7.86 Sample C.17.2. Standard petrographic photomicrograph. [x100mag. XPL]

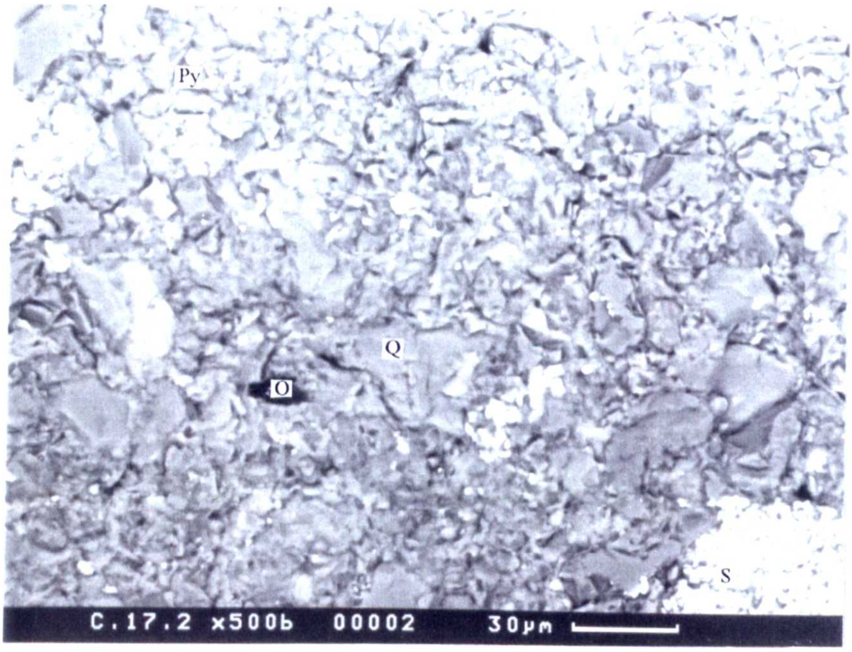


Plate 7.87 Sample C.17.2. BSI photomicrograph. [x500mag.]

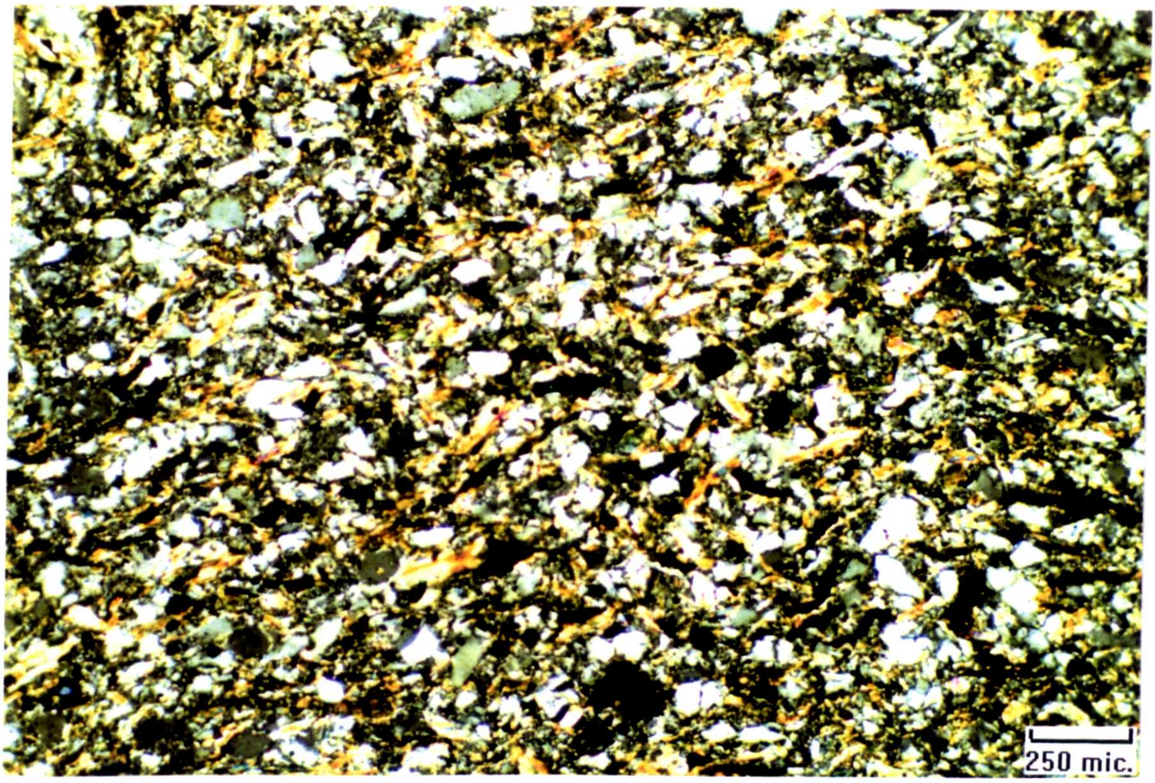


Plate 7.88 Sample C.18.1. Standard petrographic photomicrograph. [x100mag. XPL]

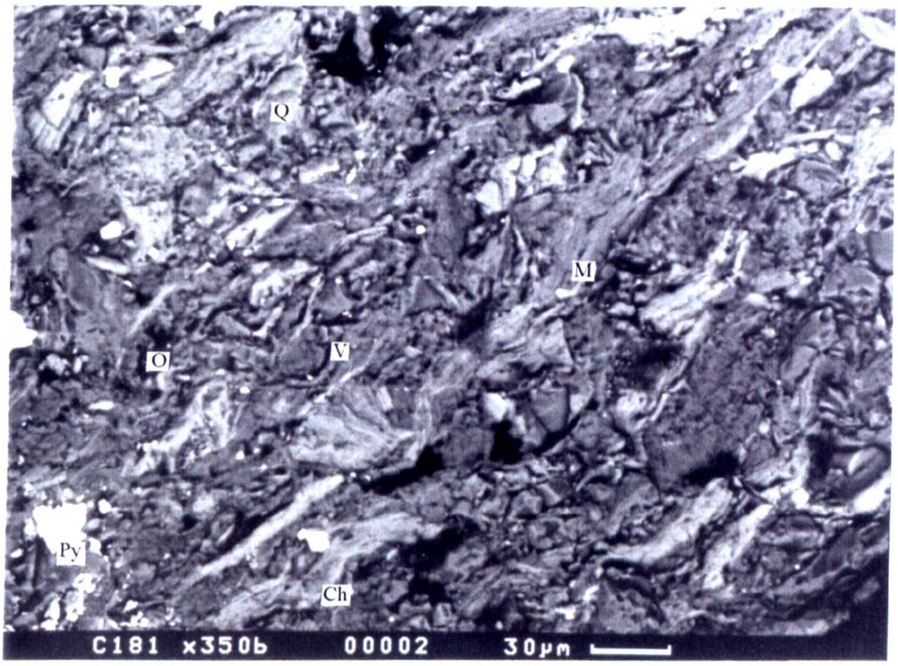


Plate 7.89 Sample C.18.1. BSI photomicrograph. [x350mag.]

# Chapter 8

# Natural and simulated, monitored weathering experiments.

## 8.1. Introduction.

Natural weathering experiments were carried out to evaluate breakdown of selected mudrock samples under natural conditions. The aims of these experiments, which were to further the work of Campbell (1993), were two-fold:

1. To evaluate whether laboratory conducted slaking experiments are useful in predicting breakdown rates and breakdown extents of mudrocks within the natural environment.
2. To investigate the process of breakdown and evaluate selected chemical reagents for potential use in assisting and accelerating mudrock breakdown.

Campbell (1993) conducted natural weathering experiments as a means of validating laboratory simulated natural weathering experiments. In addition he performed simple jar slake experiments using a series of chemical reagents including:-

- Distilled water.
- NaCl solution - to maximise the thickness of the clay particle double layer.
- $CaCl_2$ solution - to minimise the thickness of the clay particle double layer.
- $H_2SO_4$ solution - to simulate attack by acid groundwater.
- $CCl_4$ solution - a non-polar fluid.
- Formaldehyde solution - a polar fluid which enhances the fluid - clay surface interaction.

Using these reagents he concluded that there were no appreciable differences in sample breakdown when using NaCl and $CaCl_2$ solutions compared to distilled water. Using $H_2SO_4$ in certain cases reduced breakdown, except where carbonate species were present in the samples and here the breakdown was actually increased. Carbon tetrachloride solution eliminated any breakdown of the mudrock samples whereas formaldehyde again showed no difference in breakdown compared with water.

In his natural weathering experiments Campbell (1993) found that it was difficult to correlate the results with laboratory tests, this he thought was due to the fact that the natural weathering experiments were conducted on large block samples, which contained structural features not seen in the samples tested in the laboratory.

Since the intention was to evaluate chemical treatments as a means of promoting breakdown for landfill liner construction the selection of chemical additives to be used in the weathering experiments, was influenced by the need for them to be relatively cheap in cost and present a low hazard in use. Because of this carbon tetrachloride and formaldehyde were not included.

## 8.2. Outline of the test methodology.

In view of Campbell's (1993) comments regarding homogenization of the test sample for natural weathering experiments, it was decided to conduct the tests on samples prepared in accordance with the slake durability test recommendations (Franklin and Chandra, 1972). The samples consisted of 10 pieces of the mudrock , each fragment ranging from 40 - 60g in weight, the samples were oven dried prior to testing.

Seven Carboniferous samples were selected for the natural and simulated weathering experiments. These were chosen to be typical of the study range of material as follows:-

1. C1B1 - Organic claystone with a high organic carbon content.
2. C21 - Mudstone, with a moderately high organic content and also containing pyrite, calcite and siderite.
3. C31 - Very strong, very silty mudstone, containing a high proportion of siderite cement.
4. C83 - Strong siltstone,containing small quantities of organic carbon, pyrite, siderite and calcite.
5. C92 - Canneloid claystone, with a very high organic carbon content and a moderately high siderite and pyrite content.
6. C133 - Seatearth mudstone, consisting primarily of clay minerals and detrital quartz.
7. C141 - Mudstone, considered to be an average mudstone within the study group.

It was decided to monitor the natural breakdown of the samples over a 12 month period. Each mudrock sample was allowed to weather under natural environmental conditions but subsamples were treated with the selected chemical reagents on a monthly basis for the first 6 months then once after a 2 month period and finally after a 4 month period. Reagents were chosen which had not been used previously in chemical weathering studies at Sheffield University conducted by Campbell (1993) and Anderson & Cripps (1993), and the reagents were also selected on the basis that they would be commercially widely available. The following reagents were finally selected:-

(i). HCl (1M. solution) - Hydrochloric acid was selected since it is a strong oxidising agent and was intended primarily for the removal of carbonate cement minerals from the samples. The samples were designated H or (i).

(ii). $HNO_3$ (1M. solution) - Nitric acid was selected as it is a strong chelating agent with a powerful complexing action for iron (Klamberg et al.,1989). It was specifically selected as most of the samples contained pyrite and siderite. The samples were designated N or (ii).

(iii). Sodium hexametaphosphate (made up according to BS 1377:1991) - This reagent was selected as it is a powerful deflocculant for clay mineral species along with other complex phosphates. The reagent works by reducing the charge between edge-face, face-face and edge-edge clay particle interactions (Levy et al., 1991). The samples were designated Ca or (iv).

(iv). Citric acid (1M. solution) - Citric acid was selected as it is a strong chelating agent with a tendency to increase cation solubility, especially for iron (Klumberg et al.,1989). The samples were designated C or (iii).

(v). Na-EDTA (0.1M. solution) - The use of this reagent was suggested by Mr. D. Banks (hydrogeological and geochemical consultant) since it is a strong chelating agent with a powerful complexing action for metal ions such as Fe, Ca and Al (Bassett et al. 1978). Only 3 samples were tested using Na-EDTA, as there was no further space available on the test frame which could only accommodate 39 samples. The samples tested were C1B1, C31and C141. The samples were designated E or (v).

(vi).Naturally weathered- The sample was allowed to break down under atmospheric conditions. The sample was designated Nat.

### 8.2.1. Description of the test frame apparatus.

The individual samples were placed within isolated test cells. These were constructed from 1 litre capacity UV and chemically resistant polyvinylchloride soil sample pots. The lids were replaced with 10μm diameter nylon mesh which allowed exposure of the samples to sunlight, allowed rain water access but restricted access of wind blown material such as leaves and dust.

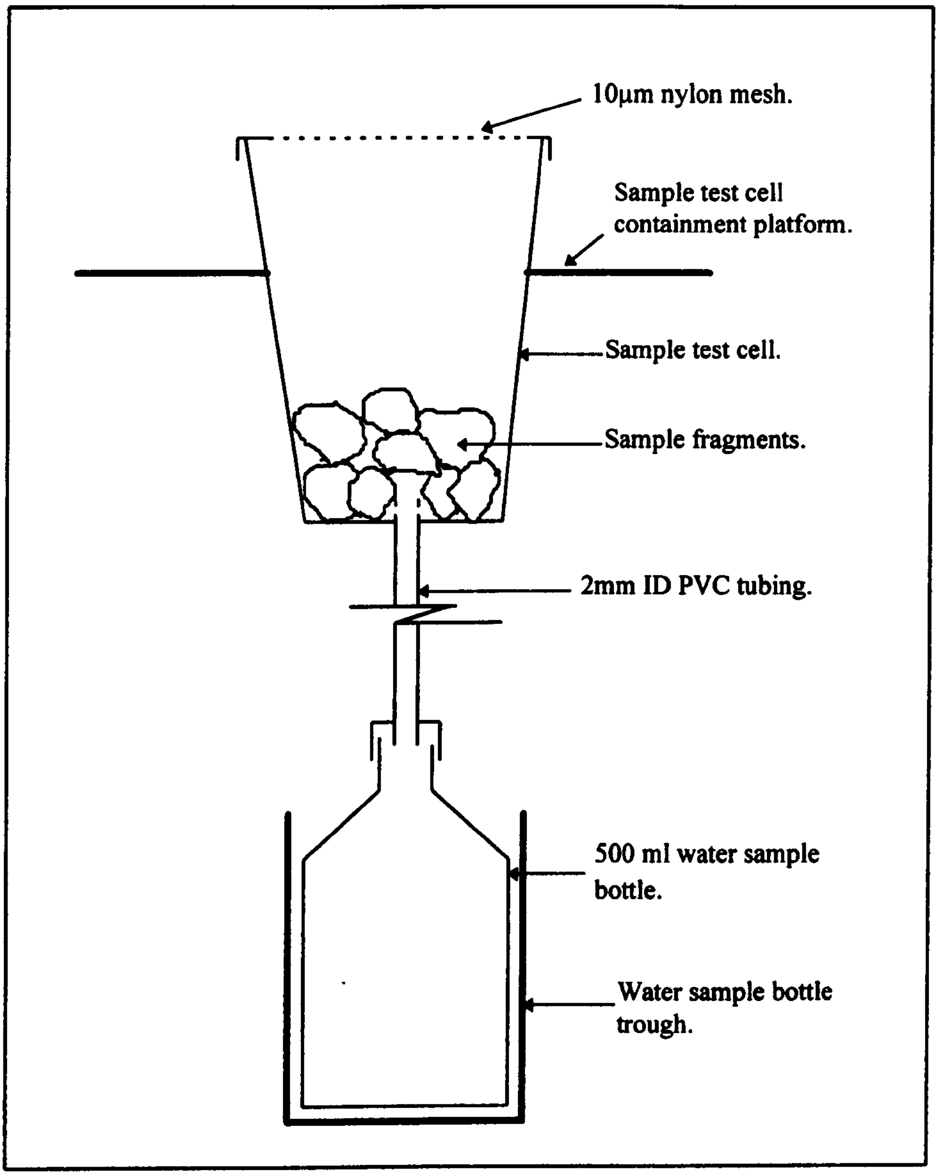


Figure 8.1 Roof weathering sample test cell design.

The samples which consisted of 10 fragments of the relevant mudrock sample were placed in the base of the sample pots around the perforated end of a 2mm ID polyvinylchloride tubing located at the base of the pot which was used for the collection of leachate and rain water.The end of the tubing was connected to a 500 ml capacity polyvinylchloride water sample bottle which had predrilled air vents through which excess solution could escape.The test cells and sampling bottles were arranged on a purpose built two tiered test frame, the top level consisting of a flat bed with precut holes into which the test cells securely fitted and the bottom level consisted of a trough in which the sample bottles were securely held.The test frame was positioned on an exposed section of the roof of the Department of Earth Sciences. The schematic picture of the sample test cell is presented in Figure 8.1 and the arrangement of the test frame can be seen in Plate 8.1.

### 8.2.2. Monitoring of the samples during testing.

To monitor the physical breakdown of the samples, monthly observations were carried out between August 1995 to January 1996 and from January every second month until July 1996. The state of breakdown of the samples was accessed according to the classification scheme devised during the modified jar slake testing programme and presented in Chapter 6. These observations are presented in Table 8.1. A qualitative accessment of the mineralogical breakdown during testing was made by means of ICP-AES analysis of the leachate collected 24 hours after reagent additions, leachate was also collected for analysis 1 month after reagent additions. The mineralogies of mudrocks are generally divided into five distinct component groups, [1] - Quartz. [2] - Carbonates. [3] - Organic material. [4] - Clay minerals. [5] - Sulphur compounds (sulphides and sulphates) (Norry et al., 1994 ; Batchelder, 1995.). Therefore it was decided only to carry out selective analysis of ion species representing these groups ie.

- Si - mainly derived from the breakdown of detrital quartz, quartz cement and clay minerals.
- Al - derived from the breakdown of clay mineral species.
- Ca - main component of carbonate species such as calcite and dolomite.
- Fe - mainly derived from siderite, pyrite and iron colloids.

The ongoing analysis of these ions was intended as a qualitative means of accessing the reaction and breakdown of the main components found in mudrocks, the results are presented numerically in Appendix C1 and graphically in Appendix C2. Analysis of the ion species was carried out monthly over the first 6 months test period, then after 8 and 12 month test periods.

On completion of the roof weathering experiment, the residual slaked sample material was collected for particle size analysis which was performed according to the recommended methods given in BS 1377:1990. This consisted mainly of wet sieve analysis with limited hydrometer determinations of the silt and clay size fractions for certain samples which provided adequate amounts of material for measurement. The particle size curves are presented in Figures 8.3 to 8.8. Upon completion of the particle size analysis representative sub-samples of the test samples were retained for XRD analysis to see if any noticable mineralogical changes had occured, these are presented along with unweathered whole rock scans for each sample in Figures 8.9 to 8.15. The subsamples were also subjected to XRF analysis and results compared with data for the original materials to observe the extent of any geochemical changes which had resulted due to the use of the reagents and so accessing their effectiveness with regards to dissolution of specific mineral components. The results for the raw XRF data are presented in Appendix C3 and corrected XRF data as presented in Table 8.3. The methods of sample preparation and analysis for XRD and XRF analysis are described in Chapter 5.

## 8.3. Physical monitoring of sample slaking as a result of weathering.

The samples were monitored visually during the testing period on a regular basis with the physical descriptions being based upon the modified jar slake classification scheme. Upon completion of the 12 months testing programme the slaked sample material was subjected to particle size distribution analysis to evaluate the extent of breakdown caused by the various reagents applied to the sub-sample material.

### 8.3.1. Visual description of the extent of sample slaking.

A good comparison is found to exist between the laboratory jar slake durability classification and the durability classification obtained from each of the natural weathering experiments. The results which are presented in Table 8.1 show that samples C1B1, C21, C92, and C141 have identical durability classifications catagories for the jar slake experiment and the roof weathering experiment. The extent of natural breakdown for each of the samples subjected to the roof weathering experiment can be seen in Plate 8.2. Sample C31 is assigned a higher durability classification from the natural weathering experiment than for the jar slake experiment, although a comparable classification is obtained within the first 8 months period of testing. The classification assigned from the natural weathering experiment for sample C31 is higher than for the jar slake classification due to the slow progressive removal of the siderite cement which was abundant in the sample. This would not have happened during a 24 hours jar slake experiment. Samples C83 and C133 appear to have marginally higher classification values for the natural weathering experiment compared with the jar slake test results. Since these results are only marginally different they are probably due to differences in sample selection and visual evaluations under non-favourable conditions. Sample C83 also contains a small percentage of carbonate cement which may have undergone dissolution after 4 months of exposure therefore enabling slaking of the sample to occur.

The classification from the simulated weathering experiment involving the addition of the selected reagents show that for samples C1B1 and C21 there is no evident reagent effects enhancing the rate and extent of sample slaking when compared with their naturally weathered equivalents. In sample C1B1-H the use of hydrochloric acid has resulted in a more rapid rate of breakdown when compared against the results using the other reagents. In sample C92 there is a slight enhanced state of breakdown using the reagents, especially HCl and $NHO_3$. The rate and extent of slaking in sample C31 appears to be similar for all the reagents used and is comparable to the rate of breakdown in the natural experiment. However, treatment with EDTA has induced more rapid rate and greater extent of slaking. This effect is due to EDTA being a strong chelating agent having an affinity to form Fe compounds and Fe in the form of siderite is a major component of the sample. Sample C83 shows a faster rate of slaking when

| Sample | Aug95 | Sep95 | Oct95 | Nov95 | Dec95 | Jan96 | Mar96 | May96 | Jul96 | Ij' |
|---|---|---|---|---|---|---|---|---|---|---|
| C1B1-H | 1 | 2-3 | 3-4 | 4 | 4 | 4-5 | 5 | 4-5 | 5 | 5 |
| C1B1-N | 1 | 2 | 2-3 | 3 | 3-4 | 4 | 4 | 4-5 | 4-5 | 5 |
| C1B1-C | 1 | 2 | 2 | 2 | 2-3 | 3-4 | 4 | 4-5 | 4-5 | 5 |
| C1B1-Ca | 1 | 2 | 2 | 3 | 3 | 3-4 | 4 | 4-5 | 5 | 5 |
| C1B1-E | 1 | 2 | 2-3 | 3-4 | 4 | 4 | 5 | 5 | 5 | 5 |
| C21-H | 1 | 4 | 4-5 | 5 | 5 | 5-6 | 6 | 6 | 6-7 | 7 |
| C21-N | 1 | 4 | 4-5 | 5 | 5 | 6 | 6-7 | 6-7 | 6-7 | 7 |
| C21-C | 1 | 2-3 | 4-5 | 5 | 5 | 5 | 6 | 6-7 | 6-7 | 7 |
| C21-Ca | 1 | 4-5 | 5 | 5 | 5 | 5 | 6 | 6-7 | 6-7 | 7 |
| C31-H | 1 | 2 | 2 | 2 | 3 | 4 | 4 | 5 | 5 | 3-4 |
| C31-N | 1 | 1-2 | 2 | 2 | 2 | 2 | 3 | 5 | 5 | 3-4 |
| C31-C | 1 | 1-2 | 2 | 2-3 | 2-3 | 3 | 4 | 4 | 4-5 | 3-4 |
| C31-Ca | 1 | 1-2 | 2 | 2 | 3 | 3 | 4 | 5 | 5 | 3-4 |
| C31-E | 1 | 2 | 2-3 | 2-3 | 5 | 5 | 5 | 5-6 | 5-6 | 3-4 |
| C83-H | 1 | 2-3 | 2-3 | 4 | 5 | 5-6 | 6 | 6-7 | 6-7 | 2 |
| C83-N | 1 | 1-2 | 2-3 | 4 | 4 | 5 | 5-6 | 6 | 6 | 2 |
| C83-C | 1 | 3-4 | 3-4 | 5 | 5 | 5-6 | 6 | 6 | 6-7 | 2 |
| C83-Ca | 1 | 3-4 | 4 | 4-5 | 5 | 6 | 6 | 6 | 6 | 2 |
| C92-H | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2-3 | 3-4 | 2 |
| C92-N | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2-3 | 3-4 | 2 |
| C92-C | 1 | 1 | 1-2 | 2 | 2 | 2 | 2 | 2-3 | 3 | 2 |
| C92-Ca | 1 | 1 | 1-2 | 2 | 2 | 2 | 2 | 2-3 | 3 | 2 |
| C133-H | 1 | 5-6 | 6 | 6 | 6 | 7 | 7 | 7-8 | 7-8 | 6 |
| C133-N | 1 | 5 | 6 | 6 | 6-7 | 7 | 7 | 7-8 | 7-8 | 6 |
| C133-C | 1 | 5 | 5-6 | 6 | 6 | 6-7 | 7 | 7 | 7 | 6 |
| C133-Ca | 1 | 5-6 | 6 | 6-7 | 7 | 7 | 7 | 7-8 | 8 | 6 |
| C141-H | 1 | 5-6 | 6-7 | 7 | 7 | 7 | 7 | 7-8 | 7-8 | 7 |
| C141-N | 1 | 6 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
| C141-C | 1 | 4-5 | 5-6 | 6 | 6 | 6-7 | 6-7 | 7 | 7 | 7 |
| C141-Ca | 1 | 6 | 6-7 | 7 | 7 | 8 | 8 |  |  | 7 |
| C141-E | 1 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
| C1B1-Nat | 1 | 2 | 2-3 | 3-4 | 4 | 4 | 5 | 5 | 5 | 5 |
| C21-Nat | 1 | 4-5 | 5-6 | 6-7 | 6-7 | 7 | 7 | 7 | 7 | 7 |
| C31-Nat | 1 | 1 | 1-2 | 2-3 | 2-3 | 2-3 | 3 | 5-6 | 5-6 | 3-4 |
| C83-Nat | 1 | 1-2 | 1-2 | 2 | 2 | 2-3 | 2-3 | 3 | 3 | 2 |
| C92-Nat | 1 | 1-2 | 1-2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| C133-Nat | 1 | 3-4 | 4 | 5 | 5-6 | 5-6 | 6 | 6-7 | 7 | 6 |
| C141-Nat | 1 | 4 | 5 | 5 | 5-6 | 6 | 6 | 7 | 7 | 7 |

Table 8.1. Roof weathering sample descriptions using the modified jar slake classification scheme.

treated with hydrochloric acid, citric acid and calgon than for nitric acid. All the classifications for the experiments involving reagent additions to sample C83 are higher than for the natural weathering and jar slake experiments. Sample C83 is a siltstone containing a clay and carbonate cement matrix which is more susceptible to slaking in the prescence of the reagents. In samples C133 and C141 the rates and extent of slaking appear to be higher for all the experiments involving the addition of reagents than for the natural weathering experiment and the jar slake test. The majority of slaking took place within the first 2-3 months of testing. It appears evident that calgon is the most effective reagent inducing the most rapid and highest degree of slaking for all the reagents used in these samples which have a higher clay mineral component than the other samples tested. clearly, deflocculating the clay minerals has led to slaking of the sample. Samples C1B1 and C21 also contain a high clay mineral component but these two samples also contain a large organic content. A high organic content within mudrocks tends to result in a hydrophobic organic film forming around clay minerals or pockets of clay minerals thus inhibiting the access of water and the reagents used to accelerate slaking. Therefore, the rate and extent of slaking remains the same as for naturally weathered sub-samples. In sample C141-E , the use of EDTA appears to have induced a more rapid rate and extent of slaking, this effect is also apparent in sample C31-E. Both these samples contain siderite cement which would be the source of dissolution for the EDTA.

The effects of natural and simulated weathering and the extent of sample slaking are shown in Plates 8.3 to 8.47. Photographs for samples C21, C31, C133 and C141 are presented for all the sub-samples and reagent additions after 6 and 12 months of testing because these samples tended to show the most evident visual changes. Plates 8.3 to 8.5 for sample C1B1-E are only presented as a representative example of the minimal extent of slaking exhibited by this sample. Plates 8.25 to 8.27 for sample C83-H are also presented as representatives showing the typical extent of slaking of this sample. No photographs of sample C92 have been presented as there was no evident slaking seen on any of the sub-samples tested. For each sample a photograph of the initial state of the sample at the start of testing is presented for comparative purposes. From the photographs presented a progressive change in the extent of slaking can be seen for samples C1B1, C21, C31 and C83, whereas for samples C133 and C141 the majority of slaking has resulted within the first 6 months of testing with minimal changes after this period. The most striking physical changes are evident in samples C133-Ca (Plates 8.35 and 8.36) and sample C141-Ca (Plates 8.44 and 8.45) where calgon was used as the slaking reagent. Here the final affects have been to reduce the samples to the state of residual soils, in sample C141-Ca this occurred within the first 6 months of testing and therefore the sample had to be removed from testing.

### 8.3.2. Particle size analysis of the slaked material.

On completion of the 12 month roof weathering experiment the slaked material was subjected to particle size analysis. The results are presented in Figures 8.2 to 8.8 where the data are presented as percent of material passing and the largest sieve size was of 19mm effective diameter. Silt and clay size determinations by the hydrometer method were only conducted on samples C133 and C141 which were the only samples to have undergone major breakdown resulting in sufficient fines for testing. The particle size for the 40 to 60g pieces of mudrock at the commencement of the experiment of the experiment was approximately 20 to 70mm. Figure 8.2 (sample C1B1) and Figure 8.6 (sample C92) show that there has been a limited amount of slaking producing fragments smaller than the maximum sieve size of 19mm diameter. The particle distribution curves for the naturally weathered samples and reagent assisted samples show that a similar distribution of slaked material has resulted for C1B1 and C92. These samples are both organic rich and the organic material acts as cementing medium resistant to slaking therefore resulting in more durable samples (Ratsey, 1973 ; Campbell, 1993). It can be seen in Figure 8.3 for sample C21 that the slaked material consists of fragments in the size range between 1 and 19mm in diameter, this being the sand to gravel size range. From these curves it appears that the addition of citric acid has resulted in marginally less sample breakdown than obtained from the other reagents used. In Figure 8.4 for sample C31 it can be seen that a similar fragment size distribution has resulted from the use of all the reagent except EDTA which appears to have resulted in a lesser degree of sample slaking with 33% of the residual material remaining as fragment sizes greater than 19mm diameter. Sample C83 (Figure 8.5) shows that a minimum of slaking has resulted from the use of the reagents although of the reagents hydrochloric acid has produced the greatest slaking, probably due to the dissolution of the carbonate cement present in C83. In Figure 8.7 (sample C133) and Figure 8.8 (sample C141) it is evident

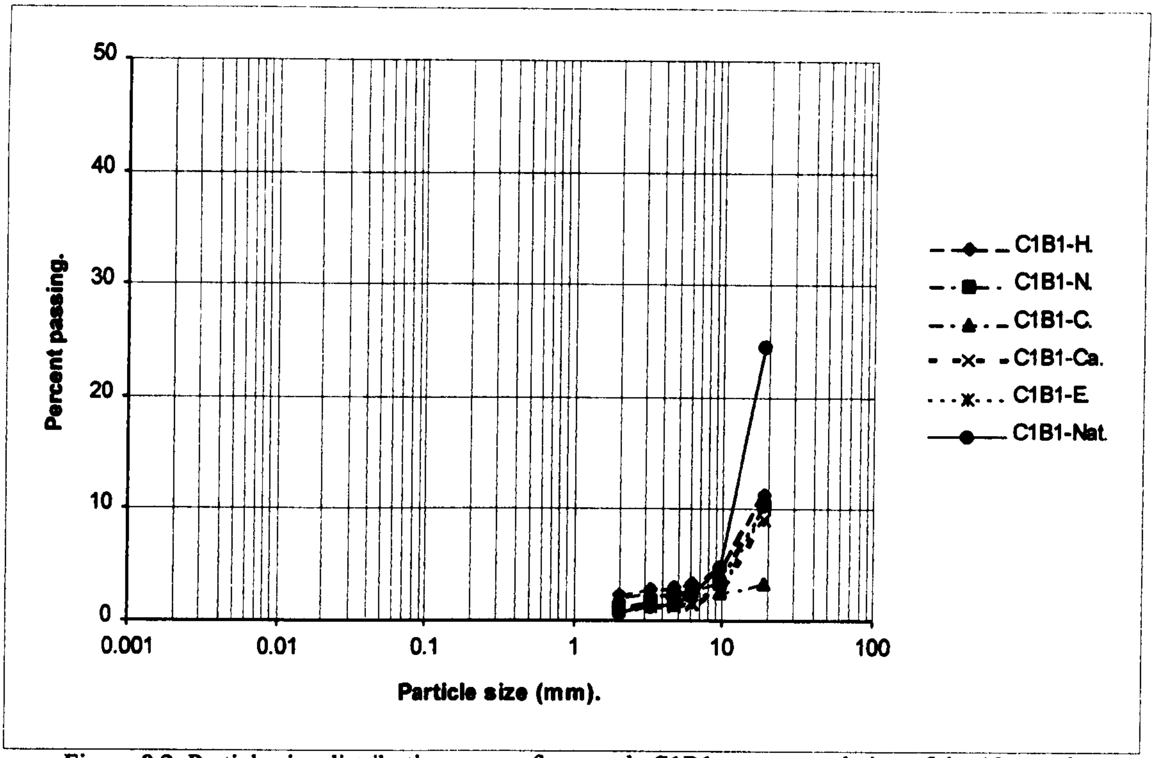


Figure 8.2. Particle size distribution curves for sample C1B1 upon completion of the 12 month weathering experiment.

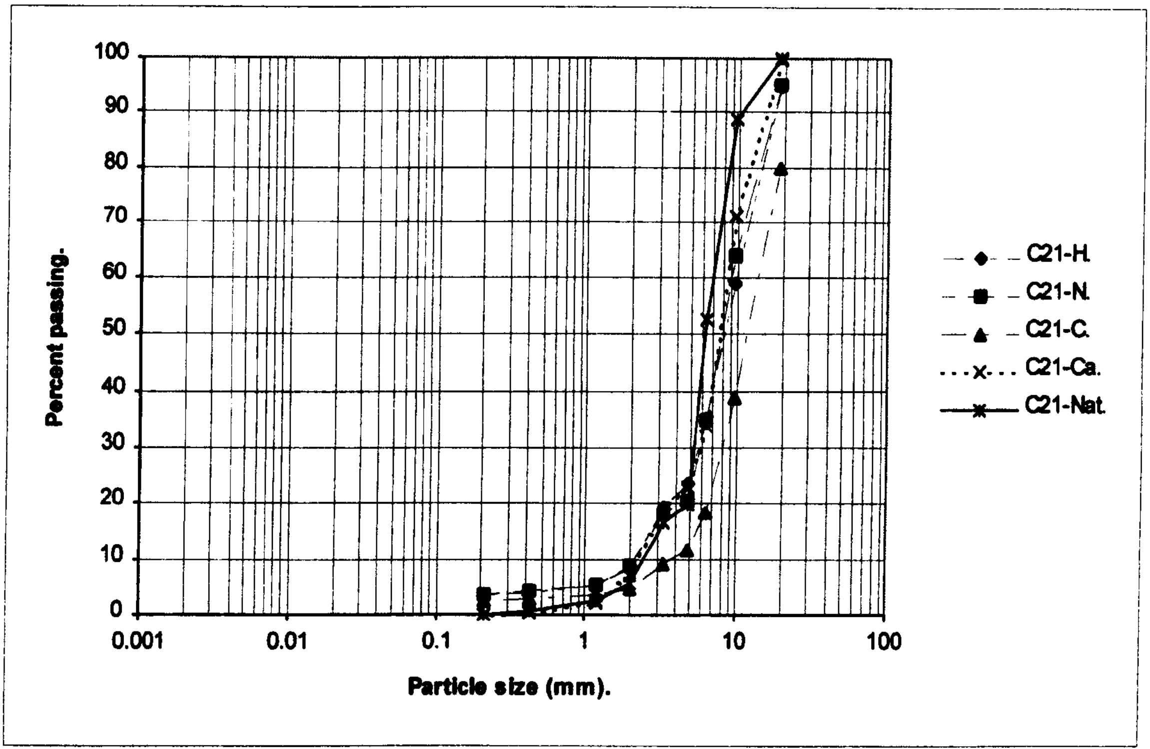


Figure 8.3. Particle size distribution curves for sample C21 upon completion of the 12 month weathering experiment.

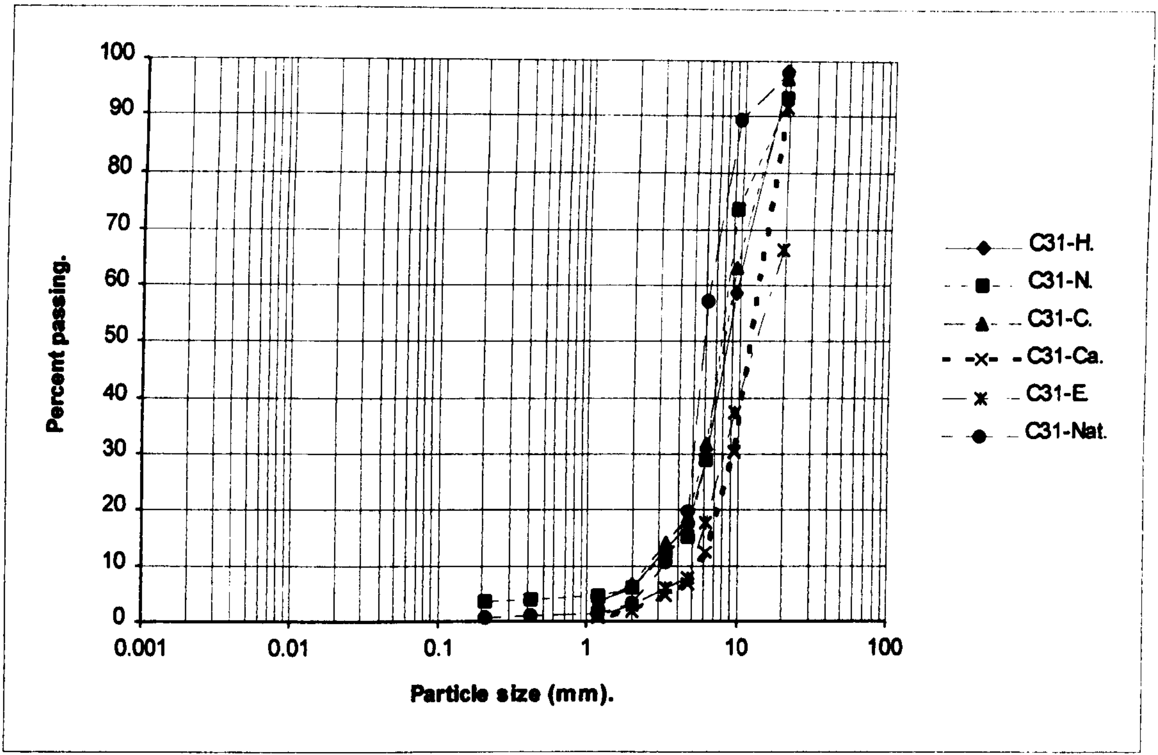


Figure 8.4. Particle size distribution curves for sample C31 upon completion of the 12 month weathering experiment.

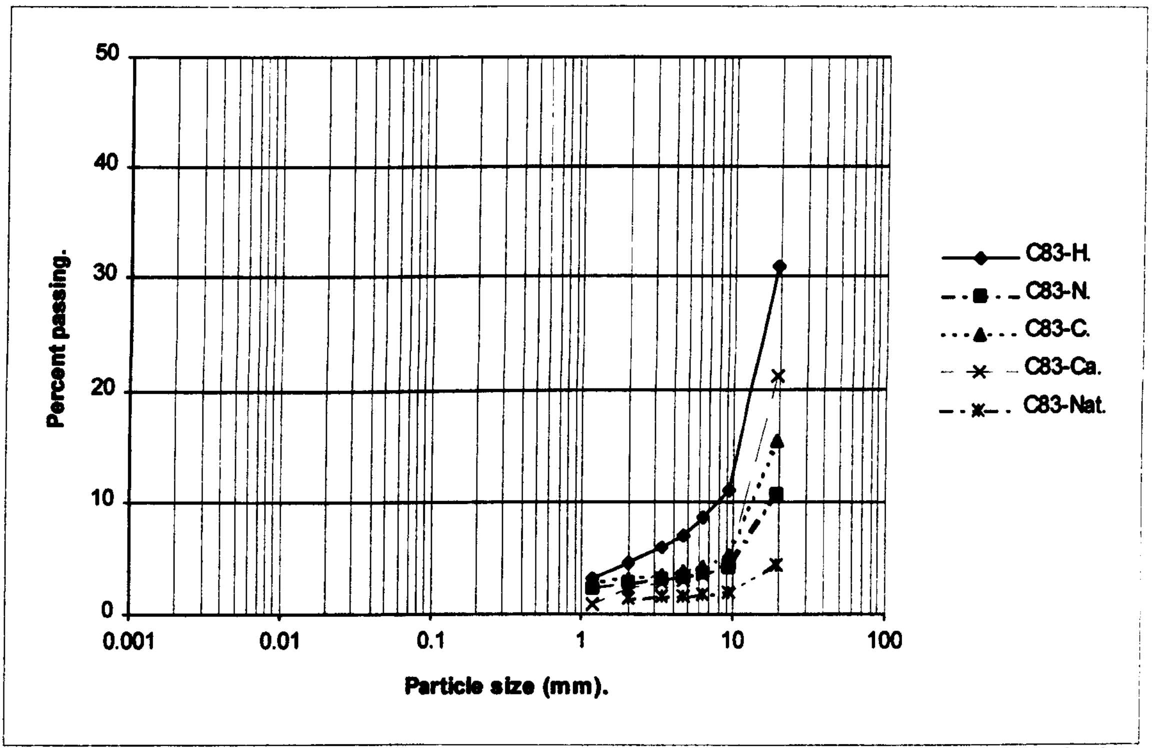


Figure 8.5. Particle size distribution curves for sample C83 upon completion of the 12 month weathering experiment.

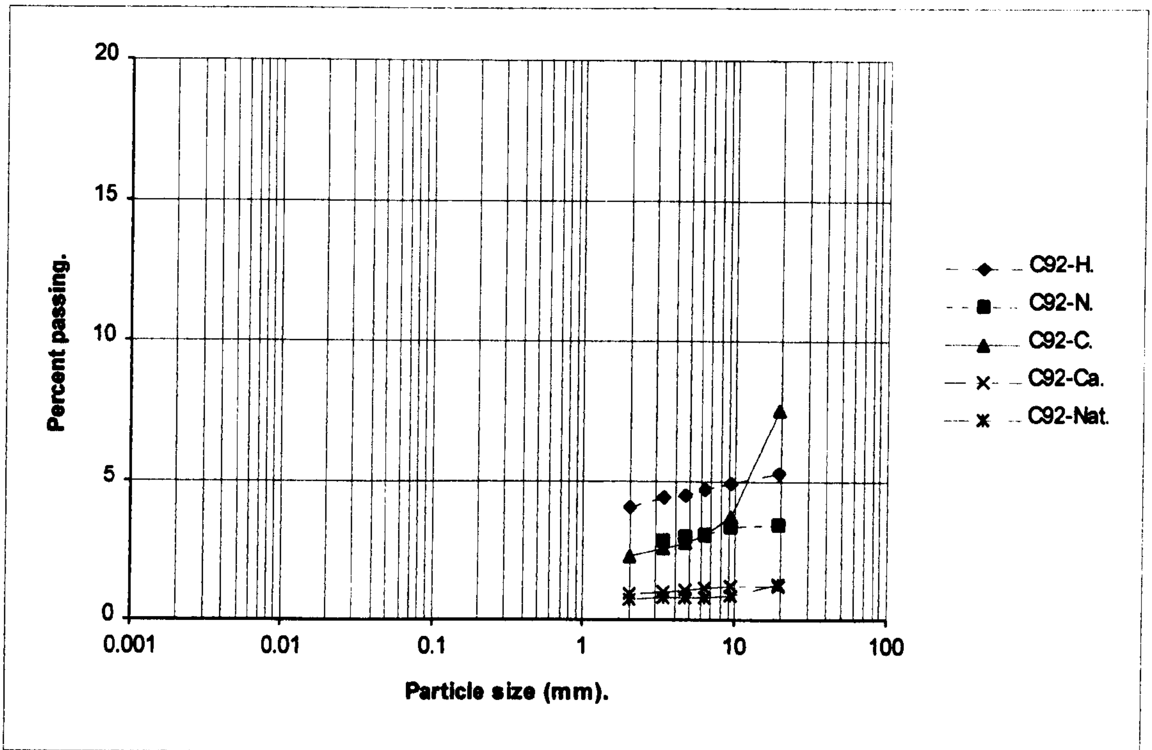


Figure 8.6. Particle size distribution curves for sample C92 upon completion of the 12 month weathering experiment.

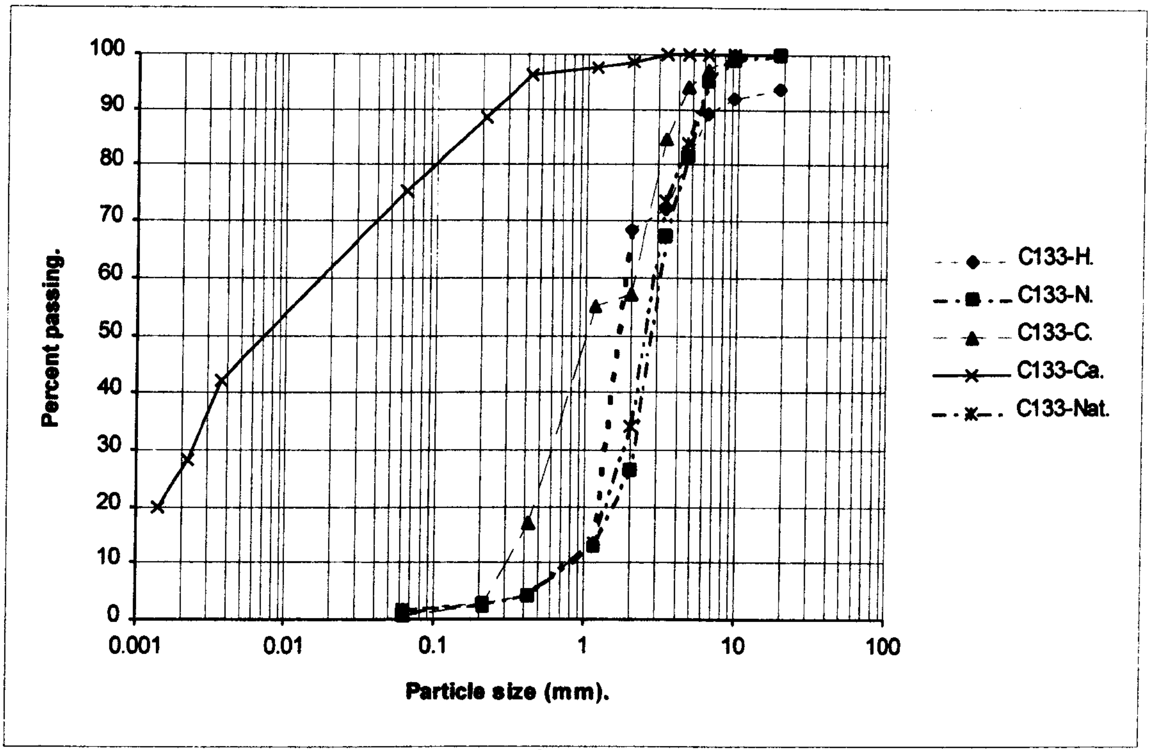


Figure 8.7. Particle size distribution curves for sample C133 upon completion of the 12 month weathering experiment.

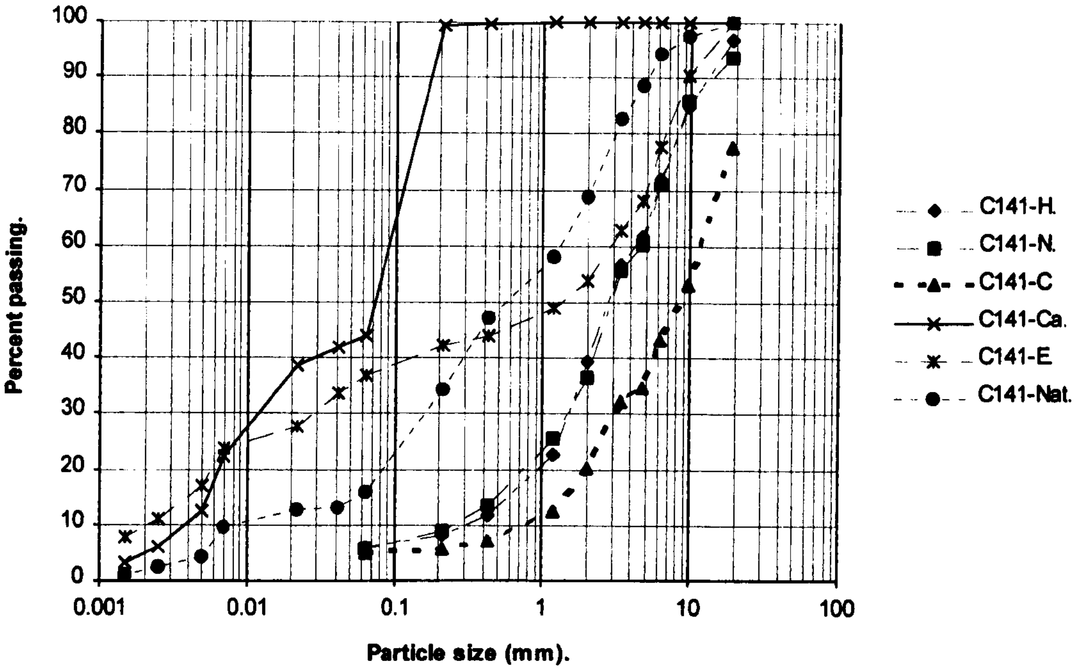


Figure 8.8. Particle size distribution curves for sample C141 upon completion of the 12 month weathering experiment.

that calgon has produced the largest amount of sample slaking. In sample C133 the other reagents have all produced similar size range distributions for the slaked material, whereas for sample C141 there is a larger scatter of the size range distribution curves for the slaked material. In C141 EDTA appears to have been the most effective slaking reagent after calgon with citric acid having the least effect on sample breakdown.

## 8.4. Mineralogical and chemical analysis of the weathered samples.

During the course of the weathering experiment samples of the leachates were collected 24 hours after the addition of the selected reagents (refered to as reagent leachates) and 1 month after the addition of the selected reagents (refered to as the periodic leachates). Analysis for Al, Ca, Fe and Si ion species concentration of the leachates was performed by ICP-AES so that a qualitative picture of which mineral species were being affected by the selected reagents during weathering could be made. On completion of the roof weathering experiment each subsample was subjected to X-ray diffraction analysis to accertain if any notable mineralogical changes had occurred.

The samples were also subjected to XRF analysis to evaluate the geochemical changes which had resulted, which would not have been evident from XRD analysis.

### 8.4.1. Chemical analysis of the leachates by ICP-AES.

In the roof weathering experiments 75 cc of the specific reagents were added to each sample at the predetermined time. This leachate material was collected after a 24 hour period and subjected to chemical analysis. The treated samples were then left to weather under natural conditions for a minimum period of 1 month after which the accumalated leachate was again collected for analysis and the next stage of reagent addition was carried out. Initially each of the reagents and rain water samples were analysed to determine their Al, Ca, Fe and Si ion concentrations, these concentrations were found to be very low, generally <5ppm and therefore corrections to the leachate analysis results were not considered to be necessary.

The chemical data for the samples are presented in Appendix C1 and graphically presented in Appendix C2, Figures C1 to C54. Comments on the findings are presented below for each sample. In general the naturally weathered samples tended to have very low concentrations of the ion species and therefore are not commented on.

Sample C1B1. Results for the analysis of the periodic leached samples (Figures C1 to C4) show that Al ion concentrations tend to be very low, generally <55ppm concentration with a marked drop after 3 months. Citric acid, HCL and $HNO_3$ tend to be the most effective reagents for the removal of Al species. Ca concentrations although moderately higher than the Al ion concentrations follow a similar trend with initial high concentrations up to 3 months, with the most effective reagents being HCl, $HNO_3$ and citric acid. Similar trends are evident for the Fe concentrations with the most effective reagent being HCL, initially producing a concentration of near 5000ppm during the 2nd month marked with a drastic drop in concentration after this initial period. Silica concentrations are low with a marked peak being evident during the eighth month towards the end of the test period, this is especially evident for citric acid and $HNO_3$. In the reagent leachate ionic analysis (Figures C5 to C8) similar trends are found for Al, Ca and Fe ions with the largest concentrations seen during first to fifth months. The highest concentration values are found for Fe ranging between 2000 - 6000 ppm, which is accountable to siderite, pyrite and possibly iron colloids. HCl and $HNO_3$ tend to be the reagents that produced the largest ion concentrations. Si ion concentration values tend to be low, with the highest concentrations being detected during the eighth month for the EDTA treatment.

Sample C21. Analysis of the periodic leached samples (Figures C9 to C13) show high ionic concentrations during the initial period up to the fourth month for Al, Ca and especially Fe, beyond the sixth month the concentrations for these ions become negligable. The most effective reagent for Al removal appears to be citric acid, whereas for Ca and Fe the reagents HCl, $HNO_3$ and citric acid all appear to be equally efficient. Si concentrations appear to be very low with a high during the eighth month resulting from the use of HCl. In the reagent leachate samples (Figures C13 to C16) a similar trend is seen for Al, Ca and Fe concentrations with initial high values dropping off after about the fourth and fifth months. The most effective reagents for Al leaching appear to be HCl, $HNO_3$ and citric acid, with $HNO_3$ producing high ionic concentrations throughout the whole duration of the experiment. Ca is most effectively leached by $HNO_3$ and HCl and Fe by HCl and $HNO_3$ producing exceptionally high ionic concentrations of around 10000 ppm during the second month. Si appears to be mostly affected by HCl, $HNO_3$ and citric acid with calgon showing a marked effect towards the latter stages of the experiment from the sixth to eighth month.

Sample C31. Analysis of the periodic leachate samples (Figures C17 to C20) show initial high ionic concentrations within the initial test period up to the sixth month for Al, Ca and Fe. The most effective reagents for mobilizing Al are respectively $HNO_3$ and citric acid, whereas for Ca it is $HNO_3$ while for Fe the reagents are $HNO_3$ and citric acid. Si remains at a low ionic concentration with a high value from the sixth to eighth month for which the most prominant reagent is $HNO_3$ with the silica values of around 3500 ppm. In the reagent leachate ionic analysis (Figures C21 to C24) similar distributions are found for Al, Ca and Fe, with HCl producing the most prominantly high concentrations. The ionic concentrations appear to fluctuate although remaining high for the test duration. In the Al analysis, $HNO_3$ also appears to be effective, whereas for Ca it is EDTA, while for Fe it is $HNO_3$. Si shows low ionic concentrations with HCl again being the most effective leaching reagent, except during the sixth to eighth month where EDTA produces high ionic concentrations.

Sample C83. Analysis of the periodic leachate samples (Figures C25 to C28) produce similar ionic concentration trends for Al, Ca and Fe with the majority of the leaching evident during the second to sixth month. The most effective reagent for Al tends to be citric acid and to a lesser extent HCl, whereas for Ca the most effective reagents are HCl, $HNO_3$ and to a lesser extent citric acid, and for iron, citric acid dominates with HCl and $HNO_3$ also being effective reagents. Si concentrations remain low with peak values occuring during the sixth to eighth month with HCl producing the most prominant results with concentrations of around 4500 ppm. In the reagent leachate ionic analysis (Figures C29 to C32), notably high ionic concentrations are evident for Al, Ca, Fe and Si during the second month, all these high concentrations being caused by the use of $HNO_3$. Beyond this period the ionic concentrations are very low. The highest ionic concentration values are noted for Ca and Fe which are present as cementing material that appears to be effectively leached by the acids.

Sample C92. Analysis of the periodic leachate samples (Figures C33 to C36) display similar trends for Al, Ca and Fe concentrations, with the highest notable ionic concentrations being seen between the second to sixth month. Concentrations for Al tend to be very low, generally <8 ppm, and otherwise the most prominant concentrations are seen for Fe and to a lesser extent for Ca. Effective reagents for Al removal tend to be mainly citric acid, whereas for Ca they are HCl and $HNO_3$ and for Fe they tend to be HCl, $HNO_3$ and citric acid. Si concentrations tend to be negligable with a sharp rise during the eighth month. Particularly, major effects are seen for HCl and more minor effects occur for calgon. In the reagent leachate analysis (Figures C37 to C40) similar trends are seen for all the ionic species, with the highest concentrations recorded during the first month for all samples, dropping to a very low concentration by the third month and rising again until the eighth month. The highest ionic concentrations are noted for Fe with values of ~ 26000 ppm showing effective pyrite and siderite dissolution. Al is most effectively leached by HCL and $HNO_3$, Ca by HCl and $HNO_3$, Fe by HCl and

$HNO_3$ and Si by HCl and $HNO_3$. The high concentrations recorded for all the ion species during the eighth month are all effectively caused by citric acid.

Sample C133. Analysis of the periodic leachate samples (Figures C41 to C44) show similar trends for the distribution of Al and Si concentrations, with the highest concentrations detected between the fifth to twelth month. This shows the effective dissolution of the clay mineral species present in the samples to be caused mainly by the use of calgon. Ca and Fe ions are present in high concentrations during the second and third months after which time there is a marked drop of these concentrations. These effects are mainly caused by $HNO_3$ which effectively dissolves the small quantities of Fe and Ca carbonate species present. The reagent leachate analysis (Figures C45 to C48) show similar curves for the Ca and Fe concentrations with the highest ionic concentrations evident during the first to fifth month, with calgon, $HNO_3$ and HCl being the most effective reagents on Ca and $HNO_3$ and HCl being the most effective reagents on Fe. Al concentrations appear to be at their highest levels during the second to fifth month, with the greatest ionic concentrations resulting from the use of HCl and $HNO_3$. Silica concentration values tend to be low except during the eighth month when an evident high concentration level results from the use of calgon.

Sample C141. Analysis of the periodic leachate samples (Figures C49 to C52) again show a similar distribution for Al and Si. The highest concentrations were recorded around the sixth month following the use of calgon. However, the highest concentrations of silica which were recorded during the eighth month resulted from the use of HCl. Ca and Fe species show moderately high ionic strength concentrations during the second to sixth month, after which the values become very low possibly after the effective removal of pyrite and carbonate species. The most effective reagents for Ca tend to be HCl, $HNO_3$ and citric acid, while for the removal of Fe, citric acid and HCl tend to be the most effective reagents. The reagent leachate analysis (Figures C53 to C56) present similar ionic concentration distributions for Al and Si, which tend to be moderately low with values of <500 ppm throughout the test duration. Very high concentration levels are recorded for Al and Si during the eighth month resulting from the use of EDTA, which is effective in degrading the clay species. (It must be pointed out that due to effective dissintegration of this sample using calgon it was removed from testing during the sixth month, and it therefore could be thought that the EDTA presents the highest dissolution concentrations but this is due to the absence of a calgon treated sample). Ca values are at high concentrations during the second to fourth month after which they become very low, where the most effective reagents proved to be HCl and $HNO_3$. Fe concentration remained moderately constant throughout the testing period with relatively high ionic concentrations ranging between 2000 - 5000 ppm, and the most effective reagents being HCl and $HNO_3$.

The effectiveness of each reagent for the removal of specific ion species is shown in Table 8.3. In the periodic leaching and reagent leaching experiments HCl and $HNO_3$ appear to be the most effective reagents as seen from the ion concentration graphs. These reagents seem most effective within the first few months of addition. They react mainly with the carbonate cement and pyrite phases exposed on the sample surfaces, and to a slower extent with the more stable silica and clay minerals present.

Citric acid also appears effective in the periodic leaching experiments for the removal of Al, Ca, and Fe ion species. In clay rich weakly cemented samples such as C133 and C141 which also contain very small quantities of organic cement, calgon appears to be the most effective reagent for the dissolution of clay minerals as is seen by the high Al and Si ionic concentrations of the leachates. EDTA also appears effective in causing dissolution of clay mineral species.

### 8.4.2. Mineralogical analysis of the slaked material by X-ray diffraction.

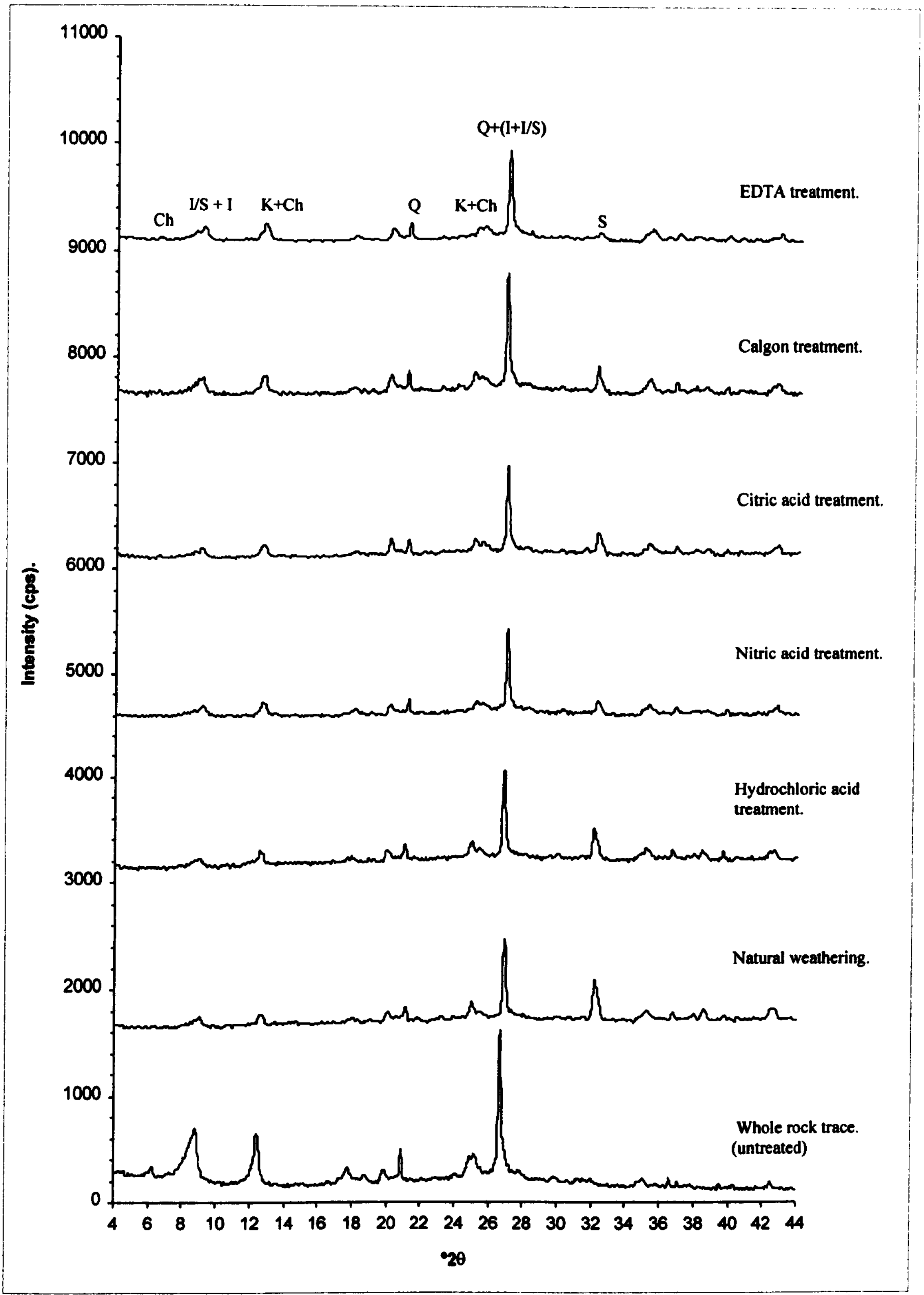
Once the slaked material from the roof weathering experiment had undergone particle size analysis, representative samples were taken for mineralogical characterization by XRD and geochemical characterization by XRF analysis. The mineralogical analysis by XRD was carried out on the whole rock samples where the preparation and analytical methodology presented in Chapter 5 was used. The traces for naturaly weathered, reagent weathered and unweathered whole rock analysis for each sample are presented on the same figure for comparative purposes (Figures 8.9 to 8.15).

It is evident from the diffraction trace for sample C1B1, Figure 8.9 that the intensities of the weathered traces tend to be weaker than for the whole rock trace, this is probably due to the degradation of the mineral species due to weathering resulting in less coherent mineral reflectors. The most notable peak change is for siderite (32.08°2θ) which does not appear to be very prominent on the whole rock trace although chemical analysis shows the sample to contain 11.4%. The siderite in the whole rock sample is probably masked by an organic or iron oxide coating which weathering and reagent treatment may have removed. The siderite peaks for $HNO_3$ and EDTA treatment appear to be the weakest, therefore these reagents have been the most effective in removing this

| | Reagent leaching. | | | | | Periodic leaching. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reagent Sample | HCL | $HNO_3$ | Cit. | Cal. | EDTA | HCL | $HNO_3$ | Cit. | Cal | EDTA |
| C1B1 - Al | **** | *** | | | * | ** | *** | **** | | |
| Ca | **** | *** | | | | **** | *** | * | | |
| Fe | **** | *** | | | | **** | ** | *** | | |
| Si | | | | | *** | | | **** | | **** |
| C21 - Al | *** | **** | *** | | | | | **** | | |
| Ca | *** | **** | * | | | *** | **** | *** | | |
| Fe | **** | **** | | | | **** | **** | **** | | |
| Si | *** | **** | * | * | | **** | | | | |
| C31 - Al | **** | * | | * | * | | **** | **** | | |
| Ca | **** | * | | | * | | **** | | | |
| Fe | **** | ** | | | * | | **** | *** | | |
| Si | *** | | | | ** | | **** | | | |
| C83 - Al | ** | **** | ** | | | *** | | **** | * | |
| Ca | ** | **** | * | | | **** | *** | ** | | |
| Fe | * | **** | * | | | *** | *** | **** | | |
| Si | * | **** | * | | | **** | | | | |
| C92 - Al | **** | *** | * | | | * | * | **** | | |
| Ca | **** | *** | * | | | **** | **** | * | | |
| Fe | **** | *** | * | | | **** | ** | ** | | |
| Si | **** | ** | * | * | | **** | | | | |
| C133 - Al | **** | ** | | * | | | * | | **** | |
| Ca | ** | ** | | **** | | | **** | | | |
| Fe | **** | *** | | * | | | **** | | | |
| Si | | | | **** | | | | * | **** | |
| C141 - Al | * | * | * | | **** | | | * | **** | |
| Ca | **** | ** | | | | **** | **** | **** | | |
| Fe | **** | ** | * | | | **** | * | **** | | |
| Si | | | | | **** | | | | **** | **** |

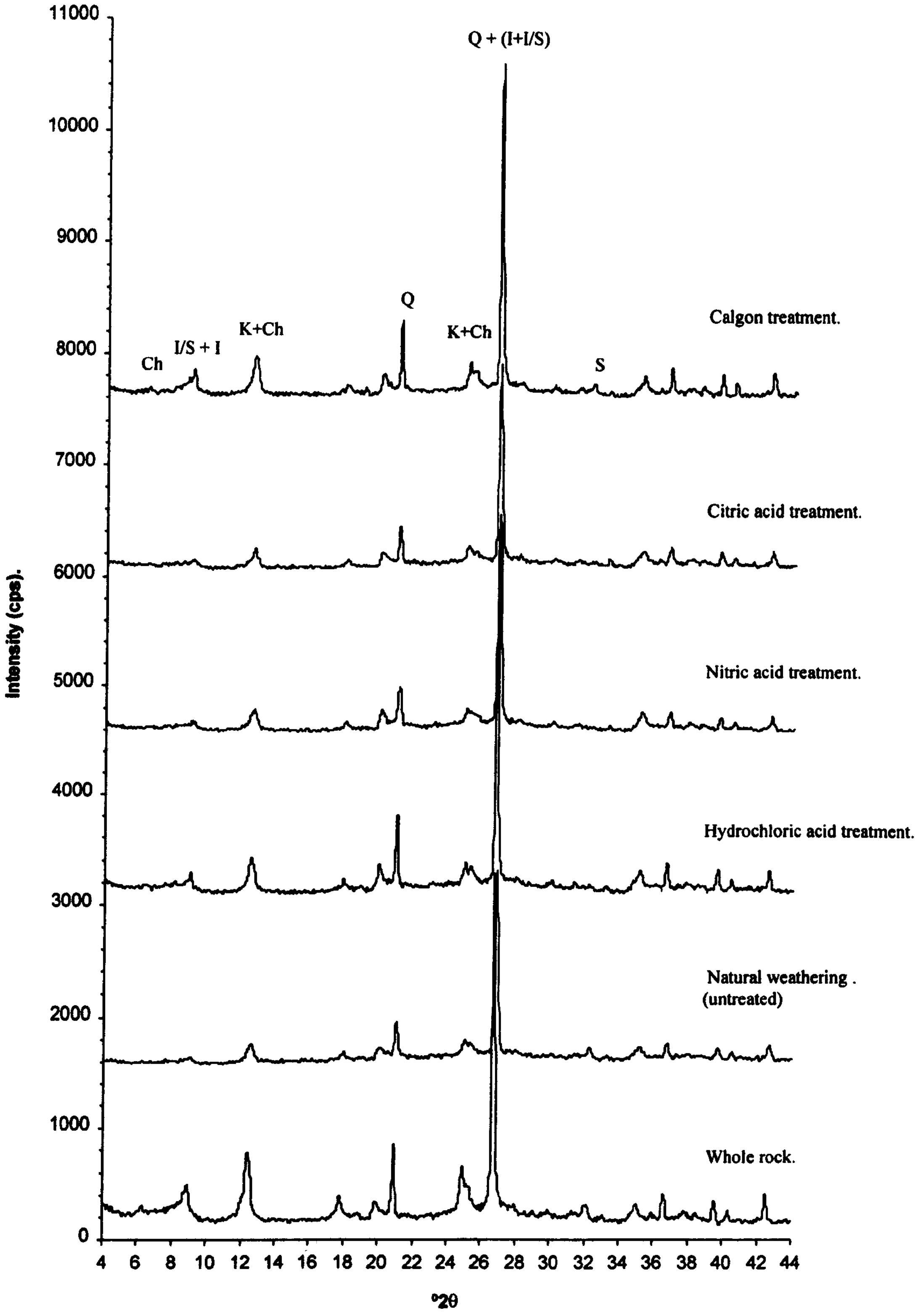
Cal. = Calgon, Cit.= Citric acid. **** = Very effective. *** = Effective.
** = Moderately effective. * = Slightly effective.

Table 8.2. Effectiveness of reagents on the leaching of specific ion species.



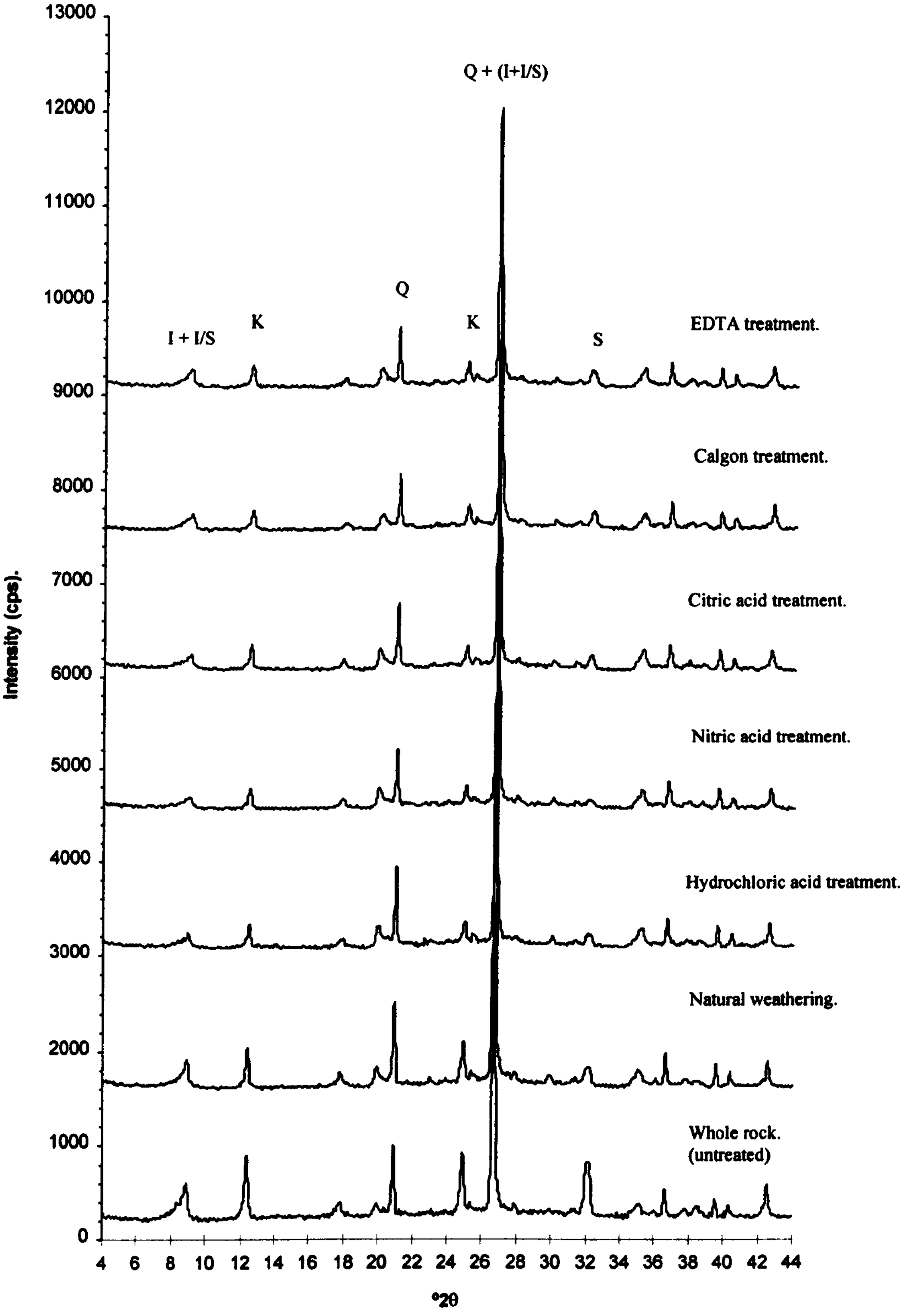
Ch = Chlorite : I/S + I = Illite with mixed layer illite-smaectite : K = Kaolinite : Q = Quartz : S = Siderite.

Figure 8.9. XRD traces of sample C1B1 upon completion of the 12 month monitored weathering experiment.



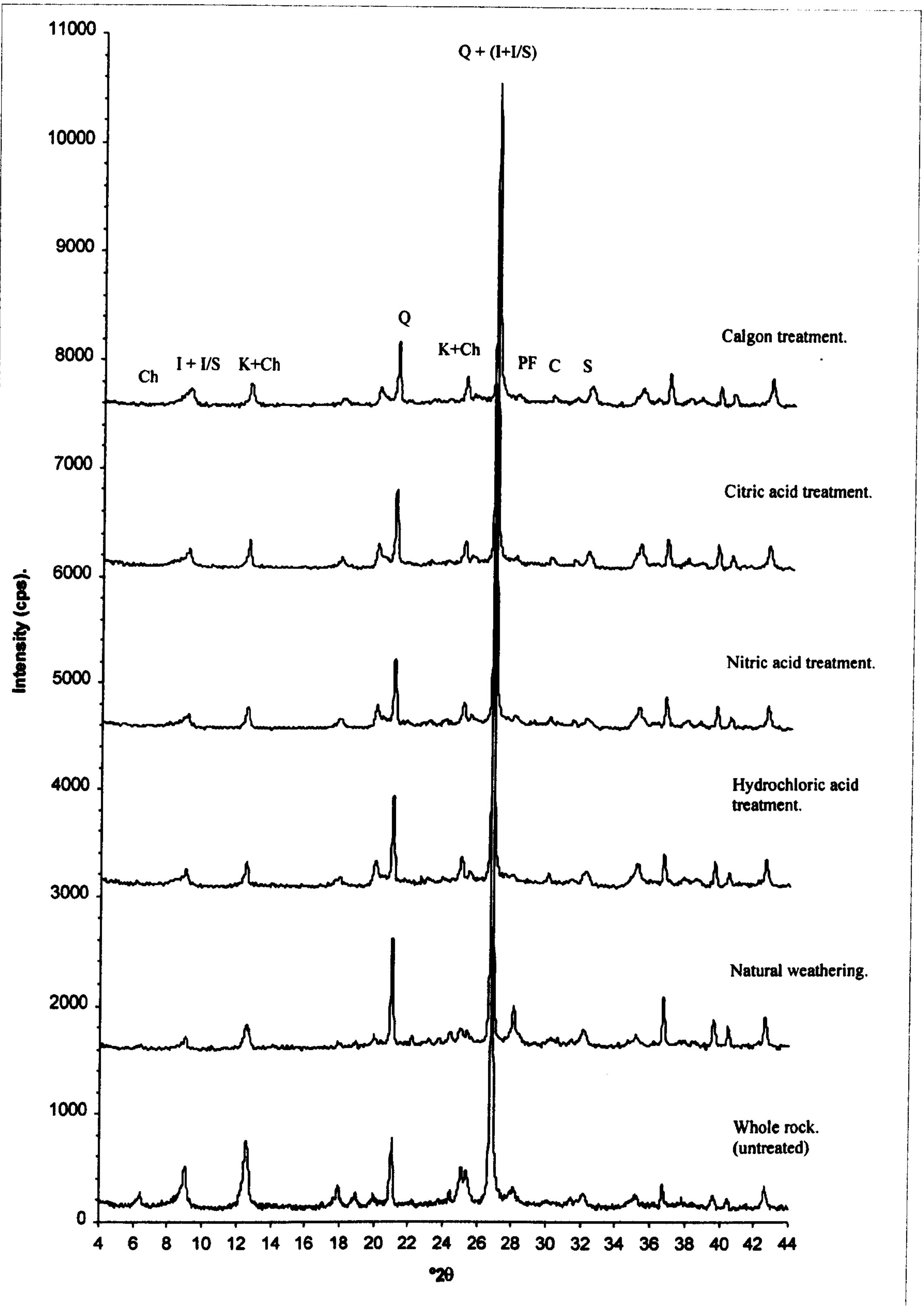
Ch = Chlorite : I/S + I = Illite with mixed layer illite-smaectite : K = Kaolinite : Q = Quartz : S = Siderite.

Figure 8.10. XRD traces of sample C21 upon completion of the 12 month monitored weathering experiment.



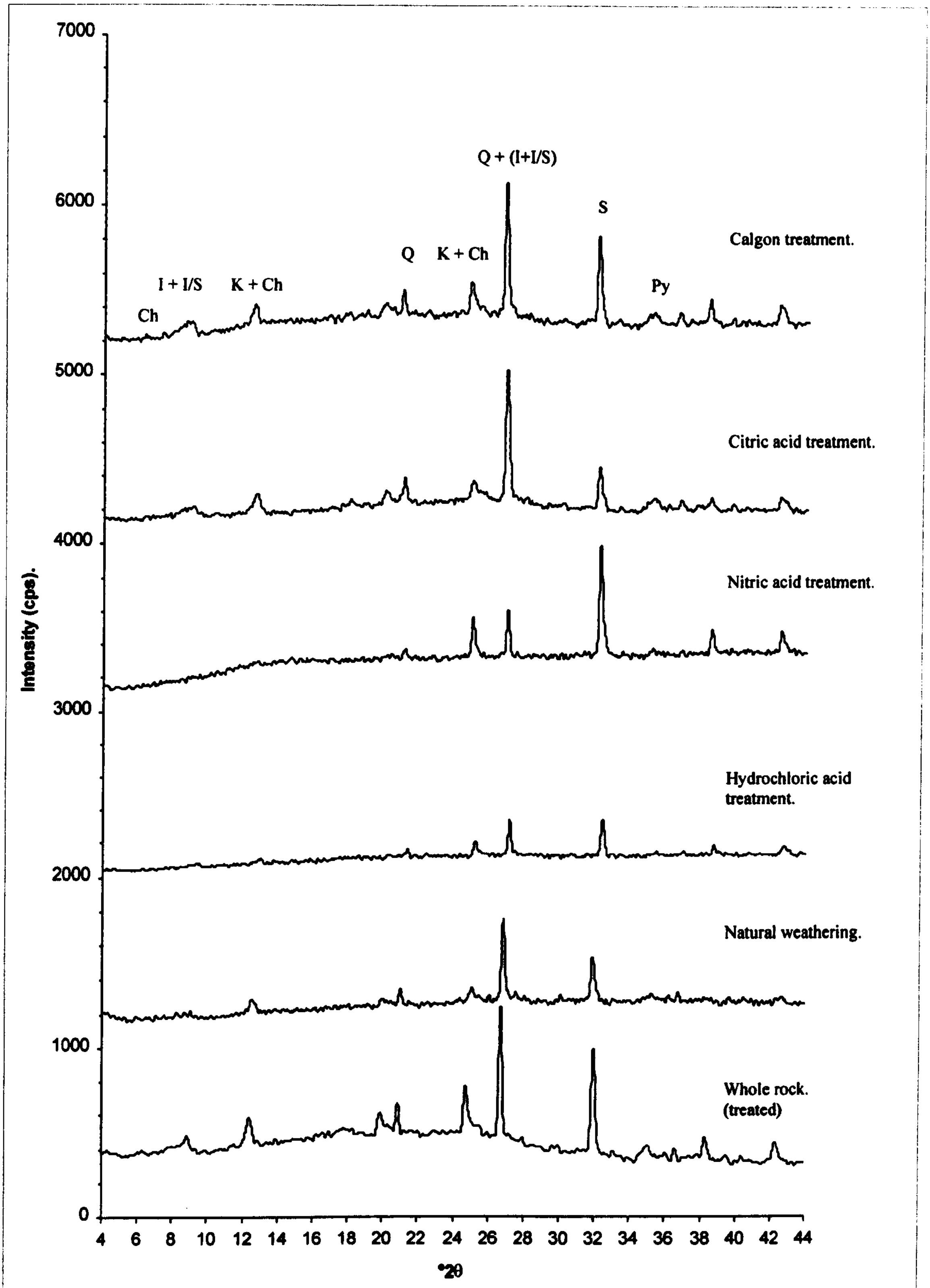
I/S + I = Illite with mixed layer illite-smaectite : K = Kaolinite : Q = Quartz : S = Siderite.

Figure 8.11. XRD traces of sample C31 upon completion of the 12 month monitored weathering experiment.



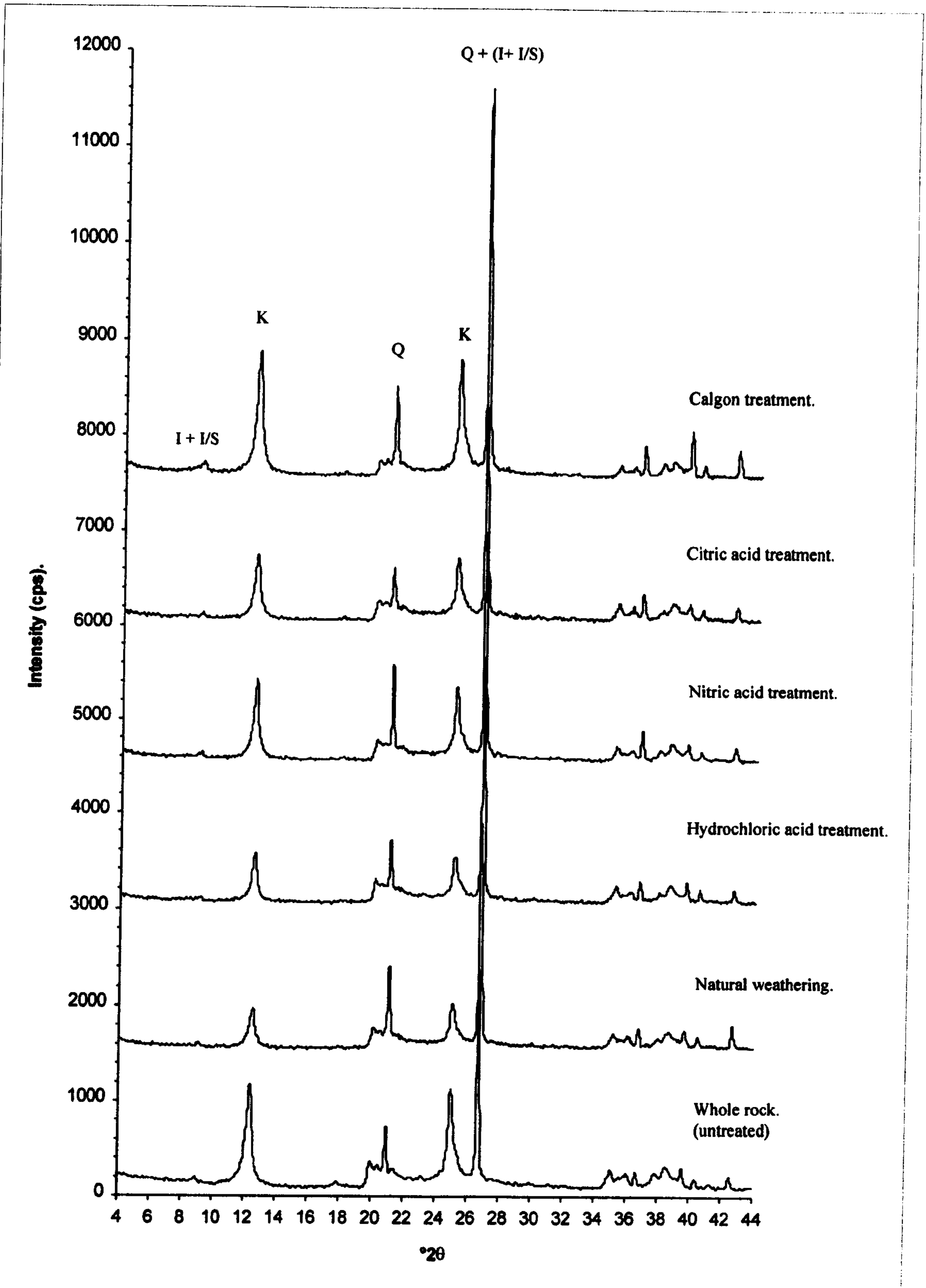
Ch = Chlorite : I/S + I = Illite with mixed layer illite-smaectite : K = Kaolinite : Q = Quartz : S = Siderite. PF = Plagioclase feldspar : C = Calcite.

Figure 8.12. XRD traces of sample C83 upon completion of the 12 month monitored weathering experiment.



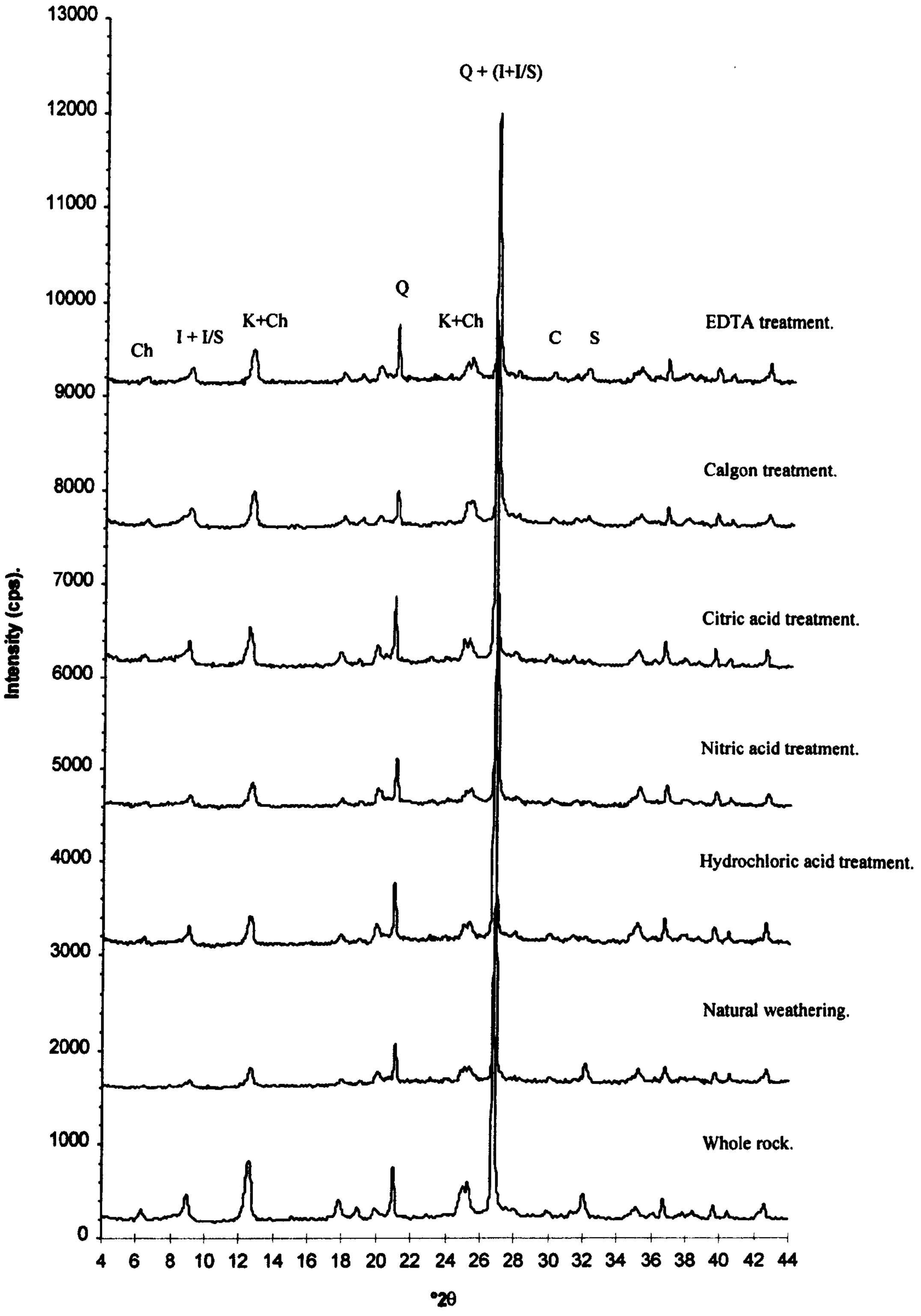
Ch = Chlorite : I/S + I = Illite with mixed layer illite-smaectite : K = Kaolinite : Q = Quartz : S = Siderite. Py = Pyrite.

Figure 8.13. XRD traces of sample C92 upon completion of the 12 month monitored weathering experiment.



I/S + I = Illite with mixed layer illite-smaectite : K = Kaolinite : Q = Quartz.

Figure 8.14. XRD traces of sample C133 upon completion of the 12 month monitored weathering experiment.



Ch = Chlorite : I/S + I = Illite with mixed layer illite-smaectite : K = Kaolinite : Q = Quartz : S = Siderite. C = Calcite.

Figure 8.15. XRD traces of sample C141 upon completion of the 12 month monitored weathering experiment.

mineral phase. The clay mineral peaks appear weaker especially for chlorite, which has been removed by the acid treatments and natural weathering, these conditions have also reduced the intensities of the illite and illite-smectite peaks.

In sample C21, Figure 8.10 the most prominent changes appear to be the removal of siderite by all of the acid treatments and also the reduction or removal of the chlorite and illite, and illite-smectite peaks by the same acid treatments.

In sample C31, Figure 8.11 there appears to be negligable changes to the carbonate peaks, here the most prominant changes appear to be due to natural weathering and $HNO_3$ treatment. The intensity of the illite and illite-smectite peak are also reduced due to the $HNO_3$ treatment.

In sample C83, Figure 8.12 there appears only to be minimal changes in the carbonate peaks, the most prominent being a reduction in peak intensities caused by HCl and $HNO_3$ treatment. The reagent treatments appear to have mainly affected chlorite which has been eliminated and illite and illite-smectite for which the peak intensities have been drastically reduced. In the naturally weathered sample the intensity of the plagioclase feldspar peak appears stronger, whereas for the acid treatment the peaks appear greatly reduced.

The trace for sample C92, Figure 8.13 shows the most effective reagent to be HCl resulting in the most evident changes to the peak intensities. Siderite does not appear to have been greatly affected by the $HNO_3$ treatment, although it has drastically reduced the clay mineral peak intensities. Citric acid treatment appears to have been the most effective in reducing the siderite content, whilst pyrite appears to have been affected mostly by the $HNO_3$ and HCl treatments.

There appears to be no major changes evident in the traces presented for sample C133, Figure 8.14 except for minor height ratio reversals for kaolinite and quartz in the naturally weathered, HCl and $HNO_3$ treated samples, in these cases these reagents may have caused minor dissolution of kaolinite.

In sample C141, Figure 8.15 there are no major differences evident between the traces for the different treatments, except for the elimination of the carbonate species when treated with HCl, $HNO_3$ and citric acid.

In the analysis of the mineralogical data it is evident that the main mineral species to have been affected by natural weathering and reagent treatment tend to be the carbonate and sulphide species when present. In many cases reduction of the chlorite and illitic clay species has occurred due to treatment with acidic reagents which are effective reagents in dissolving Fe rich clay species (Jackson,1969; Brown and Brindley,1980 and Moore and Reynolds,1989).

### 8.4.3. Geochemical analysis of the slaked material.

A fraction of the samples retained after particle size analysis for each of the weathering tests was subjected to geochemical analysis by X-ray fluorescence to qualitatively evaluate the effects of the reagents used on the major oxides. The samples were prepared and analysed according to the procedures outlined in Chapter 5. The raw data from the XRF analysis are presented in Appendix C3, and the data corrected for loss on ignition appear in Table 8.3. The corrected XRF data are also presented graphically in Figures 8.16 to 8.22 which more clearly shows the oxide phase changes which have occurred during the course of the weathering experiment.

In sample C21 (Figure 8.17) there appears to have been negligable changes in the oxide contents for the different weathering tests, with only slight reductions in the $Fe_2O_3$ content being evident in the samples subjected to treatment with acid reagents. Samples C83 (Figure 8.19) and sample C133 (Figure 8.2) show moderate reductions in $Al_2O_3$ and $SiO_2$ contents for the samples subjected to acid and calgon treatments. Samples C1B1 (Figure 8.16) and sample C141 (Figure 8.22) show a moderate reduction in the $Fe_2O_3$ content for acid treated samples. In sample C92 (Figure 8.20) there appears to be actual increases in the $SiO_2$ and $Fe_2O_3$ contents of the weathered samples, there is also a drastic reduction in the percentage of loss on ignition suggesting that the pretreatments have probably affected the carbonate, sulphide and possibly organic constituents therefore resulting in an apparent increase in the major oxide ratios during analysis.

| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | TOTAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C1B1 | 40.26 | 0.54 | 19.12 | 12.06 | 0.57 | 1.56 | 0.33 | 0.35 | 3.26 | 0.13 | 0.01 | 78.19 |
| C1B1-N | 37.13 | 0.52 | 17.87 | 14.09 | 0.63 | 1.7 | 0.42 | 0.38 | 3.07 | 0.14 | 0.02 | 75.97 |
| C1B1-H | 39.18 | 0.54 | 18.73 | 12.37 | 0.51 | 1.59 | 0.28 | 0.32 | 3.21 | 0.16 | 0.02 | 76.91 |
| C1B1-N | 40.72 | 0.54 | 19.97 | 6.96 | 0.24 | 1.32 | 0.15 | 0.35 | 3.32 | 0.11 | 0.09 | 73.77 |
| C1B1-Ci | 40.15 | 0.55 | 19.31 | 9 | 0.32 | 1.52 | 0.25 | 0.39 | 3.22 | 0.11 | 0.02 | 74.84 |
| C1B1-C | 40.54 | 0.56 | 19.7 | 7.15 | 0.26 | 1.35 | 0.19 | 0.47 | 3.37 | 0.13 | 0.01 | 73.73 |
| C1B1-E | 42.35 | 0.57 | 20.83 | 4.15 | 0.1 | 1.24 | 0.09 | 0.46 | 3.5 | 0.08 | 0.01 | 73.38 |
| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | TOTAL |
| C21 | 54.39 | 1 | 19.94 | 4.16 | 0.04 | 1.11 | 0.27 | 0.2 | 2.91 | 0.09 | 0.09 | 84.2 |
| C21-Nat. | 53.39 | 0.99 | 18.89 | 5.16 | 0.08 | 1.24 | 0.27 | 0.16 | 2.75 | 0.11 | 0.03 | 83.07 |
| C21-H | 55.85 | 1.05 | 19.67 | 3.23 | 0.02 | 0.99 | 0.02 | 0.22 | 2.85 | 0.08 | 0.02 | 84 |
| C21-N | 54.55 | 1.03 | 20.38 | 3.1 | 0.03 | 0.98 | 0.02 | 0.2 | 2.86 | 0.06 | 0.02 | 83.23 |
| C21-Ci | 55.04 | 1.04 | 20.23 | 2.92 | 0.02 | 0.91 | 0.03 | 0.34 | 2.87 | 0.05 | 0.02 | 83.47 |
| C21-Ca | 54.64 | 1.03 | 19.68 | 4.25 | 0.06 | 1.16 | 0.17 | 0.44 | 2.86 | 0.2 | 0.1 | 84.59 |
| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | TOTAL |
| C31 | 57.5 | 0.79 | 12.2 | 13.23 | 0.31 | 2.08 | 0.43 | 0.2 | 1.88 | 0.12 | 0.03 | 88.77 |
| C31-Nat. | 62.08 | 1.16 | 19.91 | 4.28 | 0.13 | 0.8 | 0.21 | 0.37 | 3.45 | 0.12 | 0.02 | 92.53 |
| C31-H | 64.35 | 1.18 | 20.05 | 3.75 | 0.1 | 0.72 | 0.07 | 0.31 | 3.4 | 0.1 | 0.02 | 94.05 |
| C31-N | 63.56 | 1.17 | 20.44 | 3.39 | 0.03 | 0.7 | 0.05 | 0.33 | 3.47 | 0.11 | 0.02 | 63.27 |
| C31-Ci | 63.96 | 1.16 | 19.96 | 3.21 | 0.1 | 0.75 | 0.11 | 0.39 | 3.4 | 0.1 | 0.02 | 93.16 |
| C31-Ca | 62.68 | 1.13 | 19.29 | 4.69 | 0.13 | 0.83 | 0.16 | 0.48 | 3.3 | 0.15 | 0.02 | 92.86 |
| C31-E | 61.94 | 1.18 | 20.02 | 4.21 | 0.11 | 0.83 | 0.13 | 0.42 | 3.47 | 0.12 | 0.02 | 92.45 |
| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | TOTAL |
| C83 | 64.65 | 1.03 | 17.01 | 5.4 | 0.1 | 1.51 | 0.31 | 1.18 | 2.83 | 0.12 | 0.06 | 94.2 |
| C83-Nat. | 67.31 | 0.83 | 12.19 | 5.26 | 0.08 | 1.15 | 0.28 | 1.11 | 1.88 | 0.12 | 0.03 | 90.24 |
| C83-H | 73.01 | 0.92 | 12.98 | 4.55 | 0.01 | 0.98 | 0.08 | 1.22 | 2.01 | 0.1 | 0.02 | 95.88 |
| C83-N | 71.6 | 0.89 | 12.74 | 5.34 | 0.1 | 1.06 | 0.19 | 1.27 | 1.98 | 0.12 | 0.02 | 95.31 |
| C83-Ci | 72.05 | 0.92 | 13.01 | 4.44 | 0.06 | 1.15 | 0.21 | 1.23 | 2.02 | 0.11 | 0.02 | 95.22 |
| C83-Ca | 70.63 | 0.9 | 12.77 | 5.52 | 0.1 | 1.18 | 0.29 | 1.22 | 1.97 | 0.2 | 0.04 | 94.82 |
| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | TOTAL |
| C92 | 15.73 | 0.25 | 6.8 | 9.77 | 0.35 | 0.59 | 0.81 | 0.14 | 1.03 | 0.43 | 0.04 | 35.94 |
| C92-Nat. | 18.46 | 0.3 | 6.77 | 31.72 | 0.81 | 0.97 | 1.17 | 0.06 | 1.08 | 0.4 | 0.1 | 61.84 |
| C92-H | 21.04 | 0.36 | 8.44 | 17.06 | 0.46 | 0.69 | 0.66 | 0.1 | 1.37 | 0.29 | 0.05 | 50.52 |
| C92-N | 17.52 | 0.23 | 6.06 | 38.61 | 1.09 | 1.37 | 1.49 | 0.07 | 0.88 | 0.53 | 0.03 | 67.88 |
| C92-Ci | 24.51 | 0.43 | 10.21 | 7.12 | 0.18 | 0.64 | 0.39 | 0.14 | 1.66 | 0.2 | 0.02 | 45.5 |
| C92-Ca | 21.16 | 0.36 | 8.4 | 15.21 | 0.36 | 0.71 | 0.77 | 0.2 | 1.33 | 0.38 | 0.01 | 48.89 |
| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | TOTAL |
| C133 | 54.59 | 1.28 | 28.89 | 1.55 | 0.01 | 0.33 | 0.06 | 0.18 | 1.14 | 0.04 | 0.02 | 88.09 |
| C133-Na | 62.27 | 1.05 | 25.35 | 1.6 | 0.01 | 0.39 | 0.04 | 0.09 | 1.1 | 0.02 | 0.04 | 91.96 |
| C133-H | 61.91 | 1.06 | 25.13 | 1.51 | 0.01 | 0.28 | 0.02 | 0.16 | 1.08 | 0.03 | 0.02 | 91.21 |
| C133-N | 62.05 | 1.08 | 25.03 | 1.5 | 0.01 | 0.33 | 0.02 | 0.09 | 1.1 | 0.03 | 0.02 | 91.26 |
| C133-Ci | 61.62 | 1.07 | 25.65 | 1.78 | 0.01 | 0.33 | 0.02 | 0.09 | 1.07 | 0.02 | 0.06 | 91.72 |
| C133-Ca | 62.32 | 1.05 | 25.13 | 1.44 | 0.01 | 0.31 | 0.02 | 0.21 | 1.05 | 0.06 | 0.02 | 91.62 |
| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | TOTAL |
| C141 | 55.45 | 0.96 | 19.29 | 9.22 | 0.24 | 1.83 | 0.54 | 0.23 | 3.24 | 0.23 | 0.04 | 91.27 |
| C141-Na | 55.83 | 0.95 | 19.57 | 8.97 | 0.21 | 1.88 | 0.51 | 0.21 | 3.25 | 0.22 | 0.08 | 91.68 |
| C141-H | 60.91 | 1.07 | 20.2 | 4.67 | 0.06 | 1.6 | 0.02 | 0.2 | 3.35 | 0.13 | 0.02 | 92.23 |
| C141-N | 61.84 | 1.07 | 20.93 | 3.96 | 0.02 | 1.58 | 0.02 | 0.1 | 3.54 | 0.11 | 0.02 | 93.19 |
| C141-Ci | 61.34 | 1.05 | 20.92 | 3.26 | 0.03 | 1.49 | 0.06 | 0.19 | 3.6 | 0.09 | 0.02 | 92.05 |
| C141-Ca | 58.14 | 1.01 | 20.2 | 5.36 | 0.1 | 1.82 | 0.33 | 0.53 | 3.35 | 0.55 | 0.02 | 91.41 |
| C141-E | 57.83 | 1.02 | 19.86 | 7.04 | 0.12 | 1.76 | 0.33 | 0.25 | 3.32 | 0.2 | 0.02 | 91.75 |

Table 8.3. Roof weathering experiment XRF major oxide data corrected for loss on ignition.

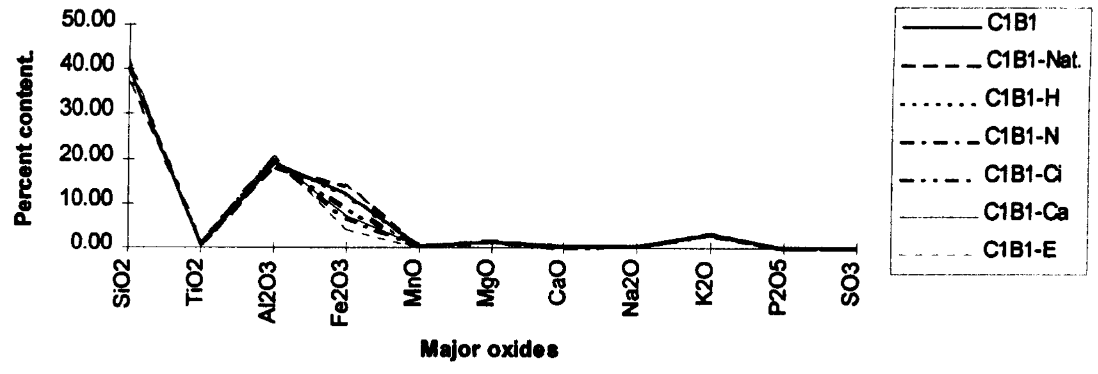


Figure 8.16. Sample C1B1 weathering experiment XRF data plot.

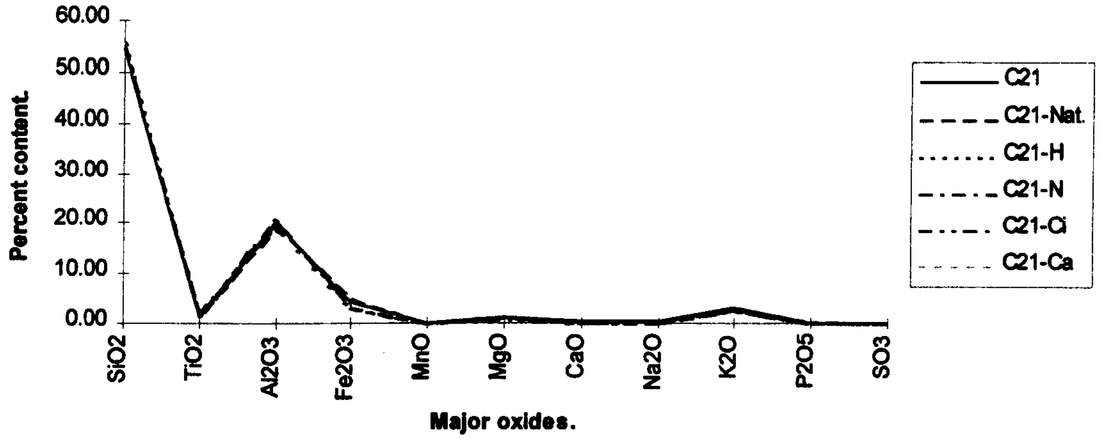


Figure 8.17. Sample C21 weathering experiment XRF data plot.

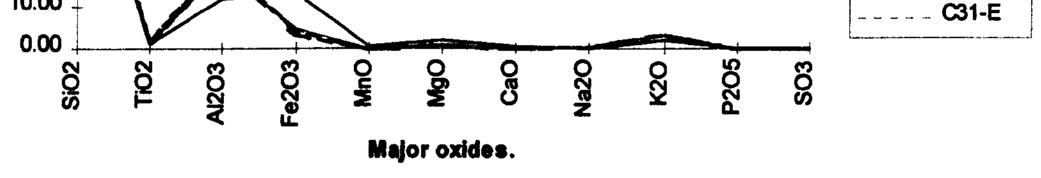


Figure 8.18. Sample C31 weathering experiment XRF data plot.

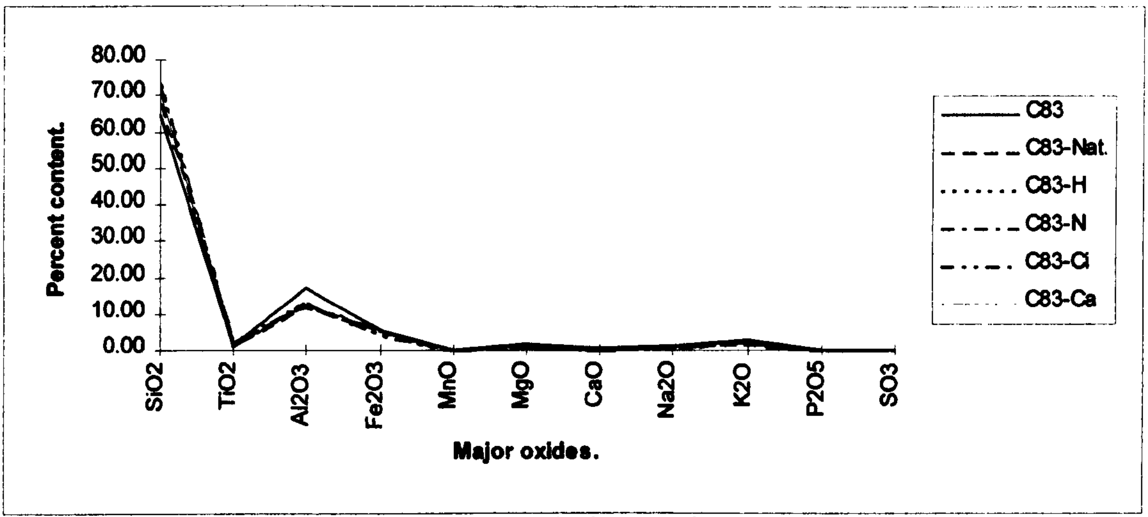


Figure 8.19. Sample C83 weathering experiment XRF data plot.

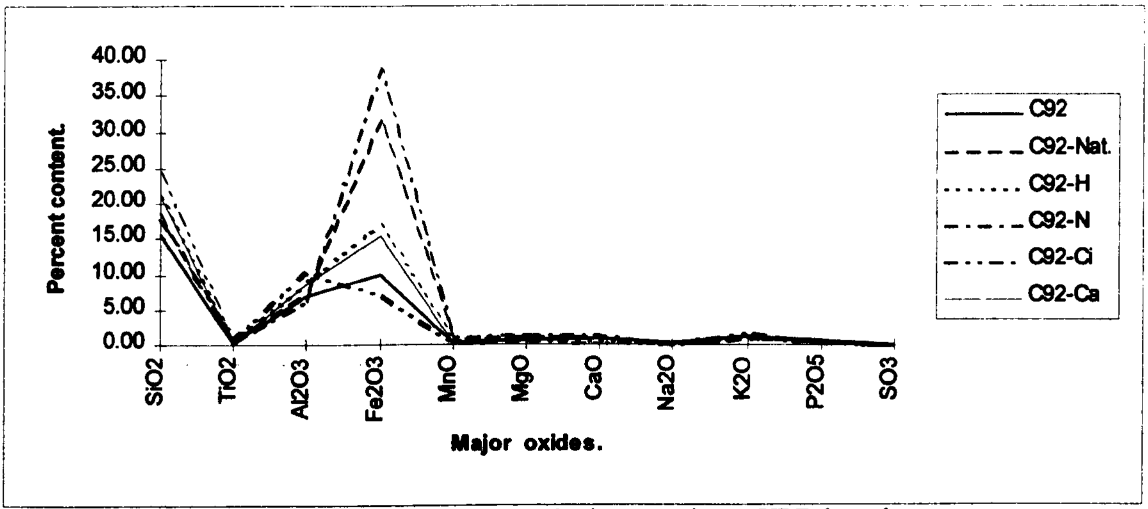


Figure 8.20. Sample C92 weathering experiment XRF data plot.

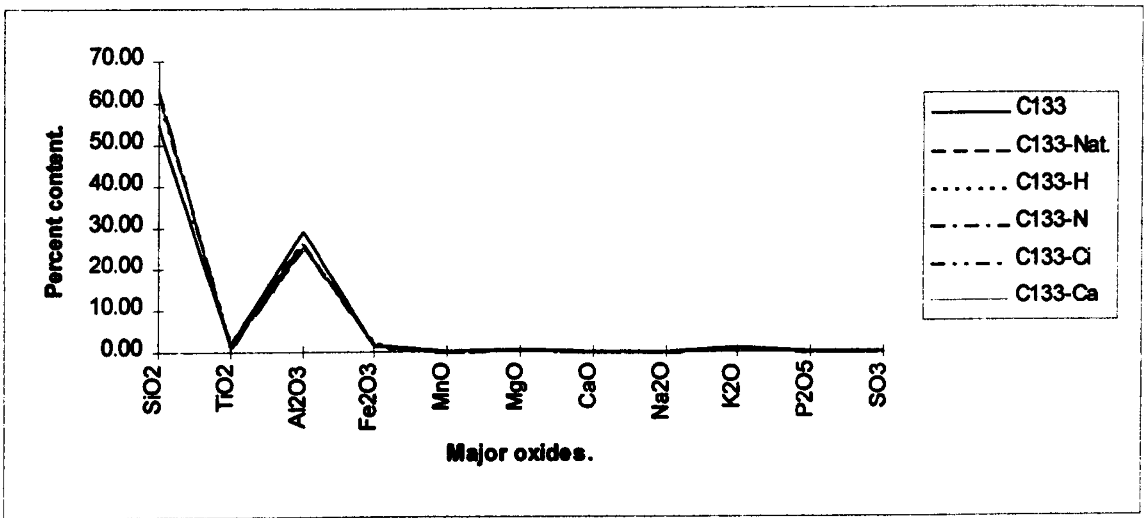


Figure 8.21. Sample C133 weathering experiment XRF data plot.

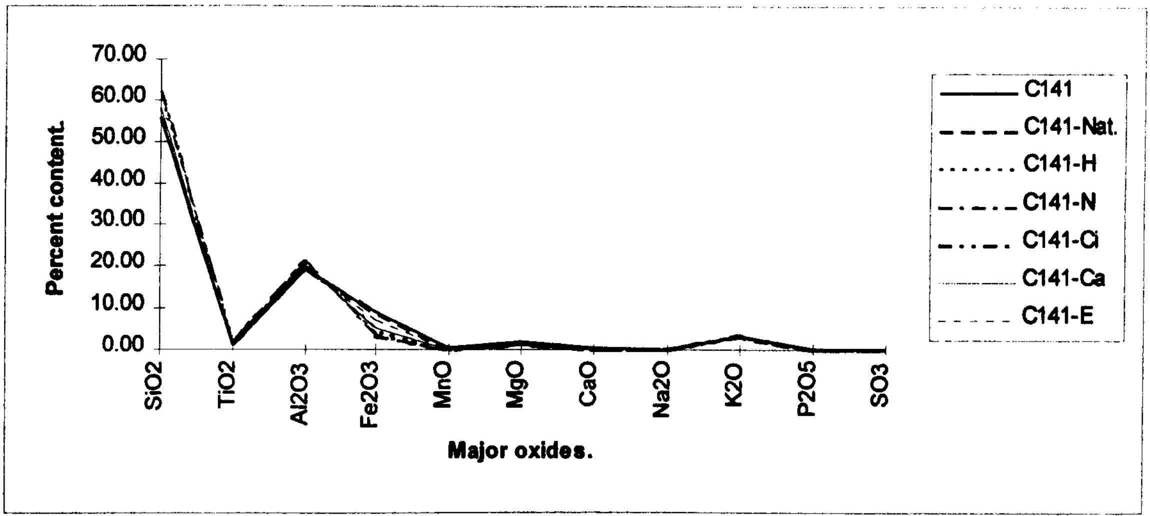


Figure 8.22. Sample C141 weathering experiment XRF data plot.

## 8.5. Comments on the weathering experiment results.

It can be seen from the analysis of the data from the roof weathering experiment that certain reagents used have proved to be moderately successful in enhancing the breakdown of certain samples during the 12 month test period. The use of the modified jar slake classification scheme has proved very successful in describing the sample states during the course of the experiment, and comparing this with laboratory analysed samples. The physical descriptions have shown that samples C1B1, C21, C31 and C141 have achieved the same level of breakdown during the course of natural weathering, as was seen in the laboratory jar slake test. Samples C31, C83, C92, C133 and C141 have achieved a greater state of breakdown by the use of the reagents. In particular acid treatments have removed carbonates in samples C31, C83 and C92 and calgon has acted on clay minerals in samples C133 and C141. It has been stated by many researchers (Badger et al., 1956; Grice, 1968; Seedsman, 1985; Sasaki et al., 1981 and Taylor, 1988) that the main mechanisms involved in the disintegration of mudrocks are due to the effects of water. These mechanisms are physical disintegration caused by air breakage resulting from capillary suction of water into voids and breakdown caused by the effects of water on expansive clay species. It was stated by Badger et al.,(1956); Sasaki et al.,(1981) and Hongxi, (1993) that the volume of voids in a mudrock control the rates and extent of rock breakdown as they allow water access into the sample. Once water accesses the sites of clay mineral species disintegration can occur due to cation exchange effects, where liquids having high dielectric constants such as water, cause cation exchange and clay mineral dispersion to proceed (Badger et al., 1956). It has also been shown that a positive correlation exists between the amount of carbonate cement and the durability of mudrocks (Lo et al., 1978 and Russell, 1982). Badger et al., (1956) also stated that organic matter and inorganic iron colloids act as binding agents. In the experiments it is seen that the removal of carbonate species by mineral acid treatments has induced breakdown of the samples, also in samples with no, or negligable quantities of cement, calgon causes dissagregation due to neutralization of clay particle charges resulting in dispersion.

Analysis of the ionic concentrations of the leachates shows that the acid treatments were most effective in the initial stages of the weathering experiment, where they generally reacted with the carbonate cement species present in the samples. Mineralogical and geochemical changes in the samples have been minor with mainly the carbonate species being affected and also dissolution of chlorite and illitic clay mineral species due to acid attack. The high Fe concentrations in the leachates is mainly derived from the siderite cement and iron colloids. It is evident from the X-ray diffraction traces that the acids effectively remove chlorite and to a lesser extent illitic phases. Evans and Adams (1975) state that chlorite and illitic phases rich in iron tend to have reduced stability in weathering, therefore their dissolution adds to the high iron concentrations of the leachates.

The primary effects of the reagents used has been to remove cement phases which result in a larger void distribution within the samples allowing greater water access into the sample and reaction sites which leads to physical disintegration of the samples. Table 8.4 presents physical and mineralogical data which is considered to have a control on sample stability, the samples are arranged with the least stable (7) to the most stable (1) samples from the weathering experiment. It can be seen that the cements specifically carbonates and organic carbon, have the most influence in controlling the extent of sample breakdown. The samples with the highest organic contents and carbonate contents appear to be the most stable with minimal slaking effects. The reagents may have proved more efficient had greater quantities been used or had they been at higher concentrations, this would have resulted in a more rapid removal of the carbonate cements and therefore allowing access to water resulting in breakdown of the samples.

| | $n_T$ | $n_e$ | $Id_3$ | $\%Cco_2$ | %Corg | Ic | %Ro |
|---|---|---|---|---|---|---|---|
| (7) C141 | 9.7 | 4.18 | 63.3 | 3.5 | 2.1 | 0.72 | 0.56 |
| (6) C133 | 4.2 | 2.44 | 10.4 | 0 | 2.0 | 2.89 | 0.54 |
| (5) C21 | 7.3 | 2.07 | 46.8 | 3.3 | 7.5 | 1.17 | 0.54 |
| (4) C83 | 9.8 | 7.35 | 81.7 | 5.0 | 2.2 | 0.56 | 0.71 |
| (3) C31 | 5.3 | 1.54 | 97.5 | 24.7 | 1.2 | 1.06 | 1.67 |
| (2)C1B1 | 4.8 | 0.78 | 97.5 | 11.4 | 15.0 | 1.11 | 1.73 |
| (1) C92 | 3.8 | 2.17 | 98.0 | 17.6 | 41.5 | 0.93 | 0.61 |

Table 8.4 . Selected physical and mineralogical properties of the roof weathering test samples.

In the mudrock samples tested weathering patterns are evident. The mudrocks can be catagorized into 4 groups: organic-mudrocks, calcareous-mudrocks, siltstones and clayey-mudrocks, in these examples the mineralogies and lithotypes control the type of weathering pattern which develops:-

- Clayey-mudrocks, (samples C133 and C141) - Substantial sample breakdown is evident in these samples within the first 2 months of exposure to weathering. The cause is considered primarily to be mechanical breakdown as a result of air breakage instigated along discontinuities by the addition of aqueous solutions and natural rain water. Selected reagents such as calgon and EDTA assist in promoting sample breakdown by affecting the clay interparticle bonding, which only results in only a slight enhancement in breakdown.
- Organic-mudrocks, (samples C1B1,C21 and C92) - The principal control on these samples is their organic content. This is evident with the rate and amount of breakdown between these three samples. Sample C21 which has the lowest organic content of the three samples ($C_{org}$=7.5%) has the largest amount of breakdown and at the fastest rate which is within 6 months. Sample C1B1 has the second highest organic content ($C_{org}$=15.0%) which experiences a lesser amount of breakdown than

sample C21 and at a progressive rate over the 12 months. Sample C92 which has the highest organic content ($C_{org}$=41.5%) the amount of breakdown is the least of all the samples and took place at a slow progressive rate over the 12 month test period. Cement removal for these samples by reagent additions is evident in the high concentrations of Ca and Fe detected in the leachates which is from pyrite, calcite and siderite cements. The breakdown mechanisms are both chemical and physico-chemical. The chemical process removes the cements allowing water access into discontinuities, voids and sites of the expandable clay mineral species. The physico-chemical mechanism occurs when the pressure exerted by expanding clay minerals and air compression in voids and discontinuities over time, due to successive wetting and drying cycles exceeds the tensile strength of the organic cement which results in slaking.

- Siltstone, (sample C83) - There is a moderately rapid rate of breakdown over the first 6 to 8 month test period, mainly evident as fractures occurring along lamination planes. The principal control being mechanical as a result of air breakage within pores and along micro-discontinuities.
- Calcareous-mudrock, (sample C31) - There is a slow progressive rate of breakdown over the initial 6 months of testing, after this period of time the breakdown is more severe. The principal control on breakdown is chemical with the progressive removal of calcareous cement which allows water access into voids and discontinuities and to the sites of expansive clay mineral species, which causes the secondary breakdown control which is physico-chemical caused by clay mineral expansion and air breakage weakening the remaining cementation causing slaking.

It can be seen that with a knowledge of the mineralogical makeup of a mudrock sample, the type of potential breakdown can assessed and additional chemical treatments may be applied to assist this process.

Plate 8.1. Photograph of the roof weathering experiment test frame.

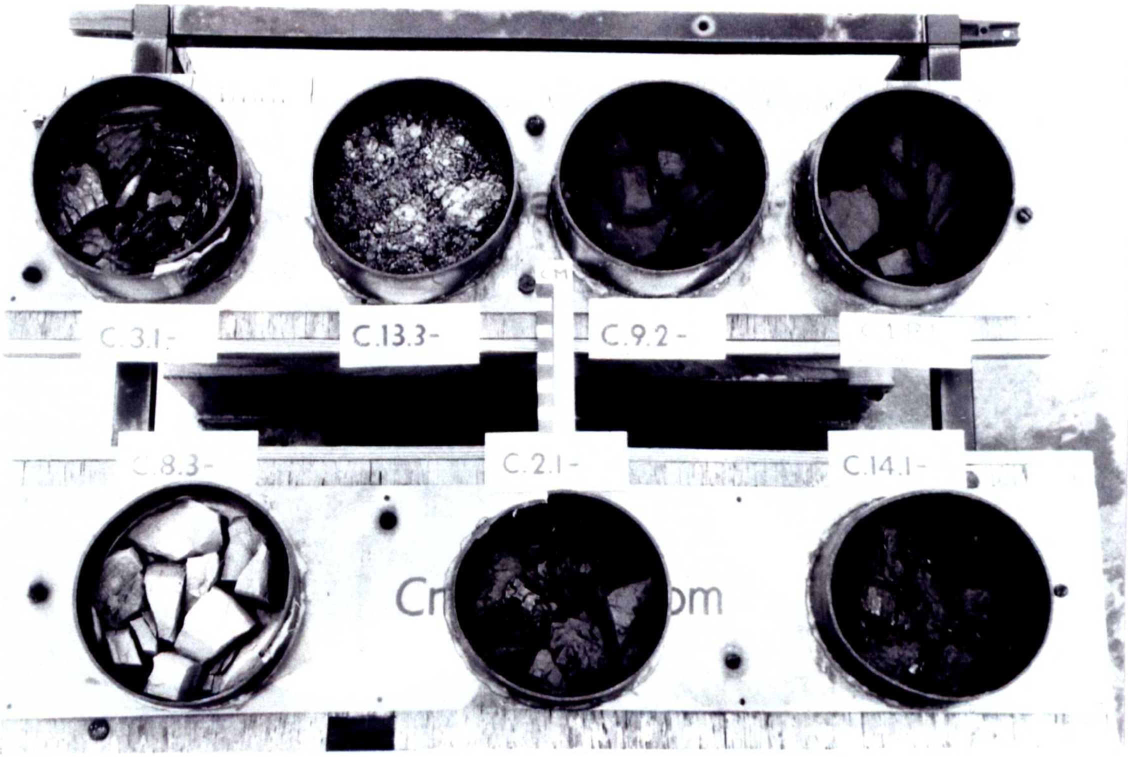


Plate 8.2. Photograph of the state of the 7 test samples after being subjected to 12 months of natural weathering.

Plate 8.3. Sample C1B1 unweathered.

Plate 8.4. Sample C1B1-E after 6 months weathering.

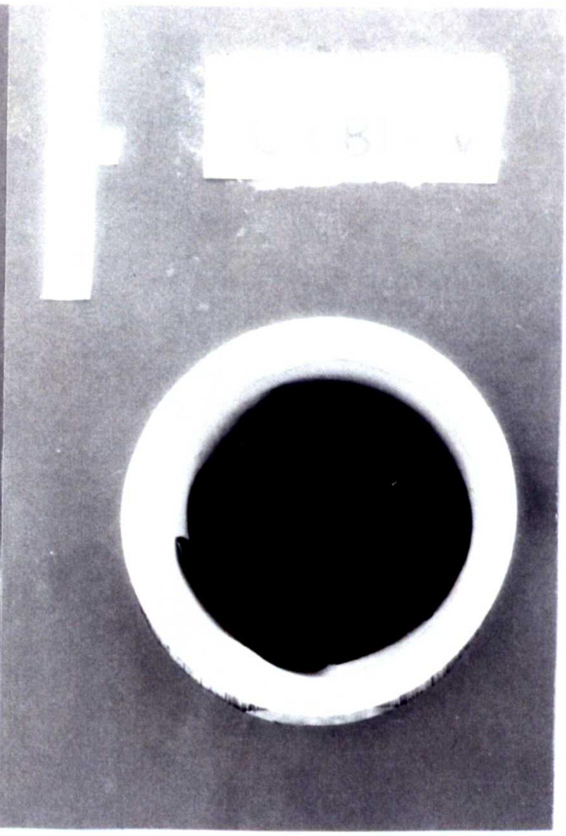


Plate 8.5. Sample C1B1-E after 12 months weathering.

Plate 8.6. Sample C21 unweathered.

Plate 8.7. Sample C21-H after 6 months weathering.

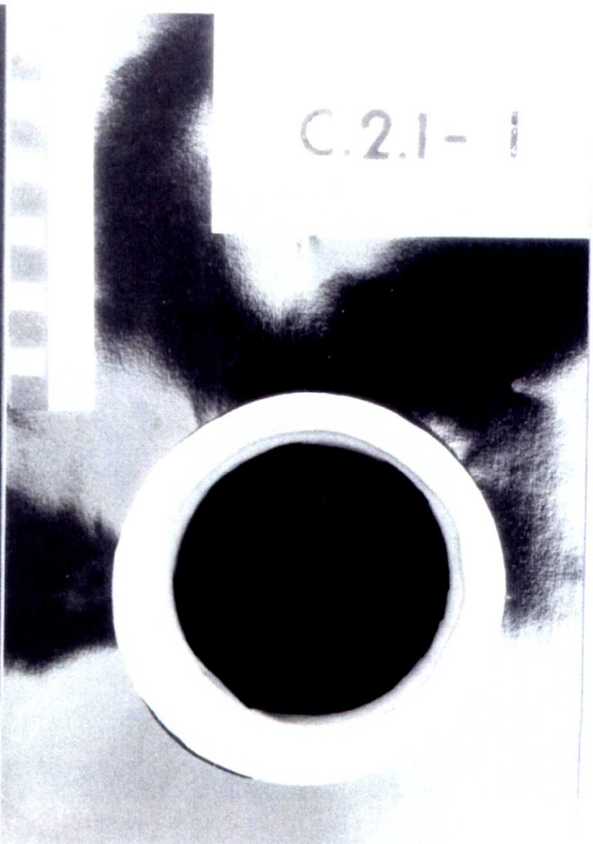


Plate 8.8. Sample C21-H after 12 months weathering.

Plate 8.9. Sample C21-N after 6 months weathering.

Plate 8.10. Sample C21-N after 12 months weathering.

Plate 8.11. Sample C21-C after 6 months weathering.

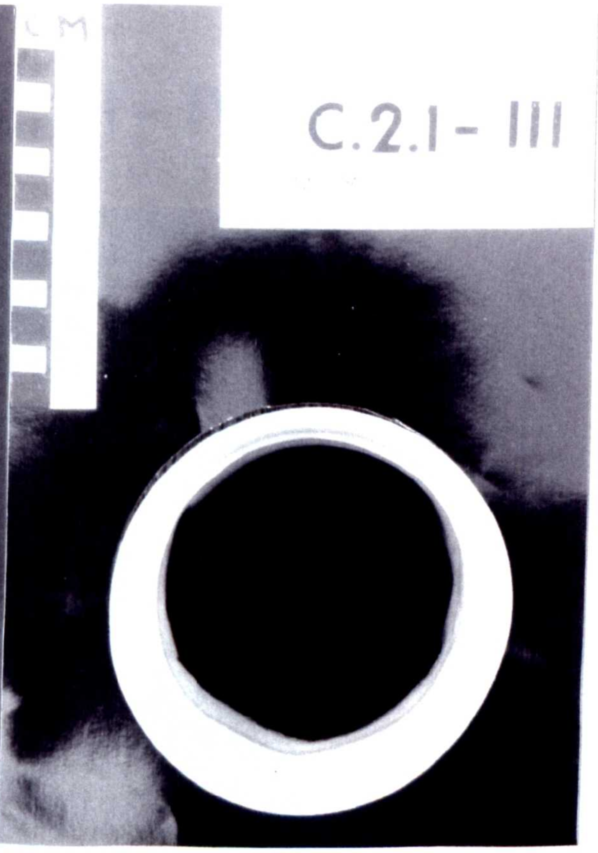


Plate 8.12. Sample C21-C after 12 months weathering.

Plate 8.13. Sample C21-Ca after 6 months weathering.

Plate 8.14. Sample C21-Ca after 12 months weathering.

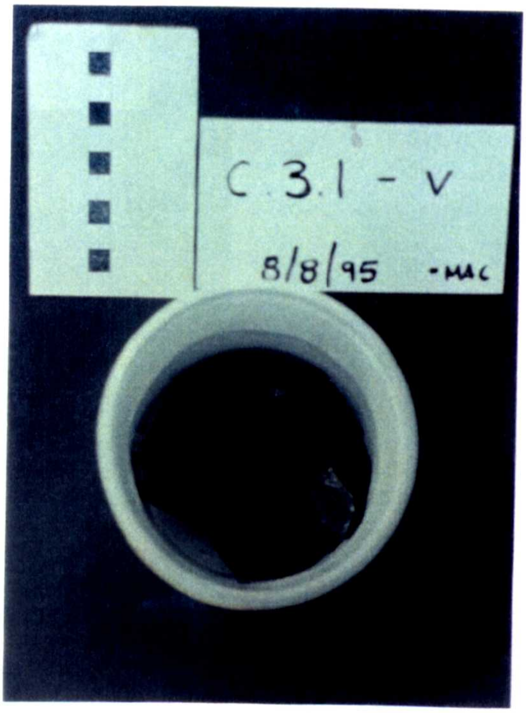


Plate 8.15. Sample C31 unweathered.

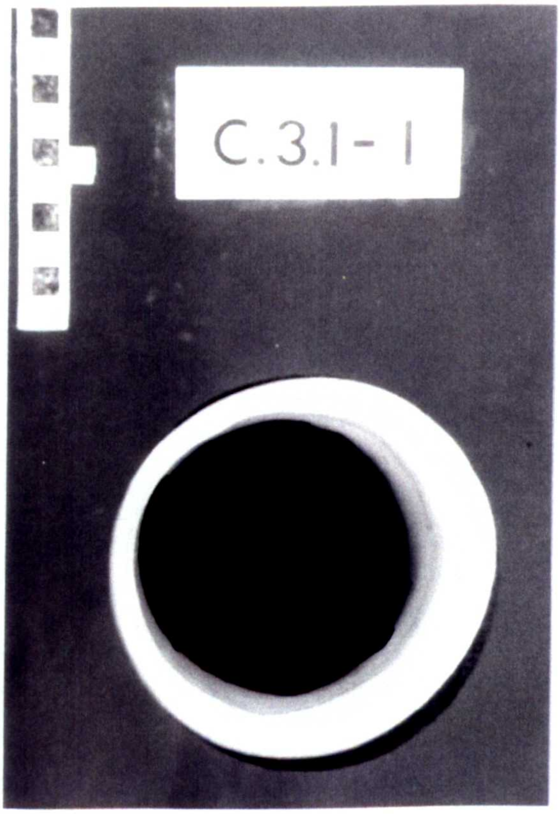


Plate 8.16. Sample C31-H after 6 months weathering.

Plate 8.17. Sample C31-H after 12 months weathering.

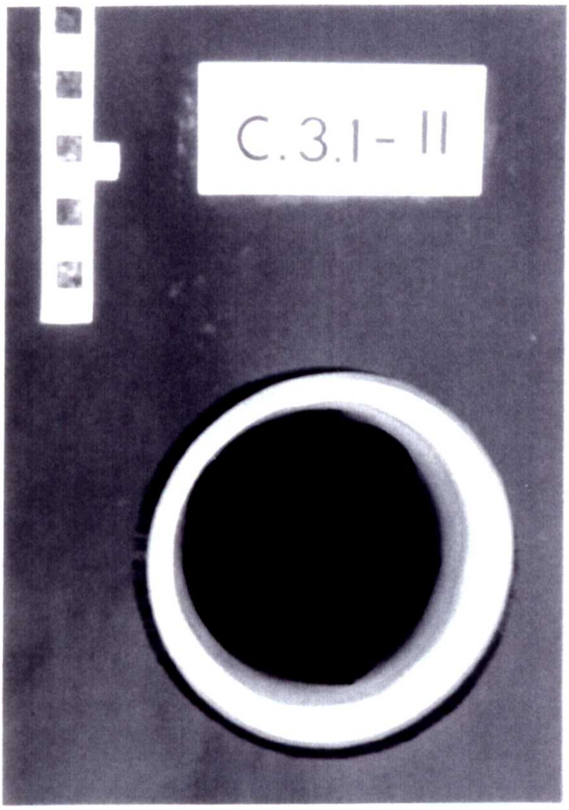


Plate 8.18. Sample C31-N after 6 months weathering.

Plate 8.19. Sample C31-N after 12 months weathering.

Plate 8.20. Sample C31-C after 6 months weathering.

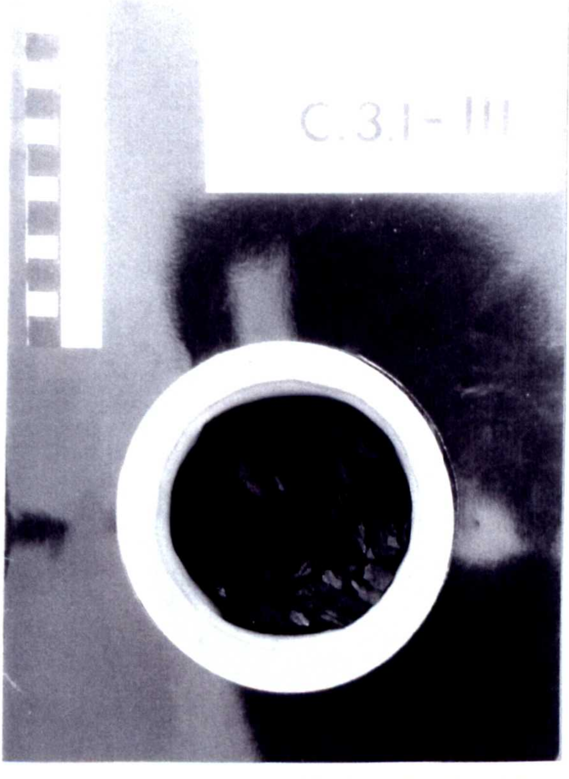


Plate 8.21. Sample C31-C after 12 months weathering.

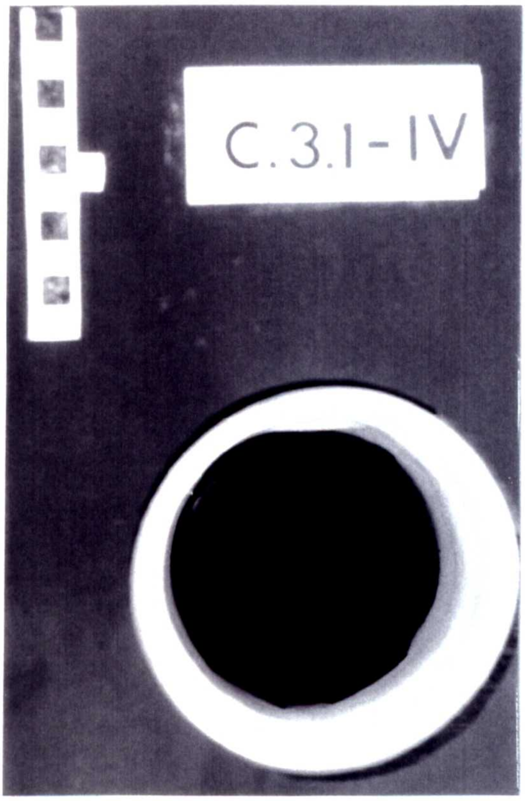


Plate 8.22. Sample C31-Ca after 6 months weathering.

Plate 8.23. Sample C31-Ca after 12 months weathering.

Plate 8.24. Sample C31-E after 6 months weathering.

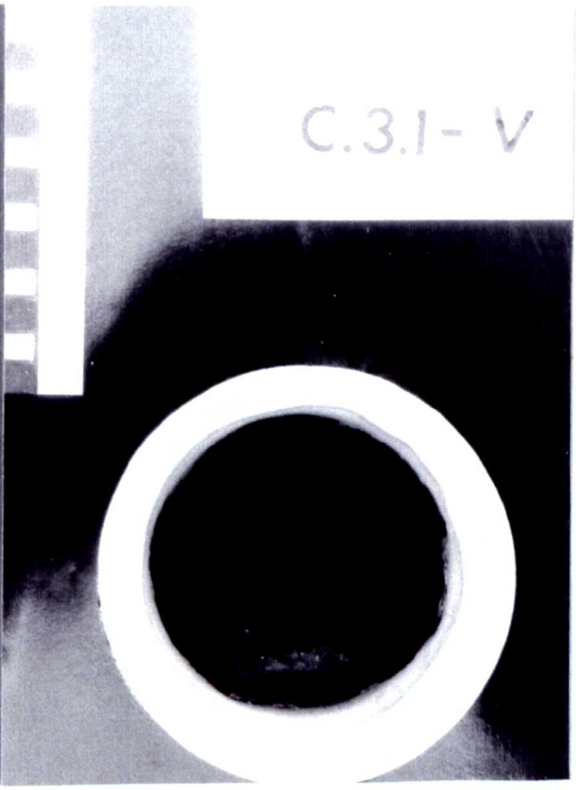


Plate 8.25. Sample C31-E after 12 months weathering.

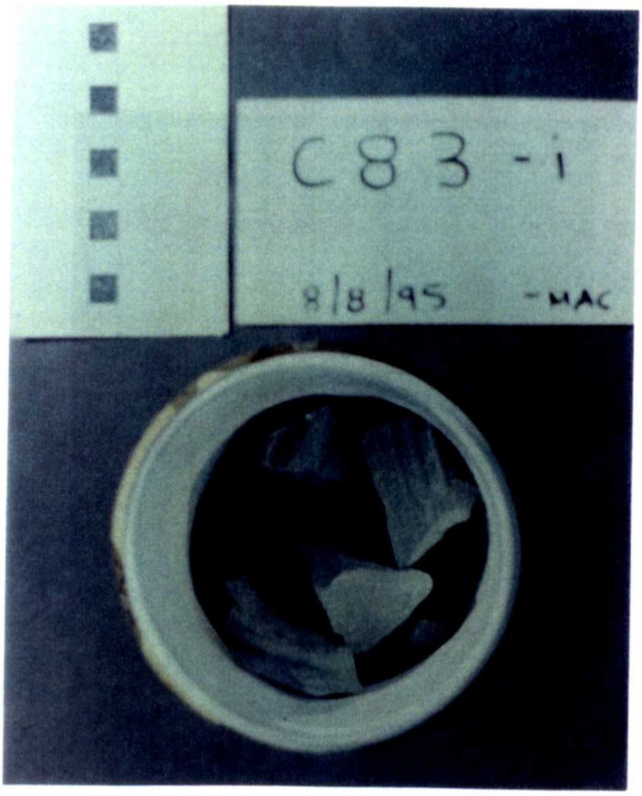


Plate 8.26. Sample C83 unweathered.

Plate 8.27. Sample C83-H after 6 months weathering.

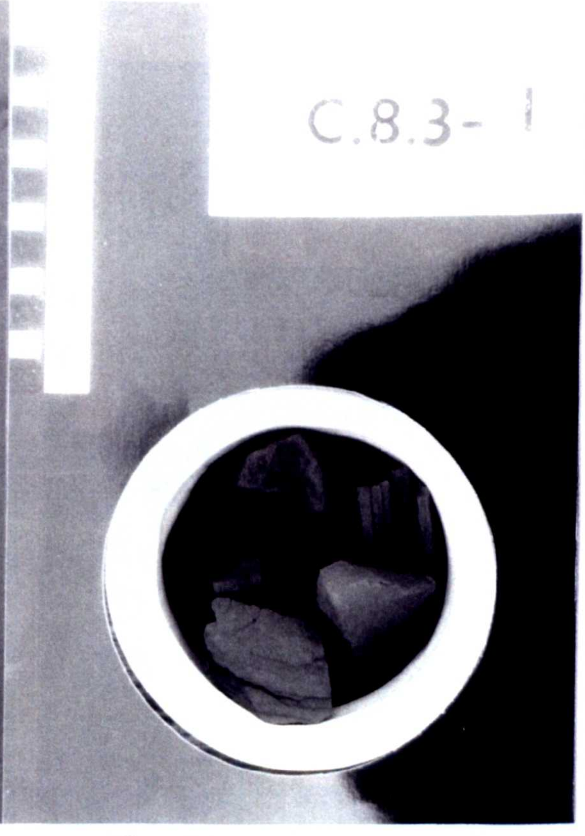


Plate 8.28. Sample C83-H after 12 months weathering.

Plate 8.29. Sample C133 unweathered.

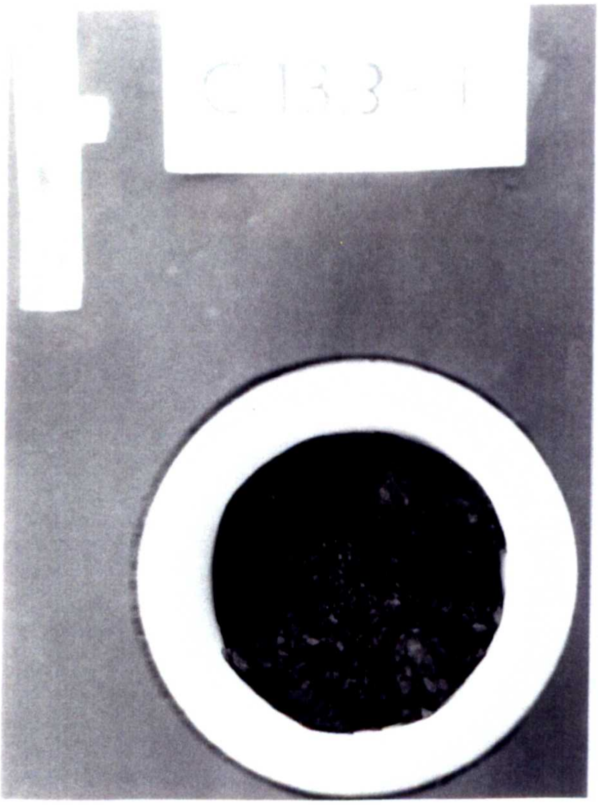


Plate 8.30. Sample C133-H after 6 months weathering.

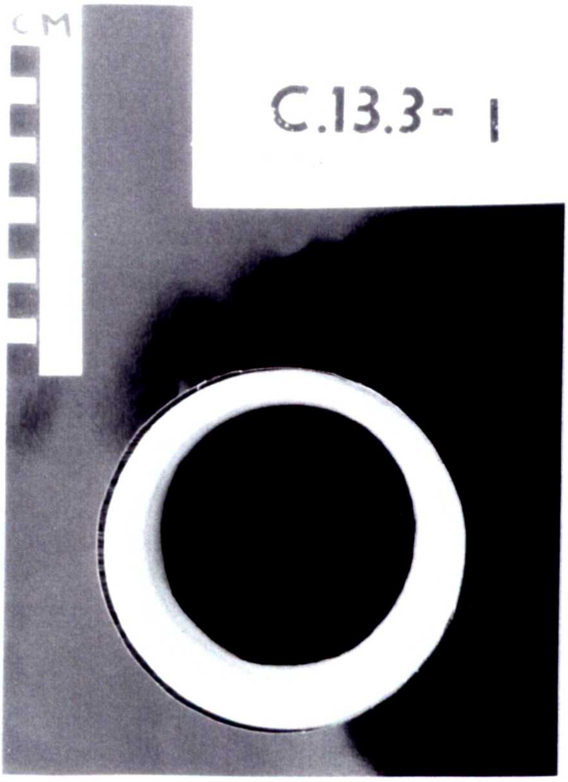


Plate 8.31. Sample C133-H after 12 months weathering.

Plate 8.32. Sample C133-N after 6 months weathering.

Plate 8.33. Sample C133-N after 12 months weathering.

Plate 8.34. Sample C133-C after 6 months weathering.

Plate 8.35. Sample C133-C after 12 months weathering.

Plate 8.36. Sample C133-Ca after 6 months weathering.

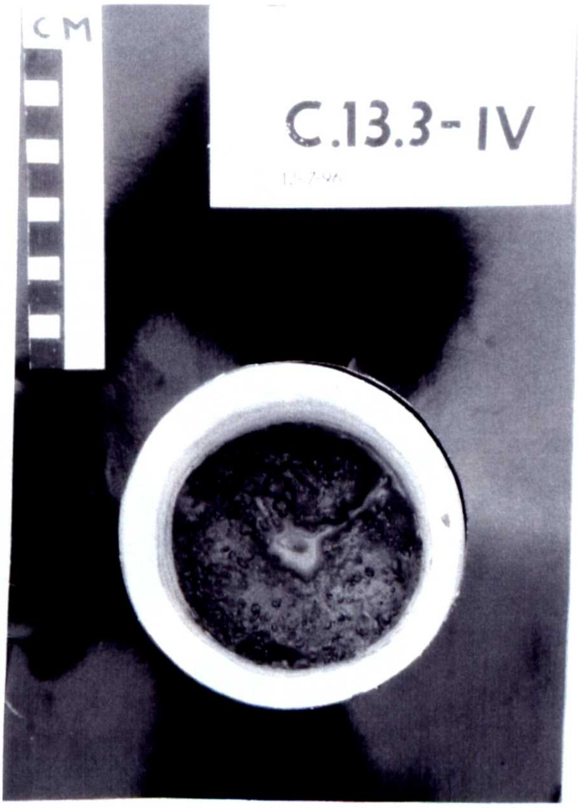


Plate 8.37. Sample C133-Ca after 12 months weathering.

Plate 8.38. Sample C141 unweathered.

Plate 8.39. Sample C141-H after 6 months weathering.

Plate 8.40. Sample C141-H after 12 months weathering.

Plate 8.41. Sample C141-N after 6 months weathering.

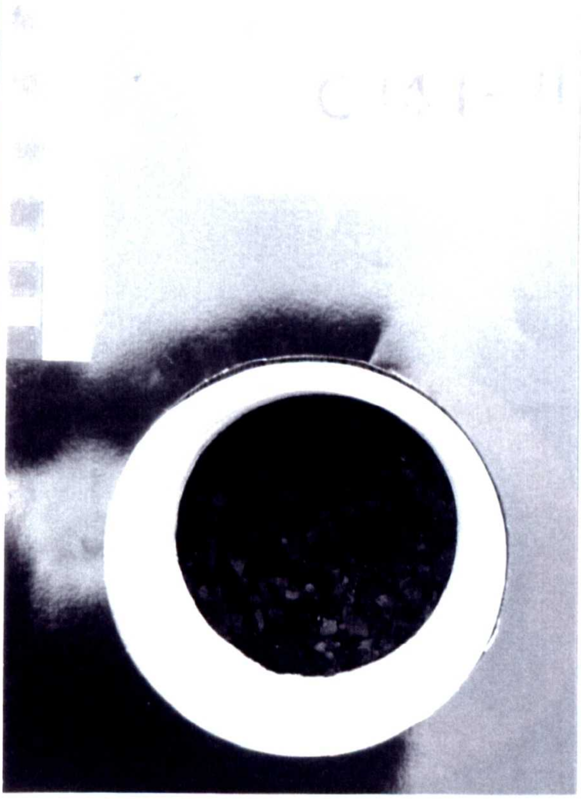


Plate 8.42. Sample C141-N after 12 months weathering.

Plate 8.43. Sample C141-C after 6 months weathering.

Plate 8.44. Sample C141-C after 12 months weathering.

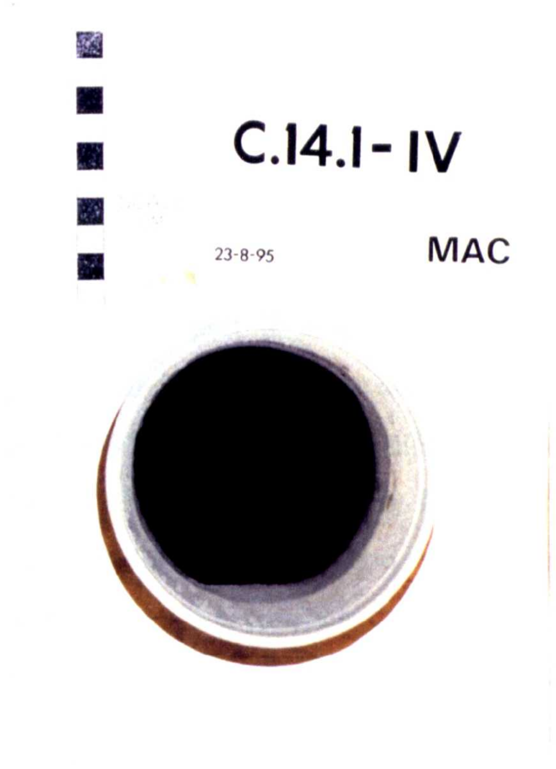


Plate 8.45. Sample C141-Ca after 6

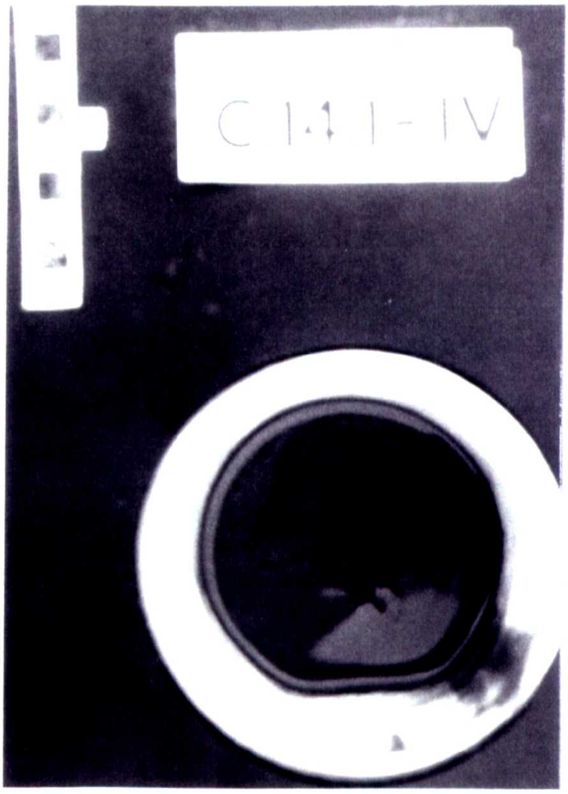


Plate 8.46. Sample C141-Ca after 12

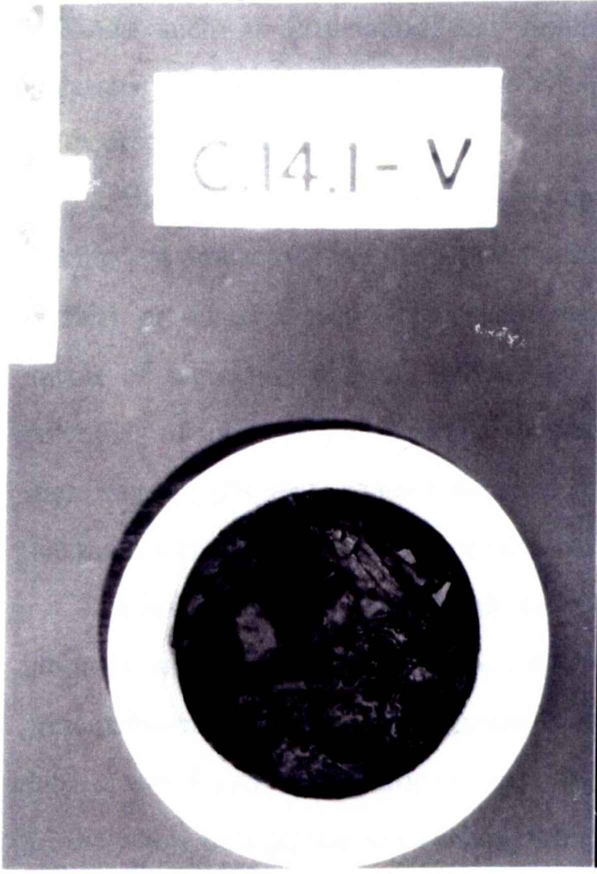


Plate 8.47. Sample C141-E after 6 months weathering.

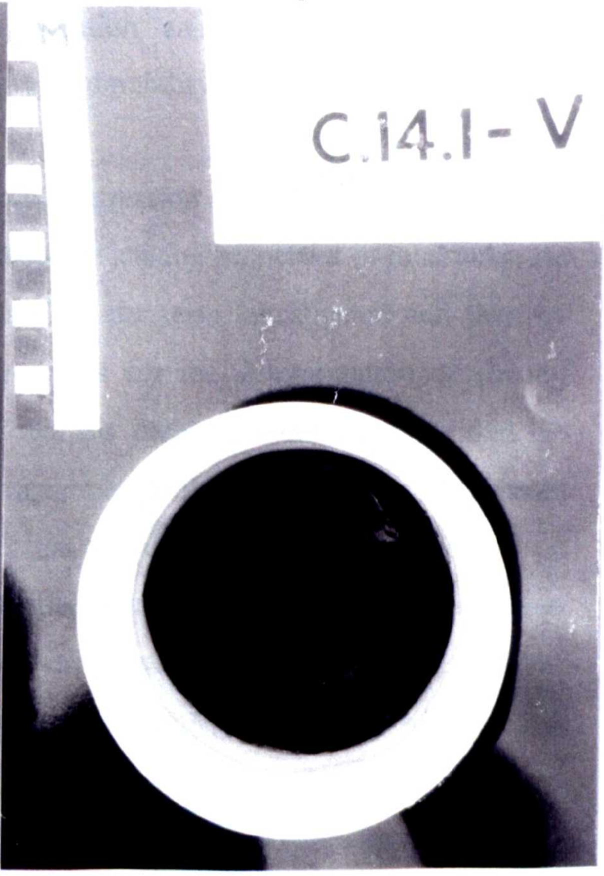


Plate 8.48. Sample C141-E after 12 months weathering.

# Chapter 9.

# Evaluation and interpretation of the test data.

## 9.1. Introduction.

In the past 40 years, numerous studies have been carried out to investigate the physical and mineralogical controls governing mudrock durability. Research by Badger et al. (1956), Gamble, (1971), Russell, (1982), Taylor and Spears, (1981), Cripps and Taylor, (1981), Hudec, (1982), Taylor and Smith, (1986), Taylor, (1988), Dick, (1992), Dick and Shakoor, (1992) and others has clearly shown that the underlying controls are mineralogy, (% expandable clay content), texture (porosity, density and microfractures) and geological (lithology, cementation and recrystallization due to diagenetic effects. In an attempt to quantify the principal controls on mudrock durability workers such as Hudec, (1982), Dick, (1992) and Sarman et al., (1994) have by the use of statistical methods such as correlation and multi-regression analysis, produced predictive equations for the determination of swelling and durability of mudrocks from simple index property relationships.

Hudec, (1982) used multivariate stepwise regression analysis to determine which slaking test procedures had the greatest influence on slaking properties of mudrocks. He initially produced a best 7 correlation matrix for the tests investigated and then by means of regression analysis derived an equation for the determination of slaking potentials of mudrocks. The results showed that the Franklin slake durability and the static wet-dry slaking tests gave the most comparable results. Hudec, (1982) concluded that mudrocks have inherent sets of properties that respond differently to each test.

Dick, (1992) in an attempt to establish quantitative relationships between lithology and durability of mudrocks, applied univariate analysis, correlation analysis, principal component, bivariate regression and multivariate regression analysis to his test data. It was found that significant correlation between test results between parameters for the whole data set was not evident, therefore he subdivided his data into lithological units for further analysis. Dick, (1992) concluded his investigation with a series of predictive slake durability equations for each mudrock lithotype based on the strongest index parameter correlations obtained from correlation analysis, the equations are as follows:

Claystone - $Id_2 = 57.3 - 32.3 \times \log C$. ($C$ = % expandable clay minerals).

Mudstone - $Id_2 = 37.0 - 127.0 \times \log I_{MF}$. ($I_{MF}$ = microfracture index).

Shale - $Id_2 = 126.0 - 7.52 \times$ Water absorption %.

Siltstone - $Id_2 = 122.1 - 7.5 \times$ Water absorption %.

The general applicability of these equations has been assessed using the data from this study. It was found that these equations were not capable of predicting the $Id_2$ values for the samples. The range of variation between the calculated slake durability results and measured slake durability results are presented in Table 9.1.

| **Mudrock type** | **Variation of predicted values to measured values** |
|---|---|
| Claystone | 16.7% to 70.4% variation |
| Mudstone | For 78% of the samples the calculated values >100%. Remainder of values, 4.4% to 4.8% variation. |
| Siltstone | For 33% of the samples the calculated values >100%. Remainder of values, 3.0% to 22.7% variation. |
| Lam/Fiss Mudstone | For 46% of the samples the calculated values >100%. Remainder of values, 0.2% to 46% variation |

Table 9.1. Range of percentage variation between calculated slake durability values using the equations of Dick (1992) and measured values.

Sarman et al. (1994) used bivariate and regression analysis to determine the volumetric swelling potentials of mudrocks. He found that texture was a principal control on swelling along with the clay mineralogy but a single property could not reliably predict the extent of volumetric swelling for samples. The equations which are as follows were based on measured values of water absorption, slake durability, void ratio, compressive strength and Atterberg limits:

All mudrocks - $\Delta V = 8.1 + 0.7(\%\ \text{absorption}) + 1.5(\%\ \text{adsorption}) - 0.1(Id_2) - 30.2(e) + 0.04(\sigma_C)$.

Claystone - $\Delta V = 42.3 + 0.4(\%\ \text{absorption}) - 14.8 \log(Id_2) - 40.6(e) - 0.1(\sigma_C)$.

Mudstone - $\Delta V = 52.5 + 0.5(\%\ \text{absorption}) - 17.5 \log(Id_2) - 137.1(e) - 0.4(\sigma_C) + 1.9$.

Shale - $\Delta V = 4.6 + 0.3(\%\ \text{absorption}) - 0.2\ (Id_2) - 7.9(e) - 0.2(\sigma_C) + 0.4\ (LL)$.

Siltstone - $\Delta V = -8.8 + 1.2(\%\ \text{absorption}) - 4 \log(Id_2) - 33(e)$.

The volumetric swelling capacities were calculated for the samples studied and again it was found that the predicted values differed greatly from the measured values as shown in Table 9.2.

| Mudrock type | Variation of predicted values to measured values |
|---|---|
| Claystone | 208% to 3121.7% variation |
| Mudstone | For 66% of the samples the calculated values gave negative values. Remainder of values gave 290% to 860% variation. |
| Siltstone | For 50% of the samples the calculated values gave negative values. Remainder of values gave 168% to 572% variation. |

Table 9.2. Range of percentage variation between calculated volumetric swelling capacities using the equations of Sarman et al. (1994) and measured values.

It can be seen that the only application of predictive equations for engineering properties of mudrocks is within the data base of samples that the equations were derived from. Mudrock properties are controlled by many variables that cannot realistically be accounted for within useable predictive equations, factors such as organic content, carbonate content, diagenetic recrystallization can have controls on the physical properties of certain samples and yet be negligable for other samples. Due to these difficulties mudrocks should be evaluated qualitatively with the additional use of simple index tests to indicate how they may perform under engineering and environmental conditions.

It has been concluded by workers such as Chandler (1969), Gamble, (1971), Spears and Taylor (1972), Russell (1982), Steward and Cripps (1983), Shakoor and Brock (1987), Taylor (1988) and Dick and Shakoor (1992) that mudrock durabilities are controlled to a large extent by clay content, rock fabric, sedimentary structure and cementation. To assess the potential durability of a mudrock, these parameters must be evaluated individually and a qualitative assessment of the mudrock concluded. This approach provides a wider applicability in engineering geology whereby it has been seen that the use of derived equations such as those of Dick (1992) and Sarman et al.(1994) have very limited and task or formation specific applications.

## 9.2. Relationships between mineralogical, lithological and physical properties of the mudrock samples.

Durability of mudrocks has been shown to be controlled by two main groups of factors which are dependent on the physical and mineralogical properties of the rock. These factors have been shown to control the engineering properties and behaviour of mudrocks, which are principally slaking properties, swelling properties and strength. These properties are further affected by the geological and diagenetic history of the rock.

To examine the relationships between the mineralogical, physical, diagenetic and engineering properties of mudrocks, the test data have been subjected to correlation analysis. This measures relationships between two data sets that are scaled to be independent of the unit of measurement. It determines whether two data sets move together, so where large values of one set are associated with large values of another data set a positive correlation is obtained and where small values of one set are associated with large values of another data set negative values result. Small values are obtained if the data sets tend to show no relationship. These correlations are linear, trends may not appear linear, as they may have cutoffs, these relationships will be evaluated where appropriate. In the analysis, very strong correlation values are taken as $r \geq 0.9$, strong correlations are taken as values of $0.9 > r \geq 0.8$, and moderately strong correlation values are taken as values of $0.8 > r \geq 0.75$, these values are suggested by Dick (1992) and Swan & Sandilands (1995). The correlation matrix for the whole data set is presented in Table 9.3 and in Table 9.4 correlation data is presented for the whole sample set excluding highly organic and calcareous samples. The intention of the correlation analysis is to distinguish the bulk physical and mineralogical parameters of the samples which strongly correlate with diagenetic parameters and engineering properties. The simple index tests are evaluated in the same way to accertain their applicability to the characterization of mudrocks. The data are initially interpreted as a whole without separating the lithological groups as suggested by Dick (1992). The samples are further analysed as lithological groups to identify which index tests are most useful in significantly characterizing the separate lithotypes.

### 9.2.1. Analysis of the whole data set.

The correlation data matrix presented in Table 9.3 for the whole data set and Table 9.4 for all the samples excluding those with high carbonate and organic carbon values present many significant correlations between the determined physical, mineralogical and engineering properties. It is also seen that some of the properties show significant interelationships between mineralogical, physical, diagenetic and engineering properties.

Methylene blue adsorption (MBA) correlates strongly with percentage mixed-layer clay (see Figure 9.1), moisture absorption (see Figure 9.2), and jar slake index (see Figure 9.3), which shows that mixed-layer clays have a significant effect on these physical properties for which the methylene blue index test is a good determinant. Strong correlation also exists with powder free swell (see Figure 9.4), which is also a good indication of the expansive clay content, diagenetic rank parameter (see Figure 9.5) and point load strength (see Figure 9.6).

The diagenetic rank parameter (DRP), as discussed in Chapter 7, is derived from an observation of mineralogical and physical properties as summarized in Table 9.5, and as such the parameter shows many strong relationships with measured index properties. It correlates strongly with percentage of mixed-layer clays (see Figure 9.7) showing that with increasing diagenesis mixed-layer clays are converted to more stable clay species, which also explains the strong relationship between MBA and DRP (see Figure 9.5). The diagenetic rank parameter also strongly correlates with moisture absorption (see Figure 9.9) and moisture adsorption (see Figure 9.10), jar slake index (see Figure 9.11), and point load strength (see Figure 9.13). This suggests that with increasing rank the engineering parameters become more favourable, with loss of expansive clays affecting adsorption and durability as measured by the jar slake index, stability due to cementation and elimination of microfractures all of which are reflected by the absorption and jar slake results. A weak correlation of (r = 0.71) is evident between the third cycle slake durability index and the diagenetic rank parameter as can be seen in

Figure 9.12, although there is much scatter of the data points. It can be seen that values of DRP<6 are for non-durable mudrocks whereas values of DRP>9.5 are obtained for extremely durable samples. In between these values there is much scatter of data which is probably due to the sensitivity limitations of the slake durability test as discussed in Chapter 6.

| | %Q+F | % Clay | % MLC | $\%C_{OR}$ | Carb's | Icrys | Dia.rank | $MC\%_{AB}$ | $MC\%_{A}$ | $MC\%_{NAT}$ | MBA | γdry | $G_s$ | e | $Id_3$ | Ij | $E_V\%$ | $E_{PD}\%$ | $Imf._{AVE}$ | Is | %MLC/10Å | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| %Q+F | 1 | | | | | | | | | | | | | | | | | | | | | |
| % Clay | -0.64 | 1 | | | | | | | | | | | | | | | | | | | | |
| % MLC | -0.45 | 0.47 | 1 | | | | | | | | | | | | | | | | | | | |
| $\%C_{ORG}$ | -0.40 | -0.21 | -0.01 | 1 | | | | | | | | | | | | | | | | | | |
| Carb's | -0.34 | -0.37 | 0.02 | 0.28 | 1 | | | | | | | | | | | | | | | | | |
| Icrys | -0.38 | 0.41 | 0.40 | 0.03 | - 0.02 | 1 | | | | | | | | | | | | | | | | |
| Dia.rank | 0.66 | -0.58 | -0.75 | -0.12 | - 0.13 | -0.67 | 1 | | | | | | | | | | | | | | | |
| $MC\%_{AB}$ | -0.51 | 0.42 | 0.73 | 0.04 | 0.16 | 0.24 | -0.75 | 1 | | | | | | | | | | | | | | |
| $MC\%_{AD}$ | -0.58 | 0.63 | 0.73 | -0.04 | 0.01 | 0.50 | -0.77 | 0.76 | 1 | | | | | | | | | | | | | |
| $MC\%_{NAT}$ | -0.55 | 0.32 | 0.62 | 0.05 | 0.35 | 0.35 | -0.61 | 0.59 | 0.57 | 1 | | | | | | | | | | | | |
| MBA | -0.55 | 0.42 | 0.80 | 0.13 | 0.18 | 0.42 | -0.82 | 0.81 | 0.78 | 0.58 | 1 | | | | | | | | | | | |
| γdry | 0.55 | -0.07 | -0.24 | -0.86 | - 0.23 | -0.22 | 0.46 | -0.30 | -0.25 | -0.24 | -0.46 | 1 | | | | | | | | | | |
| $G_s$ | 0.48 | 0.01 | -0.08 | -0.92 | - 0.19 | -0.20 | 0.33 | -0.15 | -0.13 | -0.12 | -0.29 | 0.94 | 1 | | | | | | | | | |
| e | -0.16 | 0.20 | 0.47 | -0.17 | 0.15 | 0.06 | -0.40 | 0.47 | 0.37 | 0.34 | 0.52 | -0.17 | 0.16 | 1 | | | | | | | | |
| $Id_3$ | 0.39 | -0.64 | -0.70 | 0.07 | 0.13 | -0.37 | 0.71 | -0.66 | -0.61 | -0.61 | -0.62 | 0.21 | 0.09 | -0.34 | 1 | | | | | | | |
| Ij | -0.63 | 0.82 | 0.77 | -0.10 | 0.12 | 0.49 | -0.82 | 0.80 | 0.80 | 0.61 | 0.78 | -0.18 | -0.08 | 0.31 | -0.66 | 1 | | | | | | |
| $E_V\%$ | -0.49 | 0.55 | 0.72 | 0.00 | - 0.05 | 0.19 | -0.62 | 0.82 | 0.73 | 0.31 | 0.70 | -0.18 | -0.11 | 0.22 | -0.59 | 0.79 | 1 | | | | | |
| $E_{PD}\%$ | -0.51 | 0.38 | 0.66 | 0.06 | 0.27 | 0.22 | -0.72 | 0.61 | 0.60 | 0.49 | 0.78 | -0.38 | -0.18 | 0.61 | -0.57 | 0.65 | 0.51 | 1 | | | | |
| $Imf._{AVE}$ | -0.53 | 0.42 | 0.65 | 0.06 | 0.11 | 0.46 | -0.57 | 0.52 | 0.61 | 0.64 | 0.52 | -0.14 | -0.05 | 0.27 | -0.49 | 0.66 | 0.48 | 0.33 | 1 | | | |
| Is | 0.67 | -0.54 | -0.69 | -0.21 | - 0.16 | -0.50 | 0.88 | -0.69 | -0.72 | -0.61 | -0.83 | 0.56 | 0.42 | -0.41 | 0.59 | -0.70 | -0.54 | -0.69 | -0.47 | 1 | | |
| %MLC/1 | -0.54 | 0.36 | 0.81 | 0.17 | 0.23 | 0.66 | -0.85 | 0.67 | 0.71 | 0.66 | 0.73 | -0.41 | -0.31 | 0.31 | -0.68 | 0.70 | 0.53 | 0.61 | 0.56 | -0.75 | 1 | |
| LOI | -0.54 | -0.18 | 0.05 | 0.96 | 0.49 | 0.13 | -0.24 | 0.14 | 0.05 | 0.21 | 0.23 | -0.85 | -0.90 | -0.11 | 0.00 | 0.04 | 0.05 | 0.17 | 0.14 | -0.31 | 0.30 | 1 |

Table 9.3.Correlation matrix for the whole data set.(41 samples)

| | %Q+F | % Clay | % MLC | $\%C_{OR}$ | Carb's | Icrys | Dia.rank | $MC\%_{AB}$ | $MC\%_{A}$ | $MC\%_{NAT}$ | MBA | γdry | $G_s$ | e | $Id_3$ | Ij | $E_V\%$ | $E_{PD}\%$ | $Imf._{AVE}$ | Is | %MLC/10Å | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| %Q+F | 1 | | | | | | | | | | | | | | | | | | | | | |
| % Clay | -0.97 | 1 | | | | | | | | | | | | | | | | | | | | |
| % MLC | -0.60 | 0.53 | 1 | | | | | | | | | | | | | | | | | | | |
| $\%C_{ORG}$ | -0.40 | 0.26 | 0.21 | 1 | | | | | | | | | | | | | | | | | | |
| Carb's | -0.03 | -0.11 | 0.25 | 0.17 | 1 | | | | | | | | | | | | | | | | | |
| Icrys | -0.48 | 0.47 | 0.47 | 0.03 | 0.13 | 1 | | | | | | | | | | | | | | | | |
| Dia.rank | 0.72 | -0.67 | -0.79 | -0.40 | -0.26 | -0.69 | 1 | | | | | | | | | | | | | | | |
| $MC\%_{AB}$ | -0.53 | 0.44 | 0.80 | 0.54 | 0.27 | 0.23 | -0.74 | 1 | | | | | | | | | | | | | | |
| $MC\%_{AD}$ | -0.70 | 0.59 | 0.85 | 0.39 | 0.35 | 0.51 | -0.82 | 0.82 | 1 | | | | | | | | | | | | | |
| $MC\%_{NAT}$ | -0.50 | 0.47 | 0.79 | 0.02 | 0.22 | 0.41 | -0.67 | 0.58 | 0.69 | 1 | | | | | | | | | | | | |
| MBA | -0.58 | 0.49 | 0.82 | 0.47 | 0.34 | 0.47 | -0.87 | 0.86 | 0.88 | 0.63 | 1 | | | | | | | | | | | |
| γdry | 0.53 | -0.47 | -0.43 | -0.68 | -0.34 | -0.36 | 0.76 | -0.65 | -0.60 | -0.38 | -0.71 | 1 | | | | | | | | | | |
| $G_s$ | 0.47 | -0.39 | -0.31 | -0.78 | -0.31 | -0.32 | 0.65 | -0.49 | -0.45 | -0.22 | -0.55 | 0.88 | 1 | | | | | | | | | |
| e | -0.23 | 0.24 | 0.36 | 0.04 | 0.19 | 0.17 | -0.43 | 0.51 | 0.46 | 0.40 | 0.54 | -0.53 | -0.07 | 1 | | | | | | | | |
| $Id_3$ | 0.50 | -0.48 | -0.72 | -0.25 | -0.01 | -0.35 | 0.73 | -0.68 | -0.55 | -0.70 | -0.66 | 0.52 | 0.42 | -0.33 | 1 | | | | | | | |
| Ij | -0.70 | 0.62 | 0.88 | 0.36 | 0.25 | 0.55 | -0.87 | 0.81 | 0.83 | 0.65 | 0.83 | -0.55 | -0.48 | 0.31 | -0.69 | 1 | | | | | | |
| $E_V\%$ | -0.58 | 0.49 | 0.77 | 0.59 | 0.14 | 0.20 | -0.64 | 0.90 | 0.73 | 0.39 | 0.75 | -0.48 | -0.46 | 0.19 | -0.55 | 0.79 | 1 | | | | | |
| $E_{PD}\%$ | -0.51 | 0.46 | 0.66 | 0.36 | 0.20 | 0.33 | -0.79 | 0.68 | 0.66 | 0.52 | 0.81 | -0.69 | -0.51 | 0.57 | -0.64 | 0.73 | 0.55 | 1 | | | | |
| $Imf._{AVE}$ | -0.55 | 0.50 | 0.72 | 0.02 | 0.11 | 0.46 | -0.55 | 0.53 | 0.67 | 0.80 | 0.54 | -0.15 | 0.00 | 0.32 | -0.53 | 0.67 | 0.45 | 0.37 | 1 | | | |
| Is | 0.67 | -0.61 | -0.73 | -0.35 | -0.44 | -0.51 | 0.89 | -0.71 | -0.80 | -0.65 | -0.87 | 0.76 | 0.63 | -0.47 | 0.61 | -0.77 | -0.58 | -0.71 | -0.46 | 1 | | |
| %MLC/1 | -0.63 | 0.56 | 0.89 | 0.27 | 0.37 | 0.71 | -0.88 | 0.72 | 0.82 | 0.75 | 0.81 | -0.59 | -0.51 | 0.33 | -0.75 | 0.84 | 0.63 | 0.66 | 0.62 | -0.78 | 1 | |
| LOI | -0.61 | 0.48 | 0.39 | 0.88 | 0.32 | 0.37 | -0.66 | 0.61 | 0.58 | 0.26 | 0.59 | -0.78 | -0.87 | 0.09 | -0.46 | 0.58 | 0.60 | 0.49 | 0.23 | -0.57 | 0.59 | 1 |

Table 9.4. Correlation matrix for all samples excluding those with high carbonate and organic carbon contents (30 samples)

| | Feature | Visual description | Rank |
|---|---|---|---|
| A | Mineral packing/density | Dense | 3 |
| | | moderately dense | 2 |
| | | loose to moderately dense | 1 |
| B | Clay mineral orientation | Laminar orientation | 3 |
| | | Turbostratic orientation | 2 |
| | | Continuous matrix | 1 |
| C | Clastic contact | Much point grain contact | 3 |
| | | Some point grain contact | 2 |
| | | No point contact | 1 |
| D | Degree of cementation | Much evident cementation | 3 |
| | | Some evident cementation | 2 |
| | | No evident cementation | 1 |

Table 9.5. Summary of the diagenetic rank parameter.

Moisture absorption correlates strongly with methylene blue adsorption and diagenetic rank parameter as mentioned, but also with moisture adsorption (see Figure 9.14) which accounts for the fraction of water adsorbed by clay minerals in the water absorption result. Correlation also exists between moisture absorption, jar slake index (see Figure 9.15) and volumetric free swell (see Figure 9.16), all three of these parameters being affected by the distribution of microfractures through the mudrock specimen.

Jar slake index correlates strongly with the above parameters and, in addition, with volumetric free swell (see Figure 9.17) and moisture adsorption (see Figure 9.8). The correlation coefficients for the parameters discussed are presented in Table 9.6. It is clear that durability, swelling potential and strength of mudrocks are controlled by the presence of mixed-layer clays, and the distribution of microfractures, and the extent of these two parameters is controlled by the diagenetic rank of the samples.

The degree of compaction in a mudrock is reflected by the dry density and porosity. In the whole rock correlation matrix presented in Table 9.3 it can be seen that for the indurated mudrocks studied , a strong relationship exists between dry density and specific gravity (r = 0.94), dry density and loss on ignition (r = –0.85) and dry density

| Principal parameter | Correlation parameters. |
|---|---|
| Diagenetic rank | $MC_{ABS}$(r = -0.75 ), $MC_{AD}$(r = -0.77 ), MBA(r = -0.82), $I_J$(r = -0.82), $I_S$ (r = 0.88), %MLC (r = -0.75) |
| % MLC | Dia.Rank (r = -0.75), MBA(r = 0.80), $I_J$(r = 0.77) |
| $MC_{ABS}$ | Dia.Rank (r = -0.75), $MC_{AD}$ (r = 0.76), MBA(r = 0.81), $I_J$(r = 0.80), $E_V$ (r = 0.82) |
| MBA | %MLC(r = 0.80), Dia.Rank (r = -0.82), $MC_{ABS}$ (r = 0.81 ), $MC_{AD}$(r = 0.78), $I_J$(r = 0.78), $I_S$ (r = -0.83) $I_{PD}$(r = 0.78) |
| $I_J$ | MBA(r = 0.78), Dia.Rank(r = -0.82), $MC_{ABS}$(r = 0.80), $MC_{AD}$(r = 0.80), MBA(r = 0.78), $E_V$ (r = 0.79) |

Table 9.6 Correlation coefficients between multi-related parameters within the whole data set.

and organic content (r = –0.86). This shows that for indurated mudrocks the mineralogy controls the dry density due to the rock having undergone a high degree of compaction which has drastically reduced the void space, as can be seen by the lack of correlation between porosity and dry density. The specific gravity values for minerals commonly found in mudrocks are similar, ranging from 2.65 - 2.75 (Dick and Shakoor, 1992) with the exception of organic carbon which is much lower values and pyrite which has a higher value. Hence there is a good correlation between dry density, loss on ignition and organic content.

It may be noted that an expected correlation between the microfracture index and slaking and swelling test results does not exist. This is probably due to the limitations of the test, which is performed on dry samples where microfractures may not be clearly evident.Methods of determination of this parameter in different mudrock types require further investigation as discussed in Chapter 10. However, as discussed in Chapter 6, when a wetting cycle microfracture index test is performed where the sample has been quickly wetted and dried prior to testing the microfractures are more evident for visual observation. Since this was only performed on a limited number of samples the results could not be used in the correlation analysis.

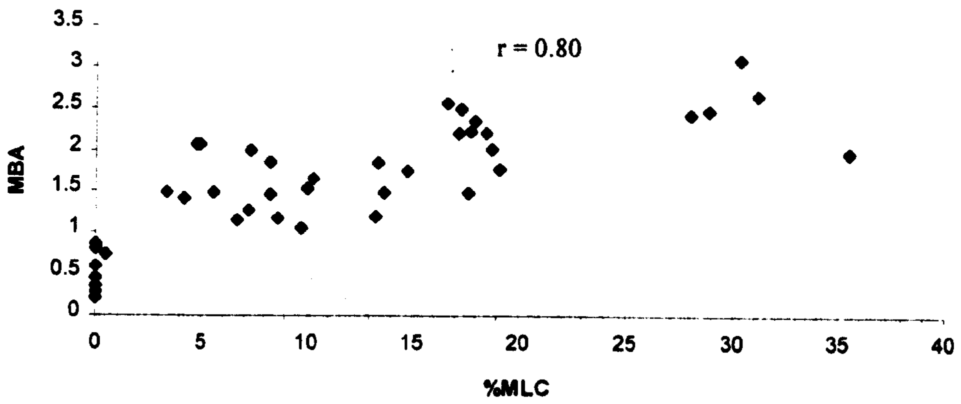


Figure 9.1. Plot of % mixed layer clay versus methylene blue adsorption.

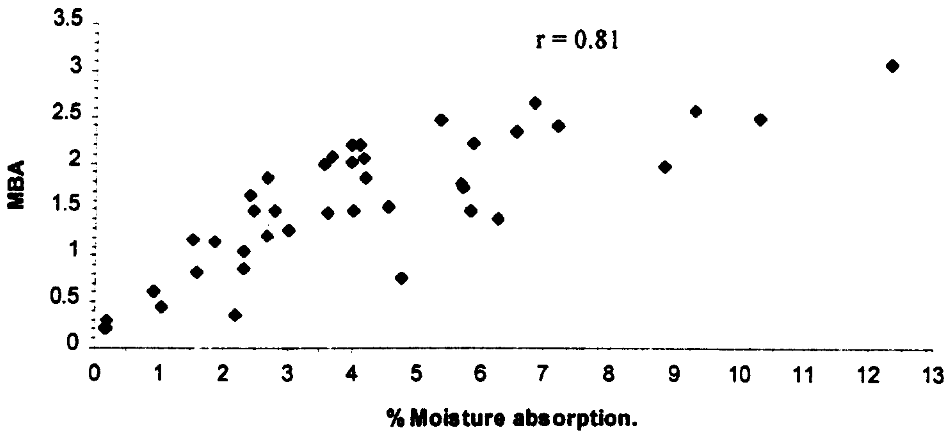


Figure 9.2. Plot of moisture absorption versus methylene blue adsorption.

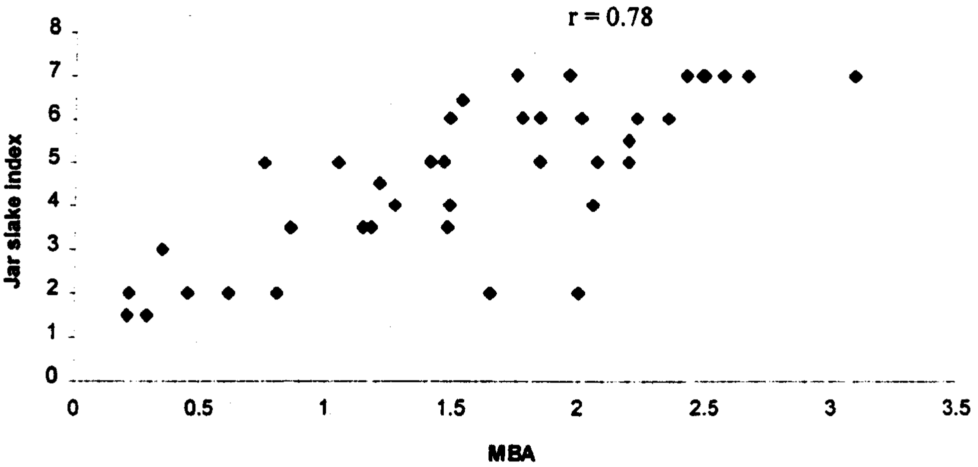


Figure 9.3. Plot of jar slake index versus methylene blue adsorption.

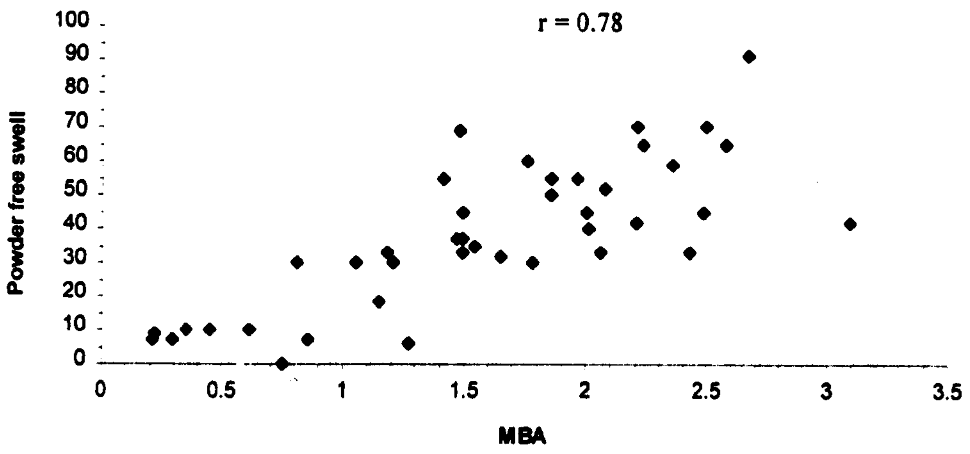


Figure 9.4. Plot of powder free swell index versus methylene blue adsorption.

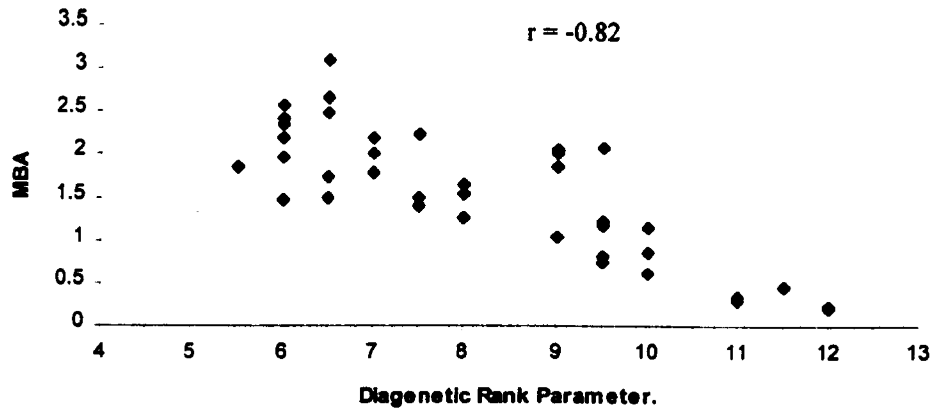


Figure 9.5. Plot of diagenetic rank parameter versus methylene blue adsorption.

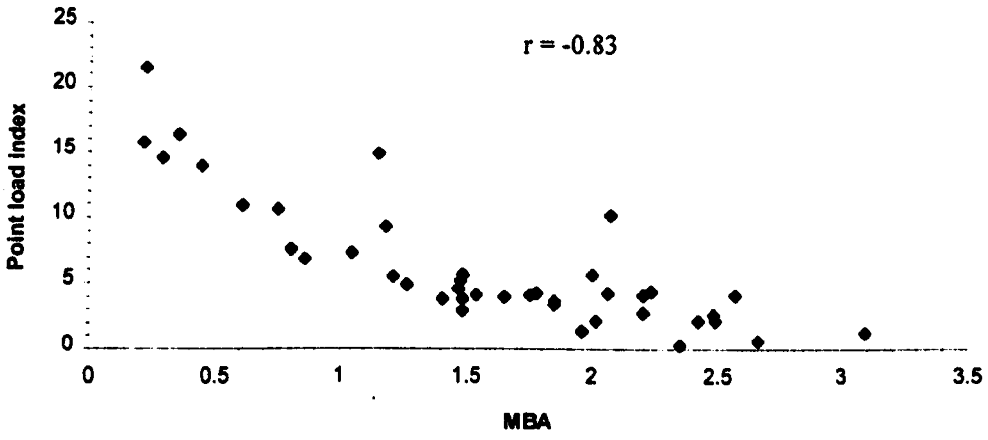


Figure 9.6. Plot of point load strength versus methylene blue adsorption.

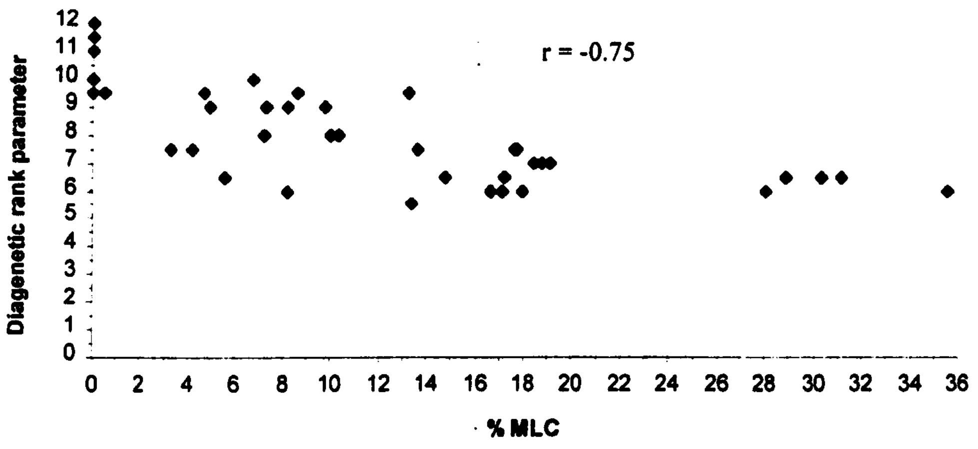


Figure 9.7. Plot of diagenetic rank parameter versus percentage of mixed layer clay.

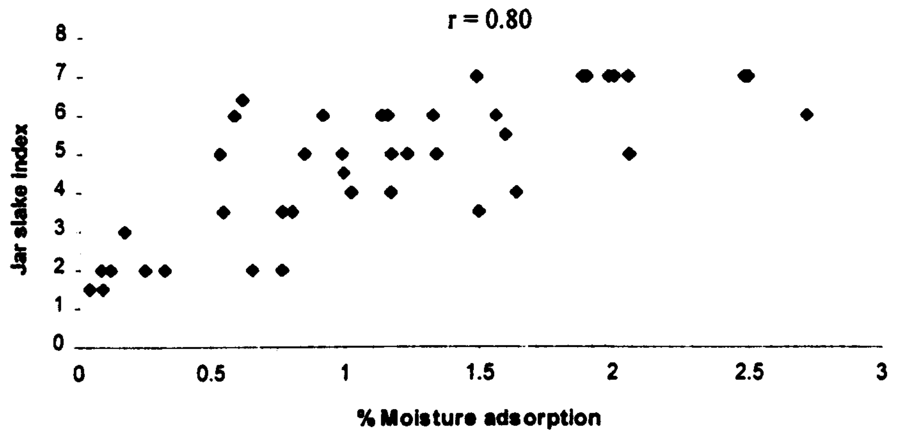


Figure 9.8. Plot of jar slake index versus moisture adsorption.

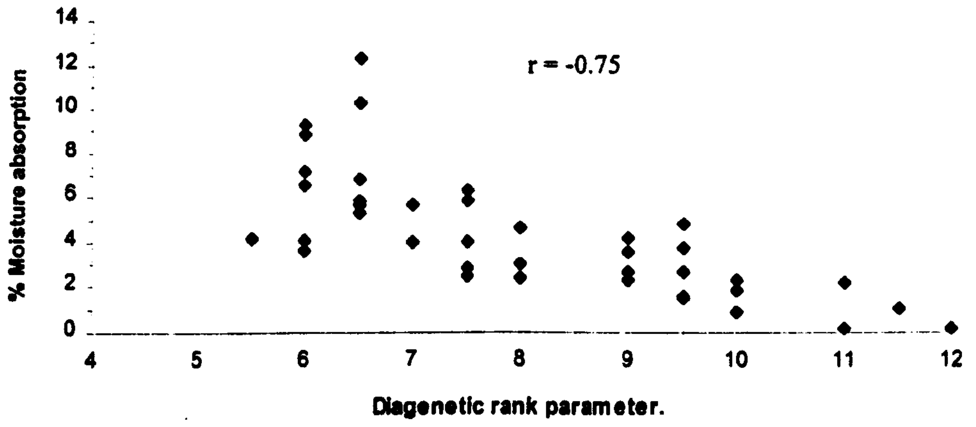


Figure 9.9. Plot of moisture absorption versus diagenetic rank parameter.

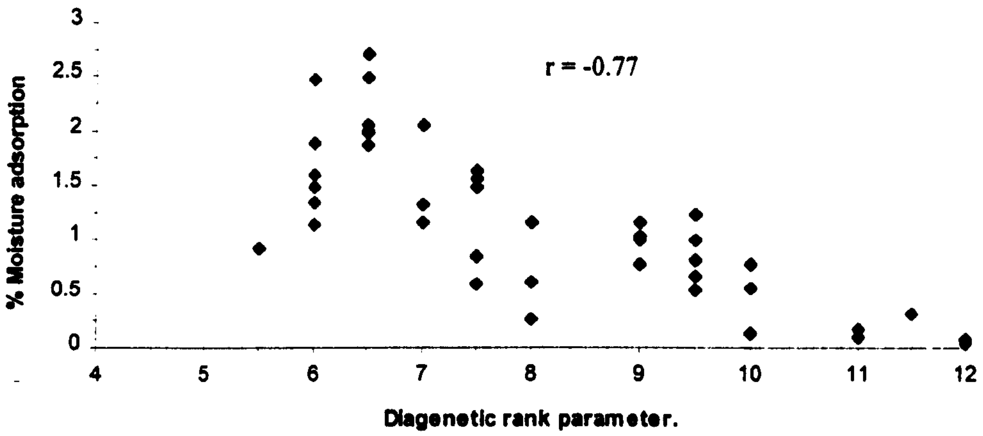


Figure 9.10. Plot of moisture adsorption versus diagenetic rank parameter.

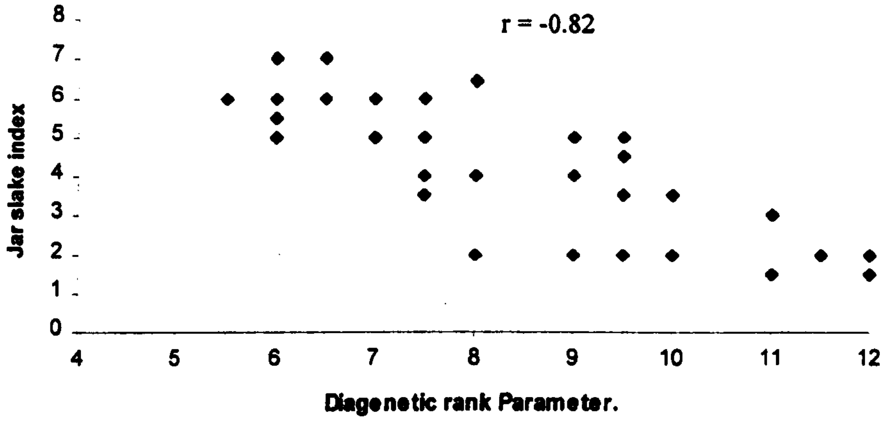


Figure 9.11. Plot of jar slake index versus diagenetic rank parameter.

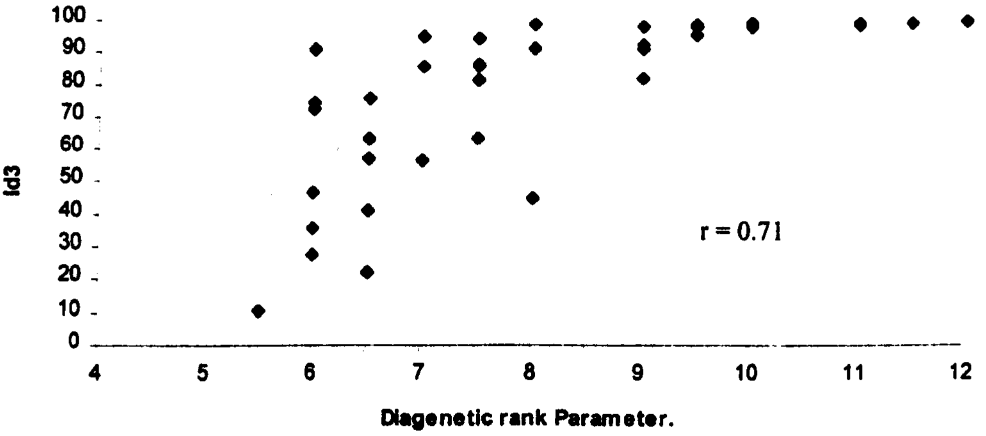


Figure 9.12. Plot of third cycle slake durability index versus diagenetic rank parameter.

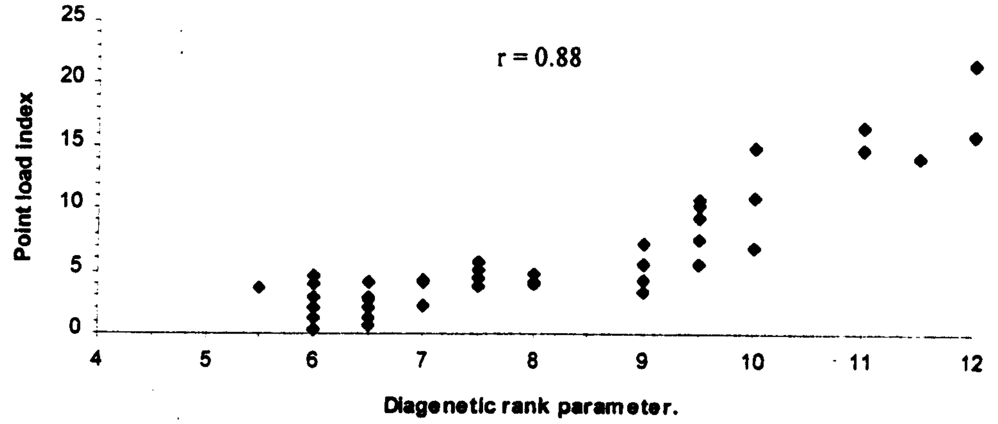


Figure 9.13. Plot of point load index versus diagenetic rank parameter.

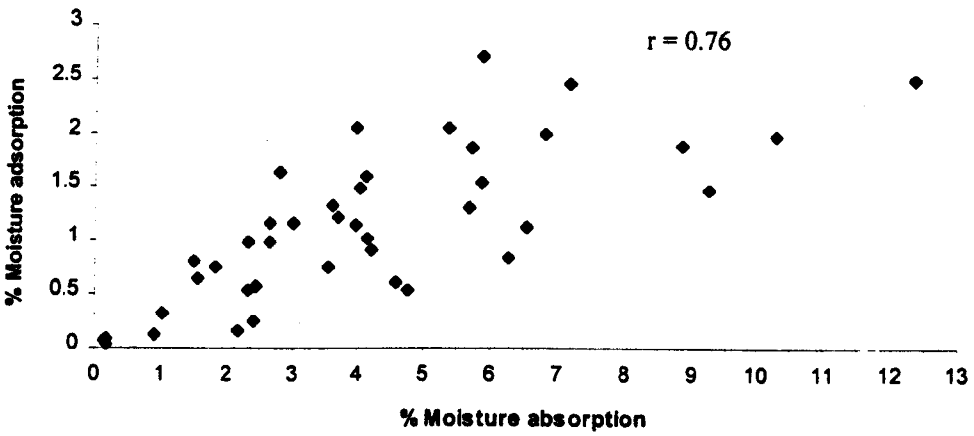


Figure 9.14. Plot of moisture adsorption versus moisture absorption.

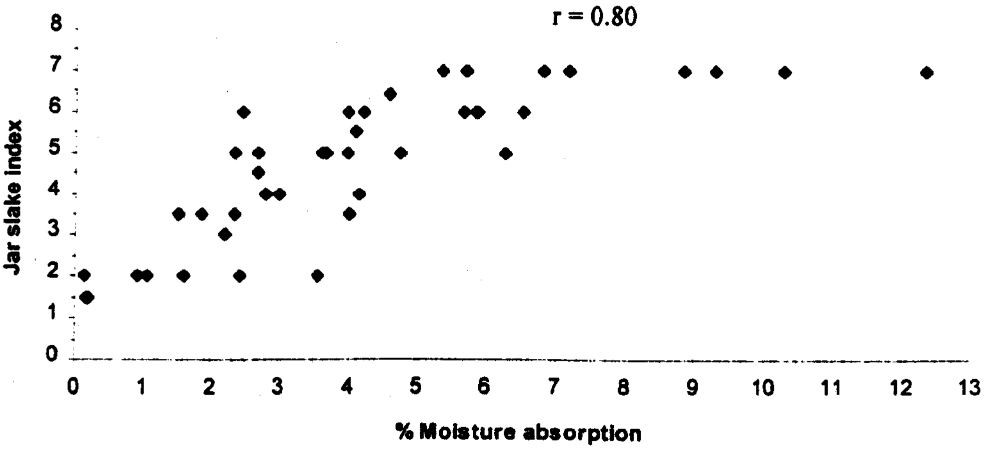


Figure 9.15. Plot of jar slake index versus moisture absorption.

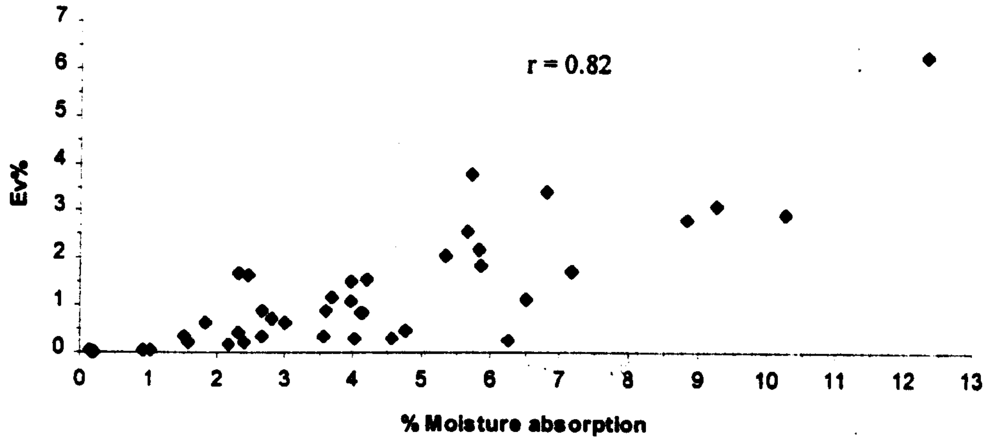


Figure 9.16. Plot of volumetric free swell versus moisture absorption.

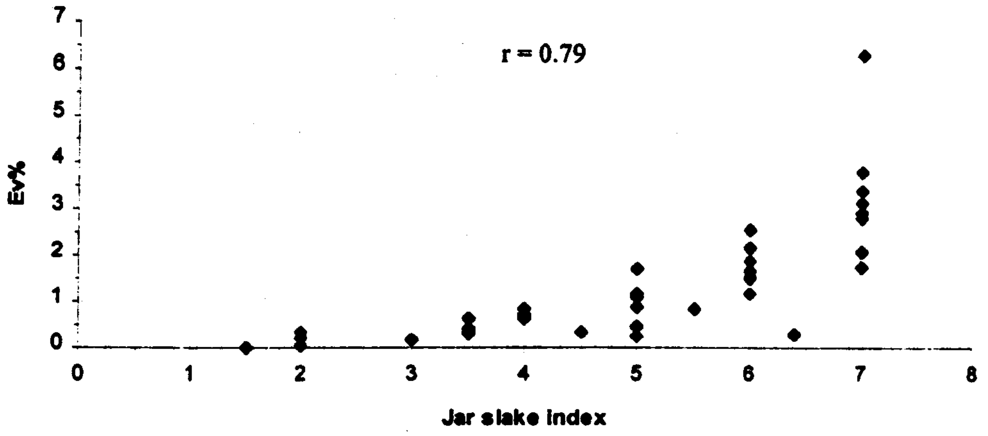


Figure 9.17. Plot of jar slake index versus volumetric free swell.

The measurement of illite 'crystallinity' shows very low correlation coefficients with physical and engineering parameters. As seen in Chapter 7, illite 'crystallinity' is useful in determining the extent of diagenetic maturity of a sample, but it cannot evaluate the controls on durability by factors such as the amount and extent of cementation in a sample, the presence and amount of swelling clays present in a sample, the fabric and the extent of development of discontinuities within a sample. The diagenetic rank parameter accesses all these and other physical parameters in a sample and is therefore a more useful diagenetic characterization index parameter.

### 9.2.2. Analysis of the whole data set excluding high carbonate and organic samples.

The test data was also analysed excluding samples which were considered to be highly organic or calcareous as discussed in Chapter 5. The results are presented in Table 9.4, from which the strong correlations which were found to exist for the whole data set are still evident although the coefficients appear to correlate with a higher degree of confidence. Additionally, strong correlations become apparent between the percentage mixed-layer clays and moisture absorption (r = 0.80), moisture adsorption (r = 0.85) and natural moisture content (r = 0.79). Diagenetic rank correlates with dry density (r = 0..76), and the powder free-swell index (r = –0.79). Moisture adsorption correlates with point load strength (r = –0.80), and percentage mixed-layer clays (r = 0.85). Methylene blue adsorption correlates with powder free-swell (r = 0.81), and the jar slake index correlates with the point load strength (r = –0.77).

From the correlation analysis it can be seen that the principal controls on the whole data set appear to be:

- Mineralogy: especially the mixed-layer clay content, which affects the durability and swelling potential of the samples.

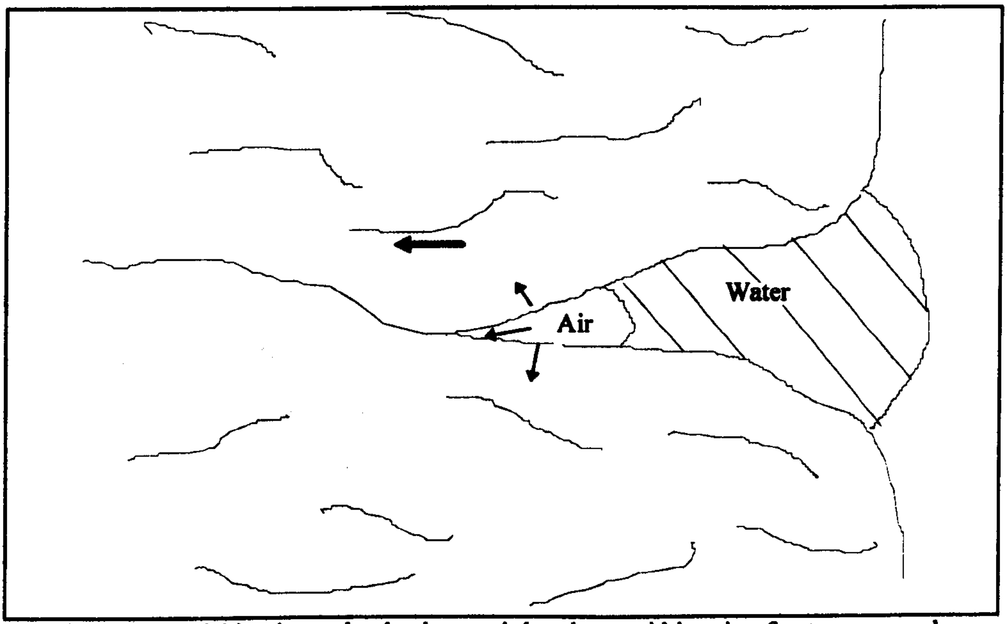


Figure 9.18. Slaking in mudrocks due to air breakage within microfractures caused by water. (Russell, 1982).

- Diagenesis: which is successfully determined by the diagenetic rank parameter, which evaluates the durability, strength and distribution of discontinuities, all of which affect the swelling potential.
- Texture: which is also determined using the diagenetic rank parameter. Textural features such as microdiscontinuities, which are seen to develop in the jar slake test and volumetric free-swell test affect the mass strength and durability of a mudrock. Discontinuities are important access routes for water into a sample causing air breakage as seen in Figure 9.18, or allowing the swelling of reactive clay phases which therefore results in slaking.

### 9.2.3. Analysis of the separate mudrock lithological units.

Statistical analysis of the mudrock lithological units consisted of dividing the samples into argillite, claystone, mudstone, fissile/laminated mudstone and siltstone groups. In each group, correlations of $r > \pm 0.8$ are selected with respect to identifying strong relationships between engineering properties (such as swelling, slaking and strength), and the mineralogical, physical and diagenetic properties which strongly affect these properties. It is also intended to identify the index tests which are most useful for evaluating these characteristics for each lithological group. Strong relationships have already been identified between properties of mudrocks for the whole data set, but as recommended by Dick (1992) and Dick and Shakoor (1992), lithological units should be evaluated individually as they found that each of the lithological groups had unique physical and mineralogical properties governing their engineering properties. From the analysis of mudrock property correlations, specific index tests are selected which are beneficial in characterizing the engineering properties of specific mudrock lithotypes are presented in section 9.4 as part of a mudrock characterization approach.

### *9.2.3.1. Assessment of argillite durability.*

The argillites studied consist of 8 samples. Correlation data presented in Table 9.7 shows many strong correlations with $r \geq 0.75$, the following being the most significant:

- $Id_3$ : $MC_{AB}$ ($r = -0.92$), $I_J$ ($r = -0.84$), $I_{MF}$ ($r = -0.81$).
- $I_J$ : Carbonates ($r = 0.91$), $MC_{AB}$ ($r = 0.96$), $MC_{NAT}$ ($r = 0.93$), $Id_3$ ($r = -0.84$), Ev% ($r = 0.86$), LOI ($r = 0.94$).
- Ev% : %MLC ($r = 0.95$), Carbonates ($r = 0.95$), $MC_{AD}$ ($r = 0.92$), MBA ($r = 0.97$), $I_J$ ($r = 0.86$), LOI ($r = 0.94$).
- $I_S$ : % Q+F ($r = 0.91$), DRP ($r = 0.87$), $\gamma$dry ($r = 0.83$).

Argillites generally do not present problems in engineering works, although problematic situations may arise, for example, samples D11 and D12 which both contain smectite as a post formational constituent, possibly derived from hydrothermal activity, may be susceptible to degradation on exposure to water due to swelling. Therefore it is prudent to access argillites for their long term stability, and it appears from the correlation data that swelling and slaking of argillites are controlled by the presence of microdiscontinuities. These properties are best determined by moisture adsorption and the jar slake test. In some samples containing swelling clays but which are cemented, swelling may be temporarilly arrested while the cement is removed by weathering processes. This is demonstrated by sample C31 which in the roof weathering experiment (see Chapter 8) displayed a short-term (~6-8 months) stability but it then underwent rapid slaking once the carbonate cement had been removed. The strength of argillites is controlled by the clastic content which mainly consists of quartz and feldspars which can be determined by X-ray diffraction or by means of the diagenetic rank parameter.

### *9.2.3.2. Assessment of claystone durability.*

The claystones studied consisted of 9 samples. The correlation coefficient matrix is presented in Table 9.8.

- $Id_3$ : $MC_{AD}$ (r = –0.80).
- $I_J$ : % Clay (r = 0.86), $\%C_{ORG}$ (r = –0.94), $MC_{AD}$ (r = 0.81), γdry (r = 0.88), Gs (r = 0.89), LOI (r = –0.98).
- Ev% : $MC_{AB}$ (r =0.82).
- $I_S$ : MBA (r = –0.78).

| | %Q+F | % Clay | % MLC | $\%C_{OR}$ | Carb's | Icrys | Dia.rank | $MC\%_{AB}$ | $MC\%_{A}$ | $MC\%_{NAT}$ | MBA | γdry | $G_s$ | e | $Id_3$ | Ij | $E_V\%$ | $E_{PD}\%$ | $Imf._{AVE}$ | Is | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| %Q+F | 1 | | | | | | | | | | | | | | | | | | | | |
| % Clay | -0.83 | 1 | | | | | | | | | | | | | | | | | | | |
| % MLC | -0.52 | 0.06 | 1 | | | | | | | | | | | | | | | | | | |
| $\%C_{ORG}$ | -0.39 | 0.45 | - 0.12 | 1 | | | | | | | | | | | | | | | | | |
| Carb's | -0.81 | 0.08 | 0.88 | 0.14 | 1 | | | | | | | | | | | | | | | | |
| Icrys | -0.86 | 0.45 | 0.38 | 0.50 | 0.49 | 1 | | | | | | | | | | | | | | | |
| Dia.rank | 0.96 | -0.70 | - 0.51 | -0.27 | -0.67 | -0.60 | 1 | | | | | | | | | | | | | | |
| $MC\%_{AB}$ | -0.78 | 0.43 | 0.54 | 0.55 | 0.82 | 0.48 | -0.81 | 1 | | | | | | | | | | | | | |
| $MC\%_{AD}$ | -0.83 | 0.47 | 0.86 | 0.09 | 0.83 | 0.53 | -0.82 | 0.71 | 1 | | | | | | | | | | | | |
| $MC\%_{NAT}$ | -0.81 | 0.38 | 0.88 | 0.40 | 0.90 | 0.59 | -0.85 | 0.94 | 0.85 | 1 | | | | | | | | | | | |
| MBA | -0.75 | 0.33 | 0.96 | 0.00 | 0.88 | 0.49 | -0.73 | 0.66 | 0.98 | 0.81 | 1 | | | | | | | | | | |
| γdry | 0.94 | -0.82 | - 0.41 | -0.48 | -0.53 | -0.46 | 0.88 | -0.80 | -0.78 | -0.90 | -0.66 | 1 | | | | | | | | | |
| $G_s$ | 0.86 | -0.59 | - 0.60 | -0.13 | -0.69 | -0.31 | 0.89 | -0.79 | -0.88 | -0.85 | -0.80 | 0.91 | 1 | | | | | | | | |
| e | -0.82 | 0.92 | 0.11 | 0.70 | 0.21 | 0.48 | -0.70 | 0.62 | 0.52 | 0.56 | 0.37 | -0.90 | -0.64 | 1 | | | | | | | |
| $Id_3$ | 0.64 | -0.34 | - 0.27 | -0.64 | -0.66 | -0.54 | 0.72 | -0.92 | -0.49 | -0.86 | -0.41 | 0.67 | 0.61 | - 0.55 | 1 | | | | | | |
| Ij | -0.66 | 0.22 | 0.69 | 0.41 | 0.91 | 0.41 | -0.71 | 0.96 | 0.73 | 0.93 | 0.74 | -0.67 | -0.73 | 0.43 | -0.84 | 1 | | | | | |
| $E_V\%$ | -0.69 | 0.21 | 0.95 | 0.04 | 0.95 | 0.43 | -0.70 | 0.75 | 0.92 | 0.85 | 0.97 | -0.61 | -0.77 | 0.30 | -0.51 | 0.86 | 1 | | | | |
| $E_{PD}\%$ | -0.59 | 0.36. | 0.83 | -0.30 | 0.57 | 0.24 | -0.54 | 0.29 | 0.86 | 0.47 | 0.88 | -0.51 | -0.67 | 0.27 | 0.03 | 0.37 | 0.77 | 1 | | | |
| $Imf._{AVE}$ | -0.58 | 0.56 | - 0.06 | 0.94 | 0.27 | 0.56 | -0.51 | 0.70 | 0.27 | 0.60 | 0.14 | -0.67 | -0.39 | 0.79 | -0.81 | 0.53 | 0.17 | -0.19 | 1 | | |
| Is | 0.91 | -0.79 | - 0.37 | -0.27 | -0.47 | -0.71 | 0.87 | -0.59 | -0.73 | -0.69 | -0.62 | 0.83 | 0.77 | - 0.71 | 0.54 | -0.43 | -0.51 | -0.50 | -0.49 | 1 | |
| LOI | -0.74 | 0.27 | 0.84 | 0.34 | 0.97 | 0.59 | -0.75 | 0.89 | 0.88 | 0.95 | 0.89 | -0.69 | -0.75 | 0.44 | -0.73 | 0.94 | 0.94 | 0.57 | 0.46 | -0.57 | 1 |

Table 9.7.Correlation matrix for the argillite samples. (8 samples)

| | %Q+F | % Clay | % MLC | $\%C_{OR}$ | Carb's | Icrys | Dia.rank | $MC\%_{AB}$ | $MC\%_{A}$ | $MC\%_{NAT}$ | MBA | γdry | $G_s$ | e | $Id_3$ | Ij | $E_V\%$ | $E_{PD}\%$ | $Imf._{AVE}$ | Is | LOI | Ro% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| %Q+F | 1 | | | | | | | | | | | | | | | | | | | | | |
| % Clay | 0.41 | 1 | | | | | | | | | | | | | | | | | | | | |
| % MLC | 0.49 | 0.53 | 1 | | | | | | | | | | | | | | | | | | | |
| $\%C_{ORG}$ | -0.69 | -0.68 | -0.43 | 1 | | | | | | | | | | | | | | | | | | |
| Carb's | -0.10 | -0.75 | -0.41 | 0.05 | 1 | | | | | | | | | | | | | | | | | |
| Icrys | -0.08 | 0.24 | 0.00 | -0.24 | -0.17 | 1 | | | | | | | | | | | | | | | | |
| Dia.rank | -0.46 | -0.43 | -0.53 | 0.62 | 0.10 | -0.38 | 1 | | | | | | | | | | | | | | | |
| $MC\%_{AB}$ | 0.47 | 0.45 | 0.57 | -0.53 | -0.18 | -0.14 | -0.62 | 1 | | | | | | | | | | | | | | |
| $MC\%_{AD}$ | 0.36 | 0.92 | 0.45 | -0.62 | -0.69 | 0.31 | -0.59 | 0.61 | 1 | | | | | | | | | | | | | |
| $MC\%_{NAT}$ | 0.16 | -0.01 | 0.22 | -0.38 | 0.34 | 0.54 | -0.38 | 0.09 | 0.09 | 1 | | | | | | | | | | | | |
| MBA | 0.33 | 0.49 | 0.94 | -0.40 | -0.35 | -0.04 | -0.45 | 0.68 | 0.43 | 0.16 | 1 | | | | | | | | | | | |
| γdry | 0.79 | 0.57 | 0.36 | -0.97 | 0.02 | 0.24 | -0.63 | 0.56 | 0.57 | 0.41 | 0.31 | 1 | | | | | | | | | | |
| $G_s$ | 0.79 | 0.56 | 0.46 | -0.98 | 0.06 | 0.19 | -0.64 | 0.51 | 0.51 | 0.44 | 0.38 | 0.98 | 1 | | | | | | | | | |
| e | 0.36 | 0.17 | 0.59 | -0.47 | 0.21 | -0.12 | -0.33 | 0.05 | -0.01 | 0.38 | 0.45 | 0.36 | 0.55 | 1 | | | | | | | | |
| $Id_3$ | -0.27 | -0.70 | -0.62 | 0.53 | 0.44 | -0.29 | 0.68 | -0.49 | -0.80 | -0.46 | -0.52 | -0.44 | -0.49 | -0.41 | 1 | | | | | | | |
| Ij | 0.66 | 0.86 | 0.60 | -0.94 | -0.36 | 0.20 | -0.67 | 0.63 | 0.81 | 0.22 | 0.56 | 0.88 | 0.89 | 0.42 | -0.68 | 1 | | | | | | |
| $E_V\%$ | 0.46 | 0.73 | 0.67 | -0.46 | -0.60 | -0.25 | -0.52 | 0.82 | 0.75 | -0.27 | 0.70 | 0.40 | 0.40 | 0.12 | -0.58 | 0.69 | 1 | | | | | |
| $E_{PD}\%$ | 0.35 | 0.20 | 0.42 | -0.54 | 0.29 | -0.30 | -0.25 | 0.14 | 0.06 | 0.34 | 0.33 | 0.43 | 0.60 | 0.92 | -0.42 | 0.46 | 0.17 | 1 | | | | |
| $Imf._{AVE}$ | 0.48 | 0.41 | 0.41 | -0.42 | -0.34 | 0.63 | -0.46 | -0.09 | 0.28 | 0.20 | 0.23 | 0.42 | 0.45 | 0.28 | -0.24 | 0.45 | 0.08 | 0.00 | 1 | | | |
| Is | -0.01 | -0.30 | -0.67 | 0.45 | -0.03 | -0.18 | 0.56 | -0.56 | -0.34 | -0.51 | -0.78 | -0.33 | -0.41 | -0.53 | 0.61 | -0.48 | -0.39 | -0.48 | -0.05 | 1 | | |
| LOI | -0.70 | -0.80 | -0.50 | 0.98 | 0.25 | -0.22 | 0.58 | -0.54 | -0.73 | -0.27 | -0.46 | -0.93 | -0.93 | -0.42 | 0.58 | -0.98 | -0.57 | -0.48 | -0.46 | 0.40 | 1 | |
| Ro% | -0.43 | 0.11 | -0.16 | 0.13 | -0.13 | -0.31 | 0.67 | -0.18 | -0.11 | -0.43 | 0.05 | -0.27 | -0.27 | -0.10 | 0.33 | -0.09 | -0.02 | 0.02 | -0.38 | 0.01 | 0.06 | 1 |

Table 9.8. Correlation matrix for the claystone samples. (9 samples)

The durability of claystone samples is governed by their mineralogy as is seen by the strong correlations between clay content, organic content, methylene blue adsorption and moisture adsorption and absorption upon the engineering properties. In addition it is seen in Table 9.8 that loss on ignition correlates significantly with percentage clay ($r = -0.80$), and % organic carbon ($r = 0.98$) and physically with dry density ($r = -0.93$). Methylene blue adsorption correlates significantly with the percentage mixed-layer clay ($r = 0.94$), but mixed-layer clay content shows very weak correlations with engineering properties suggesting that carbonate and organic carbon content controls durability by surroundin the mixed layer clays with a hydrophobic film as discussed in Chapter 3 and observed from BSI analysis in Chapter 7. The controls on durability of claystones have been noted by workers such as Ratsey (1973), Hudec (1982) and Campbell (1993), but have never been studied in detail.

### *9.2.3.3. Assessment of mudstone durability.*

The mudstones studied consisted of 8 samples. The correlation coefficient matrix is presented in Table 9.9. Strong correlations were found as follows:

- $Id_3$ : % Q+F ($r = 0.81$).
- $I_J$ : $MC_{AB}$ ($r = 0.75$).
- Ev% : $I_J$ ($r = 0.89$), $MC_{AB}$ ($r = 0.79$).
- $I_S$ : $MC_{NAT}$ ($r = -0.76$).

Strong correlations also exist between percentage mixed-layer clays, moisture absorption ($r = 0.90$), moisture adsorption ($r = 0.77$), natural moisture content ($r = 0.86$) and microfracture index ($r = 0.83$). A significant relationship exists between void ratio and moisture adsorption ($r = 0.90$). These relationships show that the durability and strength of mudstone is controlled by the mixed-layer clay content and void distribution including microdiscontinuities. Such features provide access for water to the sites of the reactive clays and also potential sites for air breakage to occur (Taylor and Spears, 1981 and Russell, 1982).

| | %Q+F | % Clay | % MLC | $\%C_{OR}$ | Carb's | Icrys | Dia.rank | $MC\%_{AS}$ | $MC\%_{A}$ | $MC\%_{NAT}$ | MBA | γdry | $G_s$ | e | $Id_3$ | Ij | $E_V\%$ | EPD% | $Imf._{AVE}$ | Is | LOI | Ro% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| %Q+F | 1 | | | | | | | | | | | | | | | | | | | | | |
| % Clay | -0.95 | 1 | | | | | | | | | | | | | | | | | | | | |
| % MLC | -0.09 | -0.05 | 1 | | | | | | | | | | | | | | | | | | | |
| $\%C_{ORG}$ | -0.34 | 0.25 | -0.26 | 1 | | | | | | | | | | | | | | | | | | |
| Carb's | 0.33 | -0.53 | 0.55 | -0.20 | 1 | | | | | | | | | | | | | | | | | |
| Icrys | -0.52 | 0.58 | -0.36 | 0.74 | -0.31 | 1 | | | | | | | | | | | | | | | | |
| Dia.rank | 0.89 | -0.87 | -0.37 | -0.21 | 0.17 | -0.53 | 1 | | | | | | | | | | | | | | | |
| $MC\%_{AS}$ | -0.23 | 0.08 | 0.90 | -0.04 | 0.34 | -0.18 | -0.47 | 1 | | | | | | | | | | | | | | |
| $MC\%_{AD}$ | -0.10 | -0.02 | 0.77 | -0.21 | 0.52 | -0.18 | -0.35 | 0.84 | 1 | | | | | | | | | | | | | |
| $MC\%_{NAT}$ | 0.03 | -0.17 | 0.86 | -0.52 | 0.77 | -0.45 | -0.23 | 0.64 | 0.73 | 1 | | | | | | | | | | | | |
| MBA | -0.57 | 0.57 | 0.35 | -0.09 | -0.19 | 0.15 | -0.67 | 0.52 | 0.67 | 0.27 | 1 | | | | | | | | | | | |
| γdry | 0.53 | -0.52 | -0.20 | -0.38 | 0.08 | -0.58 | 0.66 | -0.52 | -0.50 | 0.00 | -0.54 | 1 | | | | | | | | | | |
| $G_s$ | 0.49 | -0.49 | 0.38 | -0.78 | 0.35 | -0.78 | 0.35 | 0.20 | 0.45 | 0.57 | 0.24 | 0.46 | 1 | | | | | | | | | |
| e | -0.03 | 0.03 | 0.54 | -0.34 | 0.23 | -0.15 | -0.29 | 0.68 | 0.90 | 0.51 | 0.73 | -0.58 | 0.46 | 1 | | | | | | | | |
| $Id_3$ | 0.81 | -0.74 | -0.40 | 0.02 | 0.14 | -0.07 | 0.75 | -0.50 | -0.25 | -0.25 | -0.44 | 0.49 | 0.29 | -0.18 | 1 | | | | | | | |
| Ij | -0.48 | 0.46 | 0.73 | -0.02 | -0.13 | -0.01 | -0.70 | 0.75 | 0.42 | 0.39 | 0.52 | -0.33 | 0.03 | 0.32 | -0.62 | 1 | | | | | | |
| $E_V\%$ | -0.26 | 0.20 | 0.69 | 0.26 | -0.08 | 0.04 | -0.47 | 0.79 | 0.40 | 0.25 | 0.34 | -0.35 | -0.07 | 0.27 | -0.37 | 0.89 | 1 | | | | | |
| $E_{PD}\%$ | -0.40 | 0.54 | 0.18 | -0.41 | -0.21 | 0.13 | -0.59 | 0.29 | 0.47 | 0.23 | 0.75 | -0.58 | 0.17 | 0.72 | -0.44 | 0.32 | 0.02 | 1 | | | | |
| $Imf._{AVE}$ | -0.10 | 0.07 | 0.83 | -0.44 | 0.39 | -0.26 | -0.44 | 0.60 | 0.42 | 0.79 | 0.17 | -0.03 | 0.29 | 0.28 | -0.39 | 0.71 | 0.52 | 0.27 | 1 | | | |
| Is | 0.58 | -0.42 | -0.74 | 0.18 | -0.39 | 0.09 | 0.68 | -0.66 | -0.69 | -0.76 | -0.64 | 0.26 | -0.25 | -0.44 | 0.64 | -0.61 | -0.39 | -0.38 | -0.61 | 1 | | |
| LOI | -0.65 | 0.55 | -0.08 | 0.74 | -0.02 | 0.80 | -0.58 | 0.11 | -0.01 | -0.21 | 0.05 | -0.69 | -0.87 | -0.13 | -0.45 | 0.08 | 0.13 | 0.02 | -0.13 | -0.15 | 1 | |
| Ro% | 0.34 | -0.17 | -0.22 | 0.01 | -0.49 | -0.01 | 0.24 | -0.30 | -0.46 | -0.37 | -0.18 | 0.46 | 0.13 | -0.33 | 0.50 | 0.16 | 0.23 | -0.24 | 0.02 | 0.46 | -0.47 | 1 |

Table 9.9. Correlation matrix for the mudstone samples. (8 samples)

| | %Q+F | % Clay | % MLC | $\%C_{OR}$ | Carb's | Icrys | Dia.rank | $MC\%_{AS}$ | $MC\%_{A}$ | $MC\%_{NAT}$ | MBA | γdry | $G_s$ | e | $Id_3$ | Ij | $E_V\%$ | $E_{PD}\%$ | $Imf._{AVE}$ | Is | LOI | Ro% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| %Q+F | 1 | | | | | | | | | | | | | | | | | | | | | |
| % Clay | -0.89 | 1 | | | | | | | | | | | | | | | | | | | | |
| % MLC | -0.32 | 0.33 | 1 | | | | | | | | | | | | | | | | | | | |
| $\%C_{ORG}$ | -0.40 | 0.07 | -0.08 | 1 | | | | | | | | | | | | | | | | | | |
| Carb's | -0.09 | -0.05 | -0.37 | 0.08 | 1 | | | | | | | | | | | | | | | | | |
| Icrys | 0.02 | 0.13 | 0.38 | -0.31 | -0.04 | 1 | | | | | | | | | | | | | | | | |
| Dia.rank | 0.41 | -0.32 | -0.67 | -0.35 | 0.22 | -0.56 | 1 | | | | | | | | | | | | | | | |
| $MC\%_{AS}$ | -0.31 | 0.14 | 0.68 | 0.39 | -0.21 | 0.02 | -0.72 | 1 | | | | | | | | | | | | | | |
| $MC\%_{AD}$ | -0.51 | 0.51 | 0.83 | 0.09 | -0.43 | 0.43 | -0.81 | 0.63 | 1 | | | | | | | | | | | | | |
| $MC\%_{NAT}$ | -0.64 | 0.64 | 0.80 | -0.01 | -0.37 | 0.39 | -0.59 | 0.50 | 0.72 | 1 | | | | | | | | | | | | |
| MBA | -0.30 | 0.17 | 0.84 | 0.34 | -0.40 | 0.23 | -0.83 | 0.89 | 0.85 | 0.60 | 1 | | | | | | | | | | | |
| γdry | 0.32 | -0.05 | -0.07 | -0.88 | -0.17 | -0.08 | 0.61 | -0.50 | -0.30 | 0.00 | -0.50 | 1 | | | | | | | | | | |
| $G_s$ | 0.39 | -0.12 | 0.21 | -0.90 | -0.33 | 0.03 | 0.35 | -0.12 | -0.03 | 0.11 | -0.15 | 0.89 | 1 | | | | | | | | | |
| e | 0.19 | -0.23 | 0.56 | 0.01 | -0.33 | 0.18 | -0.56 | 0.82 | 0.52 | 0.21 | 0.76 | -0.25 | 0.21 | 1 | | | | | | | | |
| $Id_3$ | 0.60 | -0.45 | -0.77 | -0.37 | 0.21 | -0.17 | 0.69 | -0.84 | -0.68 | -0.83 | -0.81 | 0.40 | 0.16 | -0.50 | 1 | | | | | | | |
| Ij | -0.43 | 0.35 | 0.83 | 0.26 | -0.27 | 0.15 | -0.78 | 0.93 | 0.72 | 0.69 | 0.89 | -0.37 | -0.05 | 0.68 | -0.89 | 1 | | | | | | |
| $E_V\%$ | -0.33 | 0.18 | 0.61 | 0.44 | -0.11 | -0.19 | -0.59 | 0.91 | 0.48 | 0.39 | 0.78 | -0.47 | -0.19 | 0.63 | -0.75 | 0.91 | 1 | | | | | |
| $E_{PD}\%$ | -0.25 | 0.00 | 0.52 | 0.50 | -0.24 | -0.19 | -0.64 | 0.78 | 0.53 | 0.27 | 0.79 | -0.51 | -0.27 | 0.56 | -0.54 | 0.74 | 0.81 | 1 | | | | |
| $Imf._{AVE}$ | -0.50 | 0.52 | 0.88 | -0.07 | -0.39 | 0.31 | -0.56 | 0.64 | 0.71 | 0.95 | 0.69 | 0.04 | 0.25 | 0.43 | -0.88 | 0.79 | 0.54 | 0.34 | 1 | | | |
| Is | 0.51 | -0.49 | -0.60 | -0.27 | 0.29 | -0.39 | 0.85 | -0.74 | -0.87 | -0.56 | -0.79 | 0.52 | 0.20 | -0.64 | 0.69 | -0.72 | -0.55 | -0.47 | -0.58 | 1 | | |
| LOI | -0.59 | 0.27 | -0.04 | 0.92 | 0.26 | -0.06 | -0.48 | 0.36 | 0.21 | 0.14 | 0.32 | -0.90 | -0.93 | -0.06 | -0.43 | 0.27 | 0.35 | 0.41 | 0.01 | -0.40 | 1 | |
| Ro% | 0.24 | -0.20 | -0.22 | -0.32 | 0.17 | -0.50 | 0.68 | -0.55 | -0.49 | -0.33 | -0.50 | 0.57 | 0.30 | -0.55 | 0.50 | -0.43 | -0.26 | -0.15 | -0.33 | 0.81 | -0.45 | 1 |

Table 9.10. Correlation matrix for the laminated or fissile mudstone samples. (10 samples)

### *9.2.3.4. Assessment of fissile/laminated mudstone durability.*

The fissile/laminated mudstones studied consisted of 10 samples. The correlation coefficient matrix is presented in Table 9.10. There are a number of strong correlations:

- $Id_3$ : %MLC (r = –0.77), $MC_{AB}$ (r = –0.84), $I_J$ (r = –0.89), $MC_{NAT}$ (r = –0.83), MBA (r = –0.81), $I_{MF}$ (r = –0.88), Ev% (r = –0.75).
- $I_J$ : %MLC (r = 0.83), DRP (r = –0.78), $MC_{AB}$ (r = 0.93), MBA (r = 0.89), $Id_3$ (r = –0.89), Ev% (r = 0.91), $I_{MF}$ (r = 0.79).
- Ev% : $MC_{AB}$ (r = 0.91), MBA (r = 0.78), $Id_3$ (r = –0.75), $I_J$ (r = 0.91), $E_{PD}$ (r = 0.81).
- $I_S$ : DRP (r = 0.85), $MC_{AD}$ (r = –0.87), MBA (r = –0.79), %Ro (r = 0.81).

These correlations indicate that clay mineralogy and the distribution of microfractures along with rock fabric (such as particle orientation and organic laminae) control the durability of laminated and fissile mudrocks, the microfractures in this lithotype commonly develop as a result of the fissility and lamination as discussed by Ingram (1953) and Spears (1976). Additionally important correlations also exist between the mixed layer clay content and microfracture index (r = 0.88) and between natural moisture content and microfracture index (r = 0.95). These correlations also show that microfracture development could be due to stress relief effects. The results from the expansion and contraction of expansive clays and the formation of fractures due to natural exposure and weathering explains the importance of natural moisture content to $Id_3$.

### *9.2.3.5 . Assessment of siltstone durability.*

The siltstones studied consisted of 6 samples. The correlation coefficient matrix is presented in Table 9.11, and the most significant correlations are as follows:

- $Id_3$ : $MC_{NAT}$ (r = –1.00), Gs (r = 0.87).
- $I_J$ : Ev% (r = 0.78).

- Ev% : % Clay ($r = -0.85$), $I_J$ ($r = 0.78$).
- $I_S$ : DRP ($r = 0.79$), $MC_{AB}$ ($r = -0.87$), $\gamma$dry ($r = 0.77$), Gs ($r = 0.78$), $I_{MF}$ ($r = 0.93$), LOI ($r = 0.75$), %Ro ($r = 0.97$).

| | %Q+F | % Clay | % MLC | $\%C_{OR}$ | Carb's | Icrys | Dia.rank | $MC\%_{AB}$ | $MC\%_{A}$ | $MC\%_{NAT}$ | MBA | $\gamma$dry | $G_s$ | e | $Id_3$ | Ij | $E_V\%$ | $E_{PD}\%$ | $Imf._{AVE}$ | Is | LOI | Ro% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| %Q+F | 1 | | | | | | | | | | | | | | | | | | | | | |
| % Clay | -0.85 | 1 | | | | | | | | | | | | | | | | | | | | |
| % MLC | -0.62 | 0.42 | 1 | | | | | | | | | | | | | | | | | | | |
| $\%C_{ORG}$ | -0.14 | -0.13 | -0.10 | 1 | | | | | | | | | | | | | | | | | | |
| Carb's | -0.12 | -0.67 | 0.15 | 0.23 | 1 | | | | | | | | | | | | | | | | | |
| Icrys | -0.11 | -0.61 | 0.16 | -0.01 | 0.93 | 1 | | | | | | | | | | | | | | | | |
| Dia.rank | 0.35 | -0.58 | -0.86 | 0.28 | 0.32 | 0.28 | 1 | | | | | | | | | | | | | | | |
| $MC\%_{AB}$ | 0.10 | 0.18 | 0.64 | -0.08 | -0.24 | -0.24 | -0.84 | 1 | | | | | | | | | | | | | | |
| $MC\%_{AD}$ | -0.33 | 0.04 | 0.83 | 0.10 | 0.36 | 0.21 | -0.68 | 0.64 | 1 | | | | | | | | | | | | | |
| $MC\%_{NAT}$ | 0.01 | 0.42 | 0.45 | -0.43 | -0.47 | -0.22 | -0.69 | 0.69 | 0.07 | 1 | | | | | | | | | | | | |
| MBA | 0.28 | -0.14 | 0.34 | 0.44 | -0.04 | -0.19 | -0.46 | 0.82 | 0.57 | 0.27 | 1 | | | | | | | | | | | |
| $\gamma$dry | 0.23 | -0.44 | -0.72 | -0.13 | 0.28 | 0.26 | 0.84 | -0.89 | -0.53 | -0.75 | -0.71 | 1 | | | | | | | | | | |
| $G_s$ | -0.37 | -0.14 | -0.33 | 0.31 | 0.45 | 0.32 | 0.66 | -0.87 | -0.21 | -0.87 | -0.61 | 0.75 | 1 | | | | | | | | | |
| e | -0.60 | 0.45 | 0.74 | 0.53 | 0.03 | -0.07 | -0.61 | 0.57 | 0.62 | 0.30 | 0.57 | -0.81 | - 0.23 | 1 | | | | | | | | |
| $Id_3$ | 0.00 | -0.44 | -0.45 | 0.37 | 0.50 | 0.26 | 0.69 | -0.70 | -0.07 | -1.00 | -0.30 | 0.77 | 0.87 | -0.34 | 1 | | | | | | | |
| Ij | 0.27 | -0.54 | 0.40 | -0.33 | 0.54 | 0.52 | -0.29 | 0.43 | 0.67 | 0.04 | 0.34 | -0.09 | - 0.27 | -0.08 | 0.01 | 1 | | | | | | |
| $E_V\%$ | 0.57 | -0.85 | 0.00 | 0.18 | 0.60 | 0.48 | 0.10 | 0.32 | 0.43 | -0.19 | 0.58 | -0.02 | - 0.19 | -0.06 | 0.20 | 0.78 | 1 | | | | | |
| $E_{PD}\%$ | -0.54 | 0.52 | 0.90 | 0.14 | -0.07 | -0.19 | -0.87 | 0.72 | 0.85 | 0.33 | 0.55 | -0.78 | - 0.34 | 0.83 | -0.35 | 0.25 | -0.01 | 1 | | | | |
| $Imf._{AVE}$ | -0.05 | -0.59 | -0.22 | -0.04 | 0.81 | 0.89 | 0.62 | -0.64 | -0.19 | -0.43 | -0.54 | 0.62 | 0.59 | -0.38 | 0.47 | 0.22 | 0.24 | -0.54 | 1 | | | |
| Is | -0.13 | -0.43 | -0.42 | 0.07 | 0.63 | 0.68 | 0.79 | -0.87 | -0.42 | -0.59 | -0.71 | 0.77 | 0.78 | -0.44 | 0.61 | -0.12 | -0.03 | -0.66 | 0.93 | 1 | | |
| LOI | -0.02 | -0.72 | 0.18 | 0.25 | 0.98 | 0.93 | 0.25 | -0.09 | 0.39 | -0.34 | 0.12 | 0.15 | 0.28 | 0.08 | 0.36 | 0.60 | 0.70 | -0.05 | 0.75 | 0.52 | 1 | |
| Ro% | -0.08 | -0.64 | -0.11 | 0.12 | 0.89 | 0.95 | 0.55 | -0.51 | -0.05 | -0.40 | -0.35 | 0.46 | 0.52 | -0.19 | 0.43 | 0.27 | 0.36 | -0.42 | 0.97 | 0.86 | 0.86 | 1 |

Table 9.11.Correlation matrix for the siltstone samples. (6 samples)

Additional strong correlations exist between the mixed-layer clay content and powder free swell coefficient (r = 0.90), diagenetic rank parameter (r = 0.86) and moisture adsorption (r = 0.83). It is also seen that the carbonate content affects the microfracture development (r = 0.81). Therefore in siltsones there is a mineralogical control on durability. As noted by Russell (1982), the carbonate content controls the development of microfractures and the clay content affects the swelling potential. The natural moisture content provides a good indication of the potential durability of the siltstone.

## 9.3. Links between diagenesis, fabric and engineering properties of mudrocks.

The diagenetic rank of the mudstone samples was evaluated by means of measuring illite 'crystallinity', vitrinite reflectance and in conjunction with textural data by means of the diagenetic rank parameter. It can be seen in Tables 9.3 and 9.4, little correlation appears to exist between these parameters.

### 9.3.1. Illite 'crystallinity' versus vitrinite reflectance.

The correlation between these two parameters measured on 28 samples, which exclude samples with high organic and carbonate contents, gives a value of r= –0.40 the relationship can be seen in Figure 9.19.

Excluding the three samples with values in excess of %Ro = 1.5, the correlation coefficient is still only r= –0.57, there are many difficulties in correlating these two parameters, which are discussed in detail in Chapters 3 and 7. There appears to be a greater range in illite 'crystallinity' values for the mudrocks over a small range of change in vitrinite reflectance values for the samples of diagenetic rank ie. $I_C = 0.5 - 3.2$ °2θ and %Ro = 0.48 - 1.03. It is more significant to measure illite 'crystallinity' in mudrocks as this reflects upon the mineralogical state of maturity, for example, sample C31 has a %Ro = 1.67 indicating that it is late diagenetic and illite 'crystallinity' value of 1.06 °2θ suggesting an early diagenetic rank. Sample C31 is highly calcareous which has retarded the progressive development of illite 'crystallinity' due to a $K^+$ defficient environment. When subjected to the roof weathering experiment, this otherwise durable sample was found to be very unstable beyond a 6-8 month test period, when heavy slaking resulted. Of all the characterization tests performed on the samples, illite 'crystallinity' was the most capable in predicting this possible outcome.

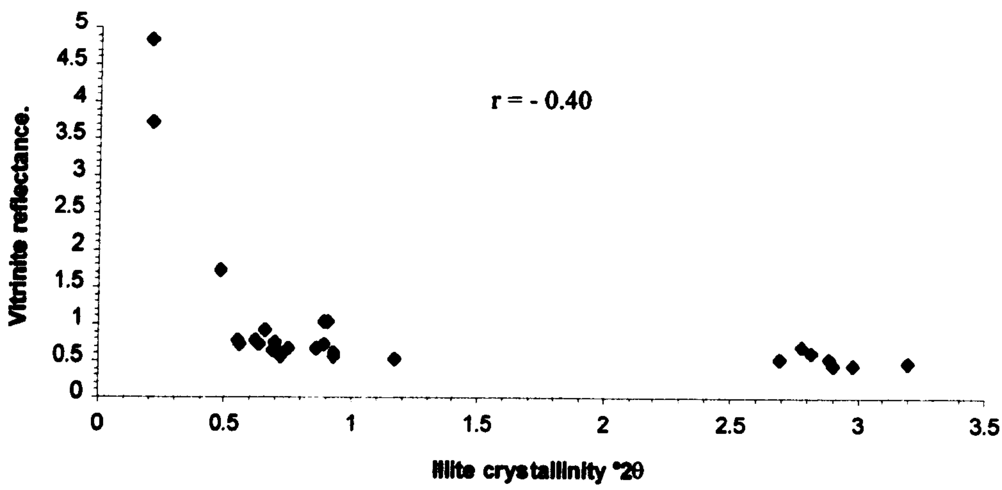


Figure 9.19. Relationship between illite 'crystallinity and vitrinite reflectance.

### 9.3.2. Illite 'crystallinity' versus diagenetic rank parameter.

A correlation of r = –0.67 exists between illite 'crystallinity' and the diagenetic rank parameter values, which does suggest a relationship exists between these two indices as seen in Figure 9.20. The diagenetic rank parameter is a measure of textural and mineralogical maturity of a sample, encompassing the state of maturity of the mineral phases present, degree of orientation of the clay minerals, extent of cementation and structural features such as voids and the distribution of microfractures. Illite 'crystallinity' only measures the state of diagenetic development of one specific mineral phase. This could be an inherent diagenetic rank dependent on the history of the source material from which the detrital illite was derived and its depositional history, or a measure of the state of change due to the diagenetic history of sedimented clay minerals. Generally, illite 'crystallinity' measurement reflects the state of development of a mudrock due to its diagenetic history. Particular geological conditions, such as a $K^+$ deficient environment, exposure to high temperature conditions of short duration, or the presence of hydrophobic mineral species such as organic carbon may affect illite 'crystallinity' development (Frey, 1987). As the diagenetic rank parameter is based on a visual evaluation of the samples level of mineral maturity and textural development as discussed previously, it is easier to apply to a sample than illite 'crystallinity' measurement, since careful sample selection is unneccessary.

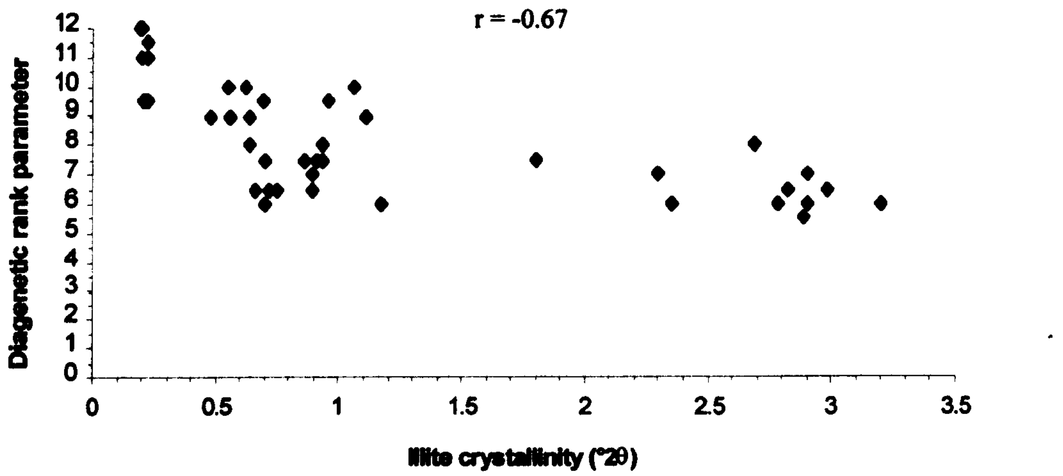


**Figure 9.20. Relationship between illite 'crystallinity and diagenetic rank parameter.**

Illite 'crystallinity' is useful for categorizing mudrocks although suitable sample selection is required and material such as siltstone, organic and carbonate rich mudrocks have to be avoided. Table 9.12, presents the categorization of the engineering properties of the samples studied. This is based on increasing diagenetic rank as defined by illite 'crystallinity', which is seen to distinguish early and mid-diagenetic mudrocks from late-diagenetic mudrocks and epizonal metamudrocks. The catagorization of the engineering properties of mudrocks is more closely defined when using the diagenetic rank parameter, as can be seen in Table 9.13. Using this parameter it is possible to separate the study samples into three catagories:

- Immature: DRP ≤ 6: These samples tend to be non-durable, weak and susceptable to swelling.
- Moderately mature: DRP 7.0 - 9.5: These samples tend to be durable, susceptable to some slaking when exposed to water, and liable to moderate swelling.

- Mature: DRP 10 - 12. These samples are highly durable, not liable to slake or swell and tend to be strong.

The diagenetic rank parameter is a very useful index in that it correlates strongly with discontinuity indices such as moisture absorption, adsorption and the jar slake index and also with mineralogical parameters, including percentage mixed-layer clay and methylene blue adsorption. It also reflects upon the durability of a sample with a strong correlation with the jar slake index and point load strength, these relationships can be seen in Figures 9.1 to 9.17 .

| Rank | No of samples | DRP | $Id_3$ % | Ij | Is (MPa) | Ev% | Ex% |
|---|---|---|---|---|---|---|---|
| Early diagenetic >1.0°2θ | 9 | 5.5-7.5 | 10.4-94.6 | 5-7 | 2.1-5.7 | 0.83-3.12 | 0.93-7.76 |
| Mid diagenetic 1.0-0.65°2θ | 7 | 6-8 | 27.8-85.6 | 3-7 | 1.3-4.5 | 0.28-6.3 | 0.74-16.6 |
| Late diagenetic 0.65-0.42°2θ | 6 | 9-10 | 81.7-98.6 | 2-5 | 4.3-7.2 | 0.32-1.69 | 0.62-4.04 |
| Anchizone 0.42-0.25°2θ | | | | | | | |
| Epizone <0.25°2θ | 6 | 9.5-12 | 98.4-99.4 | 1.5-3 | 7.6-21.6 | 0.005-0.19 | 0.016-0.57 |

Table 9.12. Engineering properties of the mudrock samples based on illite 'crystallinity' catagorization.

| | DRP | No. of samples | $Id_3$ % | Ij | Is (MPa) | Ev % |
|---|---|---|---|---|---|---|
| Immature | 5 | 1 | 10.4 | 6 | 3.6 | 1.53 |
| | 6 | 12 | 22.3-90.7 (AVE = 55.3) | 5-7 | 0.4-4.6 | 0.83-6.3 |
| Moderately mature | 7 | 8 | 63.2-94.6 (AVE = 80.6) | 3.5-6 | 2.2-5.7 | 0.26-2.55 |
| | 8 | 3 | 44.8-98 (AVE = 77.9) | 2-4 | 4.0-4.8 | 0.22-0.61 |
| | 9 | 9 | 81.7-98.4 (AVE = 93.9) | 2-5 | 3.3-10.6 | 0.33-1.69 |
| Mature | 10 | 3 | 97.5-98.6 (AVE = 98.1) | 2-3.5 | 6.9-14.8 | 0.024-0.63 |
| | 11 | 3 | 98.4-99 (AVE = 98.6) | 1.5-3 | 14-16.4 | 0.005-0.165 |
| | 12 | 2 | 99.4 (AVE = 99.4) | 1.5-2 | 15.8-21.5 | 0.046-0.08 |

Table 9.13. Mudrock classification based on the diagenetic rank parameter.

## 9.4. A systematic approach to the characterization of mudrock samples.

Detailed characterization of mudrock samples requires a systematic approach. Much information can be effectively obtained without being too costly,but the possible need for additional investigations must be recognised. Detailed characterization of mudrocks may involve the use of important and yet costly analytical techniques such as X-ray diffraction, scanning electron microscopy and mercury porosimetry. Where many samples are to be studied in a project, a representative selection of samples should be subjected to detailed laboratory characterization of the mineralogy, texture and engineering properties. In this study it is evident that certain simple index tests correlate strongly with fundamental aspects of mudrock mineralogy and texture, which control their engineering behaviour. Therefore for efficient mudrock characterization, detailed laboratory investigations on selected representative samples should be carried out in the following areas:

(A) Mudrock classification:

- A detailed classification based on the clastic content of the sample (% quartz and feldspars) as determined by X-ray diffraction (Spears, 1980 and Taylor, 1988).
- A detailed description of structural features such as laminae and the extent of fissility development, based on hand specimen descriptions using a binocular microscope, and where possible textural description using back-scattered scanning electron microscopy.
- Characterization of the diagenetic rank of the material based on illite 'crystallinity' measurement using of the terminology presented in Table 9.14.

| Illite 'crystallinity' -(°2θ) | Diagenetic rank | Descriptive term |
|---|---|---|
| >1.0 | Early diagenetic | Early diagenetic mudrock |
| 1.0 - 0.65 | Mid diagenetic | Mid diagenetic mudrock |
| 0.65 - 0.42 | Late diagenetic | Late diagenetic mudrock |
| 0.42 - 0.25 | Anchizone | Metamudrock |
| < 0.25 | Epizone | Mature metamudrock |

Table 9.14 . Diagenetic terms for mudrocks based on illite 'crystallinity' determination.

(B) Textural description:

- A detailed textural classification obtained using back-scattered scanning electron microscopy and the diagenetic rank parameter classification. This is presented in

Table 7.3 of Chapter 7. From this analysis the samples can be texturally classified according to the terms presented in Table 9.15 .

| Diagenetic rank parameter | Textural classification |
|---|---|
| <6.5 | Immature |
| 7 - 9.5 | Moderately mature |
| 10 - 12 | Mature |

Table 9.15. Textural rank classification based on the diagenetic rank parameter.

- The modified jar slake index provides an additional means of textural classification since the test monitors the extent of microfracture development according to the classification scheme presented in Table 6.5, Chapter 6.

(C) Mudrock mineralogy:

- A detailed analysis of the mineral phases is essential for the following reasons
  - Durability-classification, based on quartz and feldspar content.
  - Clay mineralogy, especially the quantity of mixed layer clays or smectite present in the sample, and the extent of conversion/recrystallization to the illite end member as determined by illite 'crystallinity'
  - Cement phases, including carbonates and organic carbon content which has been found effectively to improve the durability of mudrocks.
  - Minor potential reactive phases, including pyrite and gypsum, which have a tendency to result in swelling due to oxidation, dissolution and conversion to other mineral phases (Bell, 1992).

(D) Engineering characterization: This is based principally on-

- Slaking potential. This tends to be determined based on the Franklin slake durability test, where a value of $Id_3$ >60% is used to distinguish between non-durable and durable mudrocks. It has been found in this study that it can be also determined using the modified jar slake test since, as seen in Figure 9.21, there is a correlation between these two parameters. The respective durability classification is presented in Table 9.16. This is based on a conservative estimate of the ranking correlation seen in Figure 9.21.

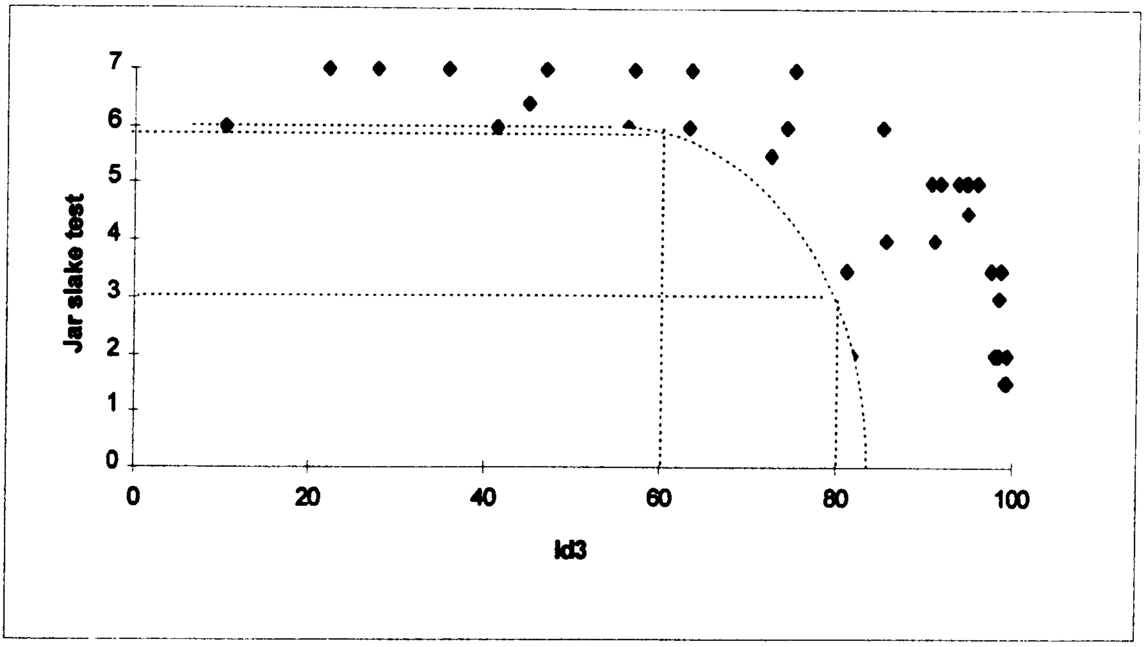


Figure 9.21. Correlation between slake durability and jar slake index.

| $Id_3$ % (after Taylor, 1988) | Ij | Durability classification |
|---|---|---|
| <60 | 6 - 8 | Non durable |
| 60 - 80 | 3 - 6 | Durable |
| >80 | 1 - 3 | Extremely durable |

Table 9.16. Correlation of durability classification based on the jar slake test and slake durability.

- Swelling potential. The susceptibility to swelling can be determined using the volumetric free swell test.
- Strength. The most effective means of determining strength of mudrocks is the point load test. This requires a minimum of sample preparation which tends to be difficult for most mudrocks due to to their susceptibility to slake when water is used to assist coring, cutting and grinding, additionally due to their brittle nature, mudrocks are proned to fracture caused by vibration. The point load test fails the sample in a tensile mode, which is controlled in mudrocks by cementation, bonding between clay mineral phases and the extent of diagenetic recrystallization of the mineral phases present in the rock. This bonding creating tensile strength is effectively the force that air breakage and swelling pressure of clay minerals has to exceed before slaking occurs.

When the initial detailed characterization of the mudrock samples has been completed, index tests can be further used to further characterize additional samples, since strong correlations have been found to exist between a number of the index tests evaluated and the mineralogical, textural and engineering properties of the mudrocks tested. From the correlation analysis for the mudrock lithotypes, the following controls were found to govern their durability. Also presented are the relevant index tests to evaluate these controls.

1. Argillites.- Their strength and durability is effectively controlled by their textural features and occasionally their mineralogy. These parameters show strong relationships with moisture absorption, jar slake index, microfracture index and methylene blue adsorption.
2. Claystones.- The major control on claystone durability is the mineralogy, principally the amount of mixed-layer clay present and the amount of organic carbon content present, and to a lesser extent the distribution of discontinuities which act as access routes for water to the sites of the expansive clays. These are most effectively determined using loss on ignition which correlates strongly with organic carbon content ($r = 0.96$ - whole data set), moisture adsorption, moisture absorption and methylene blue adsorption.
3. Mudstones.- The major controls on mudstone durability tends to be textural features such as microfractures. These are effectively determined by the jar slake index, and moisture absorption.
4. Laminated/fissile mudstones.- Their controls on durability tends to be textural and mineralogical. These controls are most effectively determined using the jar slake index, moisture absorption, methylene blue adsorption, microfracture index and moisture adsorption.
5. Siltstones.- These tend to have a strong textural control, effectively encompassing determination of porosity and microfractures. Clay mineralogy also has a slight effect on durability. These effects are determined using the jar slake index, moisture absorption, the microfracture index and methylene blue adsorption.

In the list of index characterization tests, the jar slake index, moisture absorption and methylene blue adsorption are considered to offer the highest level of confidence in characterizing mudrocks, the tests are easy to perform and the results reproducible.

Mazzoccola and Hudson (1996) produced a predictive rock mass characterization matrix for evaluating natural slope instabilities. The matrix allows selection of the control parameters which are considered to be applicable to a particular situation, and by means of a ranking system, to be evaluated. The same approach can be applied to the evaluation of mudrocks based upon simple index tests where potentially problematic material can be identified, with respect to initial detailed laboratory characterization. An example is presented below.

A simple index characterization matrix based on slake durability index, moisture absorption and methylene blue adsorption, which are ideal index tests for characterizing all mudrock lithotypes would be weighted as follows-

- Jar slake index. To monitor the slake durability of the samples, based on Figure 9.21, see Table 9.17.

| Ij | Classification | Rank |
|---|---|---|
| 1 - 3 | Extremely durable | 1 |
| 3 - 6 | Moderately durable | 2 |
| 6 - 8 | Non durable | 3 |

Table 9.17. Rank values for jar slake classification of mudrocks.

- Moisture absorption. To monitor the textural maturity of the sample, when comapred againt the diagenetic rank parameter, determined from Figure 9.22. and presented in Table 9.18.

- Methylene blue adsorption. Which is indicative of the potentially reactive mixed-layer clay content of the sample, the ranking categories are taken from Figure 9.23. A figure of 22% mixed-layer clay content was taken as the critical content after Taylor and Spears (1970), who found that effective swelling and slaking problems were commonly encountered in samples of >22% mixed layer clay. The ranking values are presented in Table 9.19.

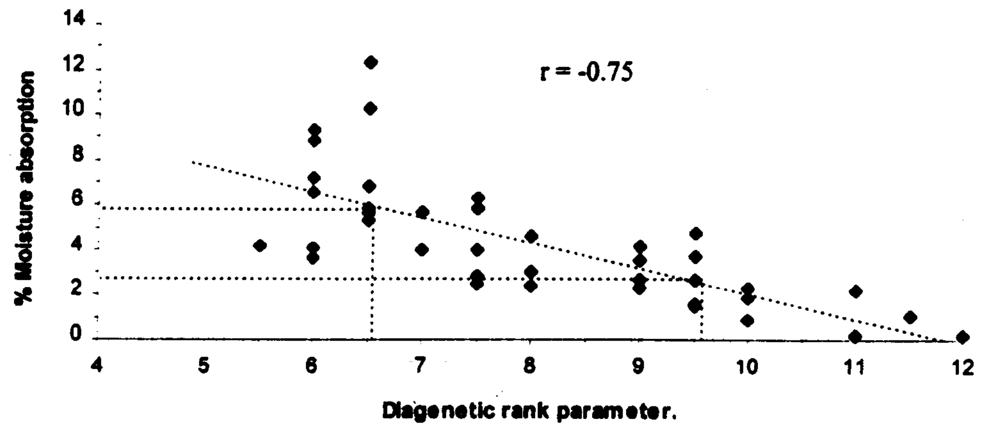


Figure 9.22. Correlation graph for ranking values of moisture absorption agains DRP.

| Moisture absorption % | Diagenetic rank parameter | Rank |
|---|---|---|
| > 6 | <6.5 | 3 |
| 3 - 6 | 7 - 9.5 | 2 |
| <3 | 10 - 12 | 1 |

Table 9.18. Rank values for moisture absorption versus DRP.

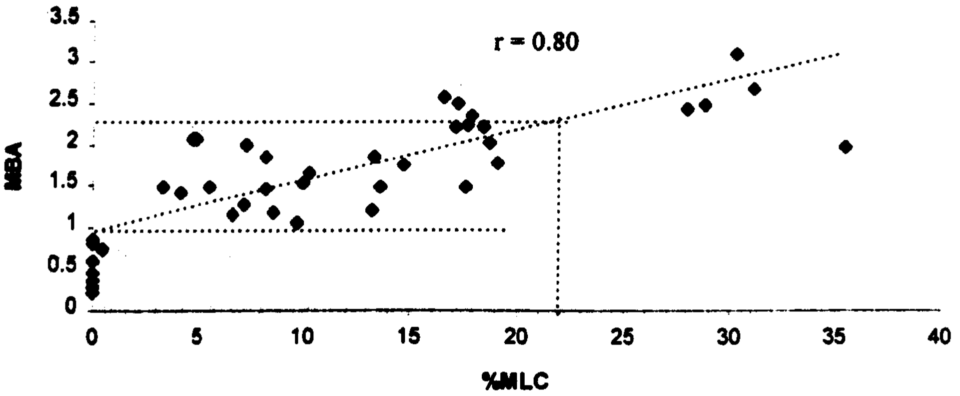


Figure 9.23. Correlation graph for ranking catagories of MBA versus % MLC.

| MBA | %MLC | Rank |
|---|---|---|
| <1 | 0 | 1 |
| 1 - 2.3 | 0 - 22 | 2 |
| >2.3 | >22 | 3 |

Table 9.19. Ranking values of MBA versus %MLC.

Using these results from the index tests a rank durability value is determined for each sample, these values are then compared with the results of the laboratory characterization tests to determine a rank value which would distinguish non-problematic mudrocks from problematic types. This kind of scheme is versatile as a selection of particular index tests can be adopted for specific lithotypes, for example the use of loss on ignition for claystones and microfracture index for laminated/fissile mudstones and siltstones. At this stage further research is required on a larger data set of mudrocks to improve this durability ranking scheme for mudrocks. This type of qualitative approach to characterization of mudrocks is considered to be more successful than the use of quantitative equations.

The rank durability values for the samples in the study were calculated and compared against measured values of $Id_3$ and Ev%, these are presented in Table 9.20. Rank values of less than 4 were classed as extremely durable samples which were not prone to swell or slake, values between 4 and 7 were classed as durable samples, and values of 7 to 9 were classed as non-durable samples. It can be seen from the results that the method was capable of identifying all the potentially problematic samples in the data set. For the durable samples, results indicate material which could exibit potential loss of durability, these samples show values of 6, and would require further characterization testing testing. The technique identifies all the extremely durable samples which can be assumed to be stable in an engineering situation. This approach is therefore useful as a cheap and rapid approach to monitoring and characterizing a large quantity of samples as would be encountered in an engineering scheme.

| Sample | Id$_3$ | Ev% | RANK | | | Rank Total Value | Classification |
|---|---|---|---|---|---|---|---|
| | | | A | B | C | | |
| Ca11 | 99.0 | 0.005 | 1 | 1 | 1 | 3 | Extremely durable |
| Ca12 | 99.4 | 0.015 | 1 | 1 | 1 | 3 | Extremely durable |
| Ca13 | 99.4 | 0.029 | 1 | 1 | 1 | 3 | Extremely durable |
| O11 | 56.9 | 2.07 | 3 | 2 | 3 | 8 | **Non-durable** |
| O12 | 35.8 | 1.73 | 3 | 3 | 3 | 9 | **Non-durable** |
| O21 | 98.5 | 0.03 | 1 | 1 | 1 | 3 | Extremely durable |
| O31 | 98.4 | 0.165 | 1 | 1 | 1 | 3 | Extremely durable |
| S11 | 94.6 | 1.08 | 2 | 2 | 2 | 6 | Durable |
| S31 | 98.6 | 0.43 | 1 | 1 | 1 | 3 | Extremely durable |
| S32 | 98.2 | 0.024 | 1 | 1 | 1 | 3 | Extremely durable |
| D11 | 94.9 | 0.46 | 2 | 2 | 1 | 5 | Durable |
| D12 | 97.6 | 1.17 | 2 | 2 | 2 | 6 | Durable |
| D21 | 98.4 | 0.19 | 1 | 1 | 1 | 3 | Extremely durable |
| C1B1 | 97.5 | 0.875 | 2 | 1 | 2 | 5 | Durable |
| C1B2 | 91.8 | 1.69 | 2 | 1 | 2 | 5 | Durable |
| C1B4 | 97.5 | 0.35 | 1 | 1 | 2 | 4 | Extremely durable |
| C1B5 | 85.0 | 1.65 | 3 | 1 | 2 | 6 | Durable |
| C21 | 46.8 | 3.12 | 3 | 3 | 3 | 9 | **Non-durable** |
| C31 | 97.5 | 0.63 | 1 | 1 | 2 | 4 | Extremely durable |
| C41 | 74.3 | 1.15 | 3 | 3 | 3 | 9 | **Non-durable** |
| C51 | 27.8 | 2.79 | 3 | 3 | 2 | 8 | **Non-durable** |
| C52 | 44.8 | 0.285 | 1 | 1 | 2 | 4 | **Non-durable** |
| C61 | 56.2 | 1.49 | 3 | 2 | 2 | 7 | **Non-durable** |
| C71 | 85.2 | 2.55 | 3 | 2 | 2 | 7 | **Non-durable** |
| C82 | 22.3 | 3.39 | 3 | 3 | 3 | 9 | **Non-durable** |
| C83 | 81.7 | 0.32 | 1 | 2 | 2 | 5 | Durable |
| C92 | 98.0 | 0.22 | 1 | 1 | 2 | 4 | Extremely durable |
| C101 | 63.2 | 1.86 | 3 | 2 | 3 | 8 | **Non-durable** |
| C111 | 56.9 | 6.3 | 3 | 3 | 3 | 9 | **Non-durable** |
| C112 | 81.2 | 0.28 | 1 | 2 | 2 | 5 | Durable |
| C121 | 75.2 | 3.79 | 3 | 2 | 2 | 7 | **Non-durable** |
| C122 | 85.6 | 0.7 | 2 | 1 | 2 | 5 | Durable |
| C131 | 41.4 | 2.18 | 3 | 2 | 2 | 7 | **Non-durable** |
| C132 | 91.0 | 0.61 | 2 | 2 | 2 | 6 | Durable |
| C133 | 10.4 | 1.53 | 3 | 2 | 2 | 7 | **Non-durable** |
| C141 | 63.3 | 2.92 | 3 | 3 | 3 | 9 | **Non-durable** |
| C151 | 72.4 | 0.83 | 2 | 2 | 2 | 6 | Durable |
| C161 | 93.8 | 0.26 | 2 | 3 | 2 | 7 | **Non-durable** |
| C171 | 91.1 | 0.84 | 2 | 2 | 2 | 6 | Durable |
| C172 | 94.8 | 0.33 | 2 | 1 | 2 | 5 | Durable |
| C181 | 90.7 | 0.87 | 2 | 2 | 2 | 6 | Durable |

A = Jar slake index : B = Moisture absorption : C = Methylene blue index.

**Table 9.20. Table of durability classification based on the rank durability approach.**

# Chapter 10.

# Conclusions.

## 10.1. General conclusions.

### 10.1.1. Overview.

The objective of the research was to determine the control diagenetic rank exerts on detailed mineralogy, texture and geotechnical properties of mudrocks. To do this indurated samples were chosen to provide a range of illite 'crystallinities' and weathering grades in mudrocks which were otherwise similar. These samples were then subjected to a rigorous laboratory testing schedule to determine their mineralogy, diagenetic rank, textural and engineering properties.

The mineralogy of the samples were analysed in detail using standard wet chemical techniques in addition to analytical techniques such as X-ray diffraction, inductive coupled plasma atomic emission spectroscopy, X-ray fluorescence and scanning electron microscope energy dispersive X-ray analysis. The diagenetic rank of the samples was determined by means of illite 'cystallinity' measurement using X-ray diffraction analysis and vitrinite reflectance measurement using microscopic analysis.

The samples were texturally evaluated by means of visual description of structural features such as lamination and fissility. In addition the samples were examined petrographically using standard optical microscopy and back-scatter electron microscopy. Textural analysis also included evaluating void distribution within the samples, which consisted of total porosity determination using index phase relationships and relative porosity determined by means of mercury *intrusion porosimetry*. The microfracture distribution in the samples was determined by visual observation.

The mudrock samples were subjected to a suite of engineering tests, concentrating specifically on determining swelling, slaking and strength properties. In addition to standard engineering testing a series of simple index tests were evaluated to determine their practical use in the characterization of mudrocks.

Selected mudrock samples were subjected to a natural weathering experiment to evaluate their slaking potential. Additional samples subjected to the natural weathering experiment were treated with regular additions of selected chemical reagents in an attempt to promote sample breakdown by the removal of cement material, and breakdown natural clay bonding forces.

The overall conclusions of each section are summarised below. In section 10.2 a critical review of the experimental programme is presented. On the basis of this work, recommendations for future research into mudrocks is outlined in section 10.3.

### 10.1.2. Classification of mudrocks.

It was generally found that different approaches to mudrock description and classification have been adopted by geoscientists specialising in different fields of geology which has lead to much confusion over nomenclature, and general application of some of the classification schemes developed.

- The use of the term shale should be avoided when describing mudrocks. Fissility and laminations in mudrocks are important features which should be described by the use of prefixes of these features before the mudrock name.
- Lithified mudrocks should not be classified by means of particle size analysis or consistency limits. These techniques are generally suitable for sediments and poorly lithified mudrocks which tend to disaggregate down to their constituent grain size with gentle aggitation in water, although observational checks are recommended. Disaggregation of lithified mudrocks tends to employ aggressive techniques which produces artificial sizes of aggregated grain size distribution which does not represent the true range of fundamental particles present. Indurated mudrocks should be classified by means of their mineralogy, specifically their clastic content ( % quartz and feldspar) as determined by X-ray diffraction techniques.

In mudrocks with high organic and carbonate contents, the terms organic and calcareous should be used as prefixes. Where the clay mineralogy of the mudrock has been evaluated and clay mineral species which are proned to swelling are detected such as smectite, mixed-layer clays and vermiculite, these should be included in the description of the sample.

### 10.1.3. Mineralogy.

The mineralogy of the mudrocks was accurately determined by employing specific wet chemical and analytical chemistry techniques specifically to quantify each non-clay mineral component.

- The clay minerals were determined by X-ray diffraction analysis of the < 2μm size fraction, which is considered more reproducible than attempting to quantify clay minerals from whole rock analysis, since clay mineral orientation of the X-ray sample preparations is critical for clay mineral quantification. The quantitative clay mineralogy of the samples was taken as constituting the remainder of the sample after determination of the non-clay mineralogy. This approach is not without problems but is considered to be more suitable than whole rocks determinations.
- Appropriate wet chemical techniques were used to quantify carbonates, organic carbon and pyrite in the samples to evaluate their effects as cements on the durability of the samples. The wet chemical methods were slightly modified to take advantage of new technology and to provide a higher level of reproducibility in the determinations without losing the ease of application of the techniques.

### 10.1.4. Diagenesis and texture.

Diagenetic rank and textural determinations were carried out by X-ray and vitrinite reflectance methods. The work allowed these parameters to be correlated with each other and other parameters.

- Illite 'crystallinity' measurement on mudrocks samples suffers from many mineralogical constraints therefore cannot be used in relation to all mudrocks. Samples need to be carefully selected avoiding where possible siltstones, carbonate rich and highly calcareous samples, in which development of illite 'crystallinity' tends to be retarded. The effects of adverse mineralogies is evident by the poor correlation between illite 'crystallinity' and the vitrinite reflectance of some of the samples.

- Illite 'crystallinity' is recommended as a means of diagenetically classifying mudrocks for engineering use in preference to vitrinite reflectance. Since illite 'crystallinity' is a reflection of the maturity of the clay mineral suite of the mudrocks, which are a major control on engineering behaviour of the samples.
- The pore size distribution of indurated mudrocks shows little correlation with diagenetic rank, since such rocks have usually undergone mass consolidation resulting in mineral rearrangement and extreme reduction in void distribution producing an inherent low porosity by the onset of lithification. Lithification also results in cementation and clay mineral recrystallisation which has occupied available pore space.
- Microfractures are an important textural feature which controls the durability of mudrocks. They tend to correlate with diagenetic rank with an overall reduction in microfractures being evident with increasing diagenetic rank due to stabilisation of the mudrock by cementation and clay mineral recrystallization.
- Classification by means of back-scattered scanning electron imagery has proved to be the most effective means of textural characterization of mudrocks, along with the specifically devised diagenetic rank parameter classification scheme. The diagenetic rank parameter has proved to be very effective in predicting geotechnical properties of mudrocks, and it is recommended that this technique should be used in routine characterization of mudrocks.
- Standard petrographic thin section analysis of mudrocks provide limited textural information, this information can be more effectively obtained by the use of back-scattered scanning electron imagery.

### 10.1.5. Engineering behaviour.

Various techniques were employed to assess the engineering performance of the material and also to provide data on the structure and nature of the samples.

- Swelling and slaking properties of mudrocks have been shown to be controlled by the distribution of microfractures, the presence of expandable clay mineral species and the extent of carbonate and calcareous cementation.

- The slake durability test is only suitable for distinguishing durable from non-durable mudrocks. The modified jar slake test is also capable of distinguishing between durable and non-durable mudrocks. In addition it proves to be more sensitive in catagorising the rate and extent of mudrocks slaking, and is therefore an invaluable index test for the durability classification of mudrocks.
- The level of diagenetic maturity of mudrocks governs their geotechnical properties. With an increase in durability resulting from the elimination of microfractures due to cementation and clay mineral recrystallization, strengthening of the rock fabric and reduction of expansive clay mineral species with increasing diagenetic rank.
- Certain simple index tests have been found to correlate strongly with more sophisticated geotechnical laboratory testing of mudrocks since they are also controlled by the rock fabric and mineralogy.

### 10.1.6. Natural slaking experiment.

Samples were exposed to natural weathering and enhanced natural weathering involving the use of reagents intended to assist the removal of cements and promote clay mineral swelling.

- The chemical reagents used to enhance mudrock breakdown were generally found not to be much more effective than natural weathering. The notable exceptions were found in the less indurated, poorly to non-cemented mudrocks. It is therefore concluded that the principal control on indurated mudrock breakdown tends to be mechanical in the form of air breakage along discontinuities.
- In the highly calcareous mudrocks the slaking rate and extent was found to be slightly enhanced with the addition of specific acids that gradually dissolved the carbonate cement. Therefore in carbonate cemented mudrocks, physico-chemical mechanisms are also an important control on breakdown.
- The organic carbon content of the mudrocks was found to enhance their natural resistance to slaking. It was found that as organic carbon content increased, then the mudrocks proved to be more durable.

- Since the slaking of indurated mudrocks was found to be mainly dominated by mechanical processes, laboratory durability testing using the modified jar slake test was found to be effective in predicting the breakdown of the mudrocks under exposure to natural weathering conditions.

### 10.1.7. Test data evaluation.

The data were examined for consistency and inter parameter correlations bearing in mind both the nature of the samples and the determinations.

- Many strong correlations were found between several factors controlling mudrock durability, therefore the evaluation of mudrock durability cannot be based upon a single characteristic property.
- Textural determinations of mudrocks using the diagenetic rank parameter proved to be the most effective characterization approach to the prediction of geotechnical properties, and therefore should be used as a routine basis of mudrock characterization. The jar slake test provides a basis of discontinuity characterization and therefore should also be adopted as a standard test method.
- Certain index tests were found to correlate strongly with mineralogical, textural and engineering properties of mudrocks. The use of these index tests in the form of a ranking matrix approach forms a cheap, reliable and accurate approach to the characterization of mudrocks. The approach can be adapted to specific situations by selecting specific index tests to monitor dominant controls for specific mudrock lithotypes.

## 10.2. Critical review of the experimental programme.

A clear connection between the diagenesis of mudrocks and their geotechnical behaviour has been established in this study, although the number of samples analysed is considered too few for such correlations to be applied universally. Some of the mudrocks tested tended to have adverse mineralogies for illite 'crystallinity' measurement, so a more rigorous sample selection procedure would have eliminated unsuitable samples, although the use of the diagenetic rank parameter overcame this problem.

A detailed mineralogical assessment of the samples was made and the effects of discrete or recrystallised form of cementation was evaluated using the diagenetic rank parameter, but the role of amorphous inorganic constituents such as sesquioxide cements was ignored. This point would need to be addressed in any future work.

Difficulties in replicate testing were encountered for a few of the less indurated samples since sample collection proved to be difficult, as poor natural exposure limited the collection of adequate block samples.

To monitor the controls of increasing diagenetic rank a selection of borehole samples collected over of depth range of a few hundred metres or over an adequate diagenetic profile require to be investigated. Unfortunately adequate material was not available as part of this study.

The roof weathering experiment was conducted as a qualitative test, since during adverse weather conditions the leachate tended to be lost due to water overflow from the 500 ml water sample containers. If the total quantity of leachate could have been collected a quantitative determination of the rate and extent of mineral breakdown could have been made, this should be addressed in future research experiments.

## 10.3. Suggestions for future research.

During the course of this research, certain potential directions for future research have been identified.

- The development of an adequate approach towards the accurate determination of the bulk clay mineralogy of mudrock samples.
- Detailed investigation of the changes in mudrock fabric during natural weathering, concentrating on the controls on fracture initiation and development, and the rates and affects of mineralogical breakdown.
- Investigation into the role of organic carbon on the durability of mudrocks, consisting of testing similar rank material with a wide range of organic content and otherwise similar mineralogies.

- To investigate the distribution and controls on durability of sulphur mineral species in mudrocks, with the development of a rigorous analytical testing procedure.
- To assist in the determination of total organic content of mudrocks the composition of organic material of varying diagenetic rank needs to be investigated.
- Determination of amorphous components and their effects on engineering behaviour and durability.
- The findings of this study have been encouraging, but the findings are based on a small number of samples, therefore additionl investigations on a larger suite of samples is recommended. Additional work is also required on anchizonal mudrocks which were not available for this study. With additional testing the mudrock characterization matrix based on index testing requires practical application to tests its validity.
- Work on similar formations which have been subjected to different geological histories.
- Work on material with the same diagenetic history but different lithologies ie. in one cyclothem.

## References.

AHN J.H. and PEACOR R.,(1986). Transmission and analytical electron microscopy of the smectite to illite transition. Clays and Clay Minerals, **34** , pp. 165-179.

ANDERSON W.F. and CRIPPS J.C.,(1993). The effects of acid leaching on the shear strength of Namurian shale. In: The Engineering Geology of Weak Rock. Engineering Geology Special Publication, **8**. (Eds. J.C.Cripps et al.) Balkema, Rotterdam, pp159 -168.

ANON (1995). The description and classification of weathered rocks for engineering purposes. Working Party Report, Q. J. eng. Geol. London, **28**, pp. 207-242.

ANON (1982). The Penguin Dictionary of Geology. Penguin, London, pp. 495.

Al-DABBAGH T.H.,(1986). A study of residual shear strength of Namurian Shale in respect of slopes in North Derbyshire. Unpublished Ph.D Thesis, University of Sheffield.

A.S.T.M.,(1987). American Society for Testing and Materials, Soils and Rock; Building Stones: annual book of ASTM standards 4.08, ASTM, Philadelphia, Pennsylvania, pp. 1189.

A.S.T.M. C837 (1986). American Society for Testing and Materials, Standard test method for methylene blue adsorption index of clay, ASTM, Philadelphia, Pennysylvania, 15.02, pp.275-276.

BADGER C.W.,CUMMINGS A.D and WHITMORE P.L.,(1956). The Dissintegration of Shales in Water. J. Inst. Fuel. **29**, pp. 417-423.

BALDWIN B.,(1971).Ways of deciphering compacted sediments. J. Sediment. Petrol., **41**, pp. 293-301.

BASSETT J., DENNEY R. C., JEFFERY G. H. and MENDHAM J.,(1978). Vogel's textbook of quantitative inorganic analysis. Longman, London, pp. 925.

BATCHELDER M.,(1995). The performance of mudrocks for leachate containment: mineralogical and chemical constraints. Unpublished PhD thesis, University of London, pp. 220.

BATES R.L and JACKSON J.A., (1987). Glossary of Geology. American Geological Institute, Virginia.

BAYLIS P.,(1986).Quantitative analysis of sedimentary minerals by powder X-ray diffraction. Powder Diffraction, **1**, pp.37-39.

BEAVINS F.C., (1989). Engineering Geology. Blackwell Scientific Publications, pp. 231.

BEAVINS E.R. and ROBINSON D.,(1992). Low-grade metamorphism. Geology Today, **8**, pp.23-27.

BELL F.G.,(1992). Engineering properties of soils and rocks. Butterworth Heinmann, pp. 345

BELL F.G (Ed).,(1992-b). Engineering in rock masses.Butterworth Heinmann Ltd., pp. 580

BELL F.G., CRIPPS J.C., CULSHAW M.G. and ENTWISTLE D.,(1993). Volume changes in weak rocks: Predictions and measurement. In: Geotechnical Engineering of Hard Soils-Soft Rocks, (Eds. Anagnostopoulos et al.), Balkema, Rotterdam pp. 925 - 932.

BERKOVITCH I., MANACKERMAN M., and POTTER N.M.,(1959). The shale breakdown problem in coal washing. Part 1- assessing the breakdown of shales in water. J. Inst. Fuel. **32**. pp. 579-589.

BISCAYE P.E.,(1965). Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. Geol. Soc. Amer. Bull., **76**, pp. 803-831.

BLATT H.,(1982). Sedimentary Petrology. W.H.Freeman and Company, USA, pp. 564.

BLATT H and SCHULTZ D.J., (1976). Size distribution of quartz in mudrock. Sedimentology. **23**. pp. 857-866.

BLATT H., MIDDLETON G.and MURRAY R., (1980). Origin of Sedimentary Rocks. Prentice-Hall, New Jersey.

BLATT H., JONES R.L. and CHARLES R.G.,(1982). Separation of quartz and feldspars from mudrocks. J. Sediment. Petrol., pp.660-662.

BLENKINSOP T.G.,(1988). Definition of low-grade metamorphic zones using illite crystallinity. J. Metamorphic Geol., **6**, pp. 623-636.

BOLES J.R. and FRANKS S.G.,(1979). Clay diagenesis in Wilcox sandstones of southwest Texas: Implications of smectite diagenesis on sandstone cementation. J. Sediment. Petrol., **49**, pp. 55-70.

BOOTH C. A.,(1996). The geochemistry, mineralogy, palynology and petrology of the Clowne coal seam, North Derbyshire. Unpublished PhD thesis, University of Sheffield, pp.386.

BOSTICK N.H.,(1974). Phytoclasts as indicators of thermal metamorphism, Franciscan Assemblage and Great Valley Sequence (Upper Mesozoic), California. Geol. Soc. Amer. Spec. Paper, **153**, pp. 1-17.

BRINDLEY G.W. and BROWN G.,(Eds) (1984). Crystal Structures of Clay Minerals and Their X-Ray identification. Mineralogical Society, London. pp. 495.

BROCH E. and FRANKLIN J.A.,(1972). The point-load strength test. Int. J. Rock Mech. Min. Sci. **9**, pp.669-697.

BROWN G. and BRINDLEY G.W.,(1980). X-ray diffraction procedures for clay mineral identification. In: Crystal structures of clay minerals and their X-ray identification (Eds. G.W. Brindley and G.Brown). Mineralogical Soc.London, pp. 305-360.

BROWN E.T., (Ed) (1981). Rock characterisation, Testing and Monitoring. Pergamon , Oxford.

BRITISH STANDARDS 5930 (1981). Code of Practice for Site Investigation. British Standards Institution, London.

BRITISH STANDARDS 1377 (1990). Methods of tests for soils for civil engineering purposes. Parts 1-9. British Standards Institution, London.

BRITISH STANDARDS 6127 (1981). Petrographic analysis of bituminous coal and anthracite. Part 5. Method of determining microscopically the reflectance of vitrinite. Parts 1-7. British Standards Institution, London.

BUCHER K. and FREY M.,(1994). Petrogenesis of Metamorphic Rocks: 6th Edition of the Complete Revision of Winklers Textbook. Blackie.

BUIST D.S et al., (1979). Engineering properties and slope stabilities of Lower Coal Measures rocks from Monks Wood Cutting, Unstone-Dronefield by-pass, Derbyshire. Engineering Geology. **14**, pp.11-28.

BURST J.F.,(1959). Post diagenetic clay mineral environmental relationships in the Gulf Coast Eocene. Clays and Clay Minerals, **6**, pp. 327-341.

BUSTIN R.M., CAMERON A.R., GRIEVE D.A. and KALKREUTH W.D.,(1985). Coal Petrology: Its principles, methods, and applications. Shourt Course Notes 2nd. edition , **3**, Victoria 1983. Geol. Assoc. Can.

BURLAND J.B.,(1984). Building on expansive soils. First National Conf. on the Science and Technology of Buildings with special reference to Buildings in Hot Climates, Khartoum, Sudan, Theme Lecture.

CAMPBELL I.M.,(1993). Mineralogical and diagenetic controls on the durability of overconsolidated clays. Unpublished PhD thesis, University of Sheffield. pp. 440.

CALIANI J.C - FERNANDEZ. and GALAN E.,(1992). Influence of tectonic factors on illite' crystallinity': A case study in the Iberian pyrite belt. Clay Minerals, 27, pp. 385 - 388.

CANCELLI A and CHINAGLIA N.,(1993). Shear strength parameters and slope stability in argillaceous rocks.In: Geotechnical Engineering of Hard soils - Softrocks. (Eds. Anagnostopoulos et al..). Balkema. Rotterdam. pp. 1087-1092.

CANFIELD D.E., RAISWELL R., WESTRICH J.T., REAVES C.M. and BERNER R.A.,(1986). The use of chromium reduction in the analysis of reduced inorganic sulphur in sediments and shales. Chem. Geol., **54**, pp. 149-155.

CARTER P.G and MILLS D.A.C.,(1976). Engineering geological investigations for the Kielder tunnels. Q. J. eng. Geol. London, **9**, pp.125-141.

CHANDLER R.J.,(1969). The degradation of Lias Clay slopes in an area of the East Midlands. Q. J. eng. Geol. London, **2**, pp.161-181.

CHANDLER R.J.,(1974). Lias Clay: the long term stability of cutting slopes. Geotechnique. **24**, pp. 21-38.

CHAO G.Y.,(1969). 2θ (Cu) table for common minerals. Geological Paper 69-2, Carlton University, Department of Geology, Ottowa, Canada.

CHAPMAN S.L.,SYERS J.K. and JACKSON M.L.,(1968). Quantitative determination of quartz in soils, sediments and rocks by pyrosulphate fusion and hydrofluosilicic acid treatment. Soil Science, **107**, pp. 348-355.

CHILINGARIAN G.V.,(1983). Compactional diagenesis. In: Sediment Diagenesis (Eds. A. Parker and B.W. Sellwood). Reidel Pub. Co., Dordrecht, pp.57-168.

COKCA E. and BIRAND A.,(1993). Determination of cation exchange capacity of clayey soils by the methylene blue index test. Geotechnical Testing Journal, GTJODJ., **16**, pp. 518 - 524.

CRIPPS J.C. and TAYLOR R.K.,(1981). The engineering properties of mudrocks. Q. J.eng. Geol. London, **14**, pp. 325-346.

COULTHARD J.M. and BELL F.G.,(1993). The influence of weathering on the engineering behaviour of Lower Lias Clay. The Engineering Geology of Weak Rocks, Cripps et al. (eds.) Balkema, Rotterdam. pp. 183-192.

CURTIS C.D.,(1977). Sedimentary geochemistry: environments and processes dominated by involvement of an aqueous phase. Phil. Trans. R. Soc. Lond. **A286**, pp. 353-372.

DEEN R.C.,(1981). The need for a scheme for the classification of transitional (Shale) materials. Geotechnical Testing Journal, GTJODJ, **4**, pp. 3-10.

DEERE D.U. and GAMBLE J.C.,(1971). Durability-plasticity classification of shales and indurated clay. Proc. 22nd Annu. Highway Geol. Symp., Norman, Okla., pp. 37-52.

DICK J.C., (1992). Relationships between durability and lithological characteristics of mudrocks. Unpublished PhD thesis, Kent State University, pp.235.

DICK J.C. and SHAKOOR A.,(1992). Lithological controls of mudrock durability.Q. J. eng. Geol. London, **25**, pp. 31-46.

DICK J.C. and SHAKOOR A.,(1995). Characterizing durability of mudrocks for slope stability purposes. Reviews in Engineering Geology, **10** , Geological Society of America. pp. 121-130.

DICK J,C., SHAKOOR A. and WELLS N.,(1994). A Geological approach towards developing a mudrock-durability classification system. Canadian Geotechnical Journal, **V.31**, No. 1, pp. 17-27.

DREVER D.I.,(1973). The preparation of oriented clay mineral specimens for X-ray diffraction analysis by a filter-membrane peel technique. Amer. Min., **58**, pp. 553-554.

DUFF D. D. Mc and SMITH A. J (Eds).,(1992). Geology of England and Wales. The Geological Society, London, pp. 651.

DUNBAR C.O. and RODGERS J.,(1957). Principals of Stratigraphy. John Wiley and Sons, Inc., New York, pp. 356.

DUNCAN N., DUNNE M. H. and PETTY S.,(1968). Swelling characteristics of rocks. Water Power, pp. 185 - 192.

DUNOYER DE SEGONZAC G., (1970). The transformation of clay minerals during diagenesis and low-grade metamorphism . Sedimentology, **15**, pp. 281-346.

DUSSEAULT M,B., CIMOLINI P., SODERBERG H, and SCAFE D,W.,(1983). Rapid index tests for transitional materials. ASTM Geotech. Test J. **6**, No. 2 pp. 64-72.

EBERL D. D. and SRODON J.,(1988). Ostwald ripening and interparticle diffraction effects for illite crystals. Amer. Min., **73**, pp. 1335 - 1345.

EBERL D.D. and VELDE B.,(1989). Beyond the Kubler index. Clay Minerals, **24**, pp. 571-577.

EBERL D.D., SRODON J., LEE M., NADEAU P. H. and NORTHROP H. R.,(1990). Sericite from the Silverton Caldera, Colorado: correlation among structure, composition, origin and particle thickness. Amer. Min., **72**, pp. 914 - 934.

ELLIOT R.E. and STRAUSS P.G., (1970). A classification of Coal Measures rocks based on quartz content. Compte Rendu de Congres Int. Strat. Geol. Carbonif. Sheffield, 1967, **2**, pp. 715-724.

EROL A.O. and DHOWAIN A.,(1990). Swell behaviour of arid climate shales from Saudi Arabia. Q. J. eng. Geol. London, **23**, pp. 243-254.

EVANS L.J. and ADAMS W.A.,(1975). Chlorite and illite in some lower Paleozoic mudstones of Mid-Wales. Clay Minerals, **10**, pp. 387-397.

FAIRBURN P. E. and ROBERTSON R. H. S.,(1956). Liquid limit and dye adsorption. Min. Soc London Clay Mins. Bull., **3**, pp. 129 - 136.

FELLOWS P.M. and SPEARS D.A.,(1978). The determination of feldspars in mudrocks using an X-ray diffraction method. Clays and Clay minerals, **25**, pp. 231-236.

FERNANDEZ - CALIANI J.C. and GALAN E.,(1992). Influence of tectonic factors on illite crystallinity: A case study in the Iberian pyrite belt. Clay Minerals, **27**, pp.385-388.

FLAWN P.T., (1953). Petrographic classification of argillaceous, sedimentary, and low-grade metamorphic rocks in subsurface. Amer. Assoc. Pet. Geol. Bull., **37**, pp. 560-565.

FOLK R.L.,(1954). The distinction between grain size and mineral composition in sedimentary rock nomenclature. Jour. Geology, **62**, pp. 344-359.

FOLK R.L., (1974). Petrology of Sedimentary Rocks. Austin, Texas, Hemphill's, pp. 182.

FOSCOLOS A.E. and KODAMA H., (1974). Diagenesis of clay minerals from Lower Cretaceous shales of northeastern British Columbia. Clays Clay Miner., **22**, pp. 319-335.

FOSCOLOS A.E. and STOTT D.F.,(1975). Degree of diagenesis, Stratographic correlations and potential sediment sources of lower Cretaceous shale of northeastern British Columbia. Energy, Mines and Resources Canada. Geological Survey Bullet in **250.**

FRANKLIN J.A.,(1970). Observations and tests for engineering description and mapping of rocks. Proc. 2nd. Congr. I.S.R.M.., Vol.1, Theme 1, No. 3, Belgium Society of Rock Mechanics, Belgrade, pp. 11-16.

FRANKLIN J.A. and CHANDRA A.,(1972). The slake durability test. Int. J. Rock Mech. Min. Sci. **9**, pp. 325-341.

FRANKLIN J.A. and DUSSEAULT M.B.,(1989). Rock Engineering. Publ. McGraw-Hill.

FREY M.,(1970). The step from diagenesis to metamorphism in pelitic rocks during Alpine orogenesis. Sedimentology, **15**, pp. 261-279.

FREY M.,(1978). Progressive low-grade metamorphism of black shale formation, Central Swiss Alps, with special reference to pyrophyllite and margarite bearing assemblages. Jour. Petrol., **19**, pp. 95-135.

FREY M.,(1987). Low Temperature Metamorphism. Blackie and Son, pp.288.

FREY M.., TEICHMULLER M., TEICHMULLER R., MULLIS J., KUNZI B., BREITSCHMID A., GRUNER U. and SCHWIZER B., (1980). Very low-grade metamorphism in external parts of the Central Alps, illite 'crystallinity', coal rank and fluid inclusion data. Eclogae Geologicae Helvetiae, 73, pp.173-203.

FREY M. and KISCH H.J.,(1987). Scope of subject. In: Low Temperature Metamorphism. (Ed. M. Frey) Blackie, Glasgow, pp.1-8.

GAMBLE J.C.,(1971). Durability-placticity classification of shales and other argillaceous rocks. Unpublished Ph.D. Thesis, University of Illinois. pp. 161.

GHARRABI M., VELDE B. and SAGON J. P.,(1996). XRD identification of two coexisting mixed layer expandable minerals in sedimentary rocks. Clays and Clay Minerals, **44**, pp. 429 - 436.

GIBBS R.J.,(1965). Error due to segregation in quantitative clay mineral X-ray diffraction mounting techniques. Amer. Mineral., **50**, pp. 741-755.

GIBBS R.J.,(1967). Quantitative X-ray diffraction analysis using clay minerals standards extracted from the samples to be analysed. Clay Minerals, **7**, pp. 79-90.

GIBBS R.J.,(1977). Clay mineral segregation in the marine environment. Jour. Sed. Petrol., **47**, pp.237-243.

GILL W.D., KHALAF F.I. and MASSOUD M.S.,(1977). Clay mineralogy as an index of the degree of metamorphism of the carbonate and terrigenous rocks in the South Wales coalfield. Sedimentology, **24**, pp. 675-691.

GRAHAM J.,(1989). Collection and analysis of field data. In: Techniques in Sedimentology (Ed. M. Tucker). Blackwell Scientific Publications.

GRAINGER P.,(1984). The classification of mudrocks for engineering purposes. Q.J.eng. Geol. Lond. **17**, pp. 381-387.

GREENSMITH J.T.,(1989). Petrology of the Sedimentary Rocks. Unwin Hyman. London. pp. 262.

GRICE R. H.,(1968). The effect of temperature-humidity on the dissintegration of nonexpansive shales. Bull. Assoc. Eng. Geol., **5**, pp. 69 - 77.

GRIFFIN O.G.,(1954). A new internal standard for the quantitative X-ray analysis of shales and mine dust. Res. Rep. No. **101**, S. Af. Mines Res. Est. Ministry of Fuel and Power, pp. 1-25.

GRIM R.E.,(1962). Applied Clay Mineralogy. McGraw-Hill, New York. pp. 422.

GRIM R.E.,(1968). Clay Mineralogy, McGraw-Hill, New York, pp. 596.

GUGGENHEIM S. and MARTIN R.T.,(1995). Definition of clay and clay mineral: Joint report of the AIPEA nomenclature and CMS nomenclature committees. Clays and Clay Minerals. 43, pp. 255-256.

HAWKINS A.B. and PINCHES G.M.,(1992). Engineering description of mudrocks. Q. J. eng. Geol. Lond. **25**, pp. 17-30.

HAWKINS A.B., LAWRENCE M.S. and PINCHES G.M., (1988). Implications of weathering on the engineering properties of the Fuller's Earth formation. Geotechnique, **38**, pp. 517-532.

HELING D.,(1974). Diagenetic alteration of smectite in argillaceous sediments of the Rhinegraben, Southwest germany. Sedimentology, **21**, pp. 463-472.

HELING D. and TEICHMULLER M.,(1974). Die grenze montmorillonit/mixed-layer minerale und ihre Beziehurig zur inkohlung in der Graven Schichten folgedes Oligozans im Oberrheingraben. Fortschr. Geol. Rheinld. u. Westf., **24**, pp. 113 - 128.

HILLIER S. and CLAYTON T.,(1989). Illite/smectite diagenesis in Devonian lacustrine mudrocks from northern Scotland and its relationship to organic maturity indicators. Clay Minerals, **24**, pp.181-196.

HILLIER S., MATYAS J., MATTER A. and VASSEUR G.,(1995). Illite/smectite diagenesis and its variable correlation with vitrinite reflectance in the Pannonian Basin. Clays and Clay Minerals, **43**, pp. 174 - 183.

HOLTZ W.G. and GIBBS J.H.,(1956). Engineering properties of expansive clays. Trans. Am. Soc. Civ. Engrs, **121**, pp. 641-663.

HONGXI L.,(1993). Physico-chemical properties of swelling soft rocks. In: Geotechnical Engineering of Hard Soils-Soft Rocks, (Ed. Anagnostopoulos et al.), Balkema, Rotterdam, pp. 665 - 670.

HOOTON D.A. and GIORGETTA N.E., (1977). Quantitative X-ray diffraction analysis by a direct calculation method. X-Ray Spectrometry, **6**, pp.2-5

HOPKINS T.C. and DEEN R.C.,(1984). Identification of Shales. Geotechnical Testing Journal. GTJODJ, 7 , pp. 10-18.

HORTON A.E., MANACKERMAN M. and REYBOULD W.E.,(1964). The shale breakdown problem in coal washing. Part 2 - some causes of shale breakdown and means for its control. J. Inst. Fuel. **37,** pp. 52-58.

HOWER J., ESLINGER E.V., HOWER M.E. and PERRY G.A.,(1975). Mechanism of burial metamorphism of argillaceous sediments:1. Mineralogical and chemical evidence. Geol. Soc. Amer. Bull., **87**, pp. 727-757.

HUDEC P.P.,(1982). Statistical analysis of shale durability factors. Transport Research Record 873, pp. 28-35.

HUGGET J.M.,(1986). An SEM study of phyllosilicate diagenesis in sandstones and mudstones in the Westphalian Coal Measures using back-scattered electron microscopy. Clay Minerals, **21**, pp.603-616.

INGRAM R.L.,(1953). Fissility of mudrocks. Geol. Soc. Amer. Bull., 64, pp. 869-878.

IRDI G. A. and BOOHER H. B.,(1995). Optical microscopic evaluation of a Pittsburg seam coal and its combustion chars. Microscopy and Analysis, pp. 29.

I.S.R.M.,(1985). Suggested method for determining point load strength. International Society of Rock Mechanics Commission on Testing Methods. Int. J. Rock Mech. Mining Science, **22**, pp. 51 - 60.

JACKSON M.L.,(1969). Soil chemical analysis: advanced course. 2nd edition. Madison.

JAEGER J.C. and COOK N.G.W.,(1979). Fundamentals of Rock Mechanics. Chapman Hall, London, pp. 576.

JEANS C.V.,(1989). Clay diagenesis in sandstones and shales: an introduction. Clay Minerals, **24**, pp.127-136.

KEELING P. S.,(1962). Some experiments on the low-temperature removal of carbonaceous material from clays. Clay Minerals, London, pp. 413 - 425.

KENNARD M.F., KNILL J.L. and VAUGHAN P.R.,(1967). The geotechnical properties and behaviour of Carboniferous shale at the Balderhead Dam. Q. J. eng. Geol. London, **1**, pp.3-24.

KIELY P.V. and JACKSON M. L.,(1965). Quartz, feldspar and mica determination for soil by sodium pyrosulfate fusion. Soil Science Society Proceedings, pp.159 - 163.

KISCH H.J.,(1980). Incipient metamorphism of Cambro-Silurian clastic rocks from the Jamtland Supergroup, Central Scandanavian Caledonides, western Sweden: illite crystallinity and vitrinite reflectance. J. Geol. Soc. London, **137**, pp. 271-288.

KISCH H.J.,(1983). Mineralogy and petrology of burial diagenesis (burial metamorphism) and incipient metamorphism in clastic rocks. In: Diagenesis in Sediments and Sedimentary Rocks. (Eds. G.Larsen and G.V. Chilingar). Elsevier, Amsterdam, pp. 289-493.

KISCH H.J.,(1990). Calibration of the anchizone: a critical comparison of illite 'crystallinity' scales used for definition. J. metamorphic Geol., **8**, pp.31-46.

KISCH H.J.,(1991). Development of slaty cleavage and degree of very-low grade metamorphism: a review. J. metamorphic Geol., **9**, pp.735-750.

KISCH H.J. and FREY M.,(1987). Appendix: Effects of sample preparation on the measured 10 Å peak width of illite 'crystallinity'. In: Low Temperature Metamorphism (Ed. M. Frey). Blackie and Son, Glasgow, pp. 301-304.

KLAMBERG H., MATTHESS G. and PEKDEGER A.,(1989). Organo-metal complexes as mobility-determining factors of inorganic toxic elements in porous media. In: Inorganic Contaminants in the Vadose Zone, (Eds. B Bar Yosefm, N. J. Barrow and J Goldsmith), Ecological Studies No. **74**, Springer Verlag, pp. 3 - 17.

KRINSLEY D.H., PYE K. and KEARSLEY A.T.,(1983). Application of backscatter electron microscopy in shale petrology. Geological Magazine, **120**, pp. 109-208.

KRINSLEY D., NAGY B., DYPVIK H. and RIGALI M.,(1993). Microtextures in mudrocks as revealed by backscattered electron imaging. Precambrian Research, **61**, pp. 191-207.

KRUMBEIN W. C.,(1947). Shales and their environmental significance. J. Sediment. Petrol., **17**, pp. 101 - 108.

KUBLER B.,(1964). Les argiles, indicateeurs de metamorphism. Revue de L'Institut Francais du Petrole, **19**, pp. 1093-1112.

KUBLER B.,(1967). La cristallinite de l'illite et les zones tout a superieures du metamorphisme. In: Etages Tectonique Cooloque de Neuchatel, 18-21 avril 1966. A la Baconniere, Neuchatel (Suisse), pp. 105-122.

KUBLER B.,(1968). Evaluation quantitative du metamorphisme par la cristallinite de l'illite. Bulletin du Centre de Recherches de Pau - SNPA, **2**, pp.385-397.

KUBLER B.,(1984). Illite crystallinity and diagenesis revisited (preprint). 5eme Congres Europeen de Sedimentologie.

LARSEN G. and CHILINGAR G.V.,(1979). Introduction - Diagenesis of sediments and rocks. In: Diagenesis in Sediments and Sedimentary Rocks. Developments in Sedimentology, 25A. (Eds. G. Larsen and G. V. Chilingar), Elsevier, pp. 1-30.

LEE C.F. and KLYM T.W.,(1978). Determination of rock squeeze potential for underground power projects. Engineering Geology. **12**, No.1 pp. 181-192.

LEE I.K., WHITE W. and INGLES O. G.,(1983). Geotechnical Engineering. Pitman.

LEEDER M.R.,(1982). Sedimentology, Processes and Products. Unwin-Hyman, London, pp.344.

LEGGETT J.K.,(1980). British lower palaezoic black shales and their palaeo-oceanographic significance. J. geol. Soc. London, **137**, pp. 137 - 156.

LEVY G. J., SHAINBERG I. and ALPEROVITCH N.,(1991). Effect of Na-hexametaphosphate on the hydraulic conductivity of kaolinite-sand mixtures. Clays and Clay Minerals, **39**, pp. 131 - 136

LEWANS M.,(1978). Laboratory classification of very fine grained sedimentary rocks. Geology, **6**, pp. 745-748.

LLOYD G. E.,(1987). Atomic number and crystallographic contrast image with the SEM: a review of backscattered electron techniques. Mineralogical Magazine, ***51***, *pp.* 3 - 19.

LO K,Y.,WAI R,S,C., PALMER J,H,L,and QUIGLEY R,M.,(1978). Time-dependent deformation of shaly rocks in Southern Ontario. Canadian Geotechnical Journal, **15**, pp. 537-547.

LORD C. J., (1982). A selective and precise method for pyrite determination in sedimentary materials. J. Sediment. Petrol., **52**, pp. 664 - 666.

LUNDEGARD P.D. and SAMUELS N.D.,(1980). Field classification of fine-grained sedimentary rocks. J. Sediment. Petrol. **50**, pp. 781-786.

LUTTON R.J.,(1977). Design and construction of compacted shale embankments. Vol. 3. Slaking Indexes for Design. U.S. Army Engineer Waterways Experiment Station, Vicksburg, Report No. **FHWA--RD-77-1** (National Technical Information Service, Springfield, Virginia 22161), pp. 88.

MADSEN F.T. and MULLER-VONMOOS M.,(1985). Swelling pressure calculated from mineralogical properties of a Jurassic opalinum shale, Switzerland. Clays and Clay Minerals. **33**, No.6 pp. 501-509.

MAXWELL J. A.,(1981). Rock and Mineral Analysis. Chemical Analysis Vol. **27**, Interscience , New York.

MAZZOCCOLA D.F.and HUDSON J.A.,(1996). A comprehensive method of rock mass characterization for indicating natural slope instability. Q. J. eng. Geol. Lond. **29**, pp. 37-56.

McKEE E.D. and WEIR G.W.,(1953). Terminology for stratification and cross-stratification in sedimentary rocks. Geol. Soc. America Bull. **64**, pp. 381-389.

McMANUS D. A.,(1991). Suggestions for authors whose manuscripts include quantitative clay mineral analysis by X-ray diffraction. Marine Geology, **98**, pp. 1 - 5.

MEAD W.J.,(1936). Engineering geology of dam sites. Trans. 2nd Int. Congr. Large Dams, Washington, DC, **4**, pp. 183-198.

MERRIMAN R.J. and ROBERTS B.,(1985). A survey of white mica crystallinity and polytypes in pelitic rocks of Snowdonia and Llyn, North Wales. Mineralogical Magazine. **49**, pp. 321-333.

MERRIMAN R.J. and KEMP S.J.,(1996). Clay minerals and sedimentary basin maturity. Mineralogical Soc. Bull. **111**, pp 7-8.

MIKI T., NAKAMUTA Y. and AIZAWA J.,(1991). Relationships between authigenic mineral transformation and variation in vitrinite reflectance during diagenesis: An example from the Tertiary of Northern Kyushu, Japan. Clay Minerals, **26**, pp.179 - 187.

MILLOT G.,(1970). The Geology of Clays. Chapman and Hall, London.

MOON V.G. and BEATTIE A.G.,(1995). Textural and microstructural influences on the durability of Waikato Coal Measures mudrocks. Q. J.eng. Geol. Lond. **28**, pp. 303-312.

MOON C.F and HURST C.W.,(1984). Fabric of muds and shales: an overview. In: Fine-grained sediments: deep-water processes and facies. (Eds. D.A.V. Stow and D.J.W. Piper). Blackwell Scientific Publications, Oxford, pp. 579-593.

MOORE D.M. and REYNOLDS R.C.Jr.,(1989). X-Ray Diffraction and the Identification and analysis of Clay Minerals. Oxford University press.

MORGENSTERN N.R. and EIGENBROD K.D.,(1974). Classification of argillaceous Soils and Rocks. Proc. Amer. Soc. Civ. Engrs. J. Geot. Div. **100**, pp.1137-1156.

MUKHOPADHYAY P. K.,(1992). Maturation of organic matter as revealed by microscopic methods: Applications and limitations of vitrinite reflectance, and continuous spectral and pulsed fluorescence spectroscopy. In: Diagenesis III, Developments in Sedimentology, **47**, (Eds. K. H. Wolf and G. V. Chilingarian) Elsevier Science Publishers, pp. 435 - 510.

NADEAU P.H., TAIT J.M., McHARDY W.J. and WILSON M.J.,(1984). Interstratified XRD characteristics of physical mixtures of elementary clay particles. Clay Minerals, **19**, pp. 67-76.

NORBURY D.R.,(1986). The point load test. In: Site Investigation Practice: Assessing BS 5930, Engineering Geology Special Publication, **2**, (Ed. A. B. Hawkins) Geological Society, London, pp.326 - 329

NORRISH K. and HUTTON J.T.,(1969). An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. Geochim. Cosmochim. Acta., **33**, pp. 431-453.

NORRY M. J., DUNHAM A. C. and HUDSON J. D.,(1994). Mineralogy and geochemistry of the Peterborough member, Oxford Clay formation, Jurassic, UK-Element fractionation during mudrock sedimentation. J. Geol. Soc. London, **151**, pp. 195 - 207.

NORTH F. K.,(1985). Petroleum Geology. Allen and Unwin, London, pp. 607.

OKAGBUE C.O.,(1984). The geotechnical characteristics and stability of a spoil heap at a Southwestern Pennsylvania coal mine U.S.A. Engineering Geology. **20**, pp. 325-341.

OLA S.A.,(1982). Geotechnical properties of a Attapulgite Clay Shale in Northwestern Nigeria. Engineering Geology. **19**, No.1 pp. 1-13.

OLIVEIRA R.,(1993). Weak rock materials. In: The Engineering Geology of Weak Rock, (Eds. Cripps et al.), Balkema, Rotterdam, pp. 5 - 14.

OLIVIER H.J.,(1979). Some aspects of the influence of mineralogy and moisture redistribution on the weathering behaviour of mudrocks. Proc. $th Int. Conf. on Rock Mech. Montreux. **3**, pp. 467-475.

OLIVIER H.J.,(1980). A new engineering-geological rock durability classification. Engineering Geology. **14**, pp. 255-279.

OLIVIER H.J.,(1990). Some Aspects of the engineering geological properties of swelling and slaking mudrocks. 6th Int. IAEG Congress.1990 Balkema, Rotterdam.

PEARCE R. B., CLAYTON T. and KEMP A. E. S.,(1991). Illitization and organic maturity in Silurian sediments from the Southern Uplands of Scotland. Clay Minerals, **26**, pp. 199 - 210.

PATERSON E., BUNCH J.L. and DUTHIE D. M. L.,(1986). Preparation of random-orientated samples for X-ray diffraction. Clay Minerals, **21**, pp. 101 - 106.

PATERSON S. R. ., YU H. and OERTEL G.,(1995). Primary and tectonic fabric intensities in mudrocks. Tectonophysics, **247**, pp.105 - 119.

PEARSON M.J., WATKINS D., and SMALL J.S.,(1982). Clay diagenesis and organic maturation in northern North Sea sediments. Proc. Inter. Clay Conf., Bologna and Pavia, pp. 665-675.

PELLS P. J. N.,(1975). The use of the point load test in predicting the compressive strength of rock materials. Australian Geomechanics Journal, pp. 54 - 56.

PENNER E., GILLOT J,E, and EDEN W,J., (1970). Investigations to heave in Billings shale by mineralogical and biogeochemical methods.Canadian Geotechnical Journal. V.7 pp. 333-338.

PETTIJOHN F.J.,(1975). Sedimentary Rocks. Harper and Row, New York. pp. 628.

PICARD M.D.,(1953). Marlstone - a misnomer as used in the Unita Basin, Utah. Bull. Amer. Assoc. Petrol. Geol., **37**, pp. 1075-1077.

PICARD M.D.,(1971). Classification of fine grained sedimentary rocks. J. Sediment. Petrol., 41, pp. 179-195.

PIERCE J. W. and SIEGAL F. R.,(1969). Quantification in clay mineral studies of sediments and sedimentary rocks. J. Sediment. Petrol., **39**, pp. 187 - 193.

POTTER P.E., MAYNARD J.B and PRYOR W.A.,(1980). The Sedimentology of Shale: A Study Guide and Reference Source. Springer Verlag, New York. pp. 306.

PRIMMER T.J. and SHAW H.F.,(1987). Diagenesis in shales: Evidence from backscattered electron microscopy and electron microprobe analysis. In: Proceedings of the International Clay Conference, Denver, 1985. (Eds. L. G. Schultz et al. ), The Clay Mineral Society , Bloomington, Indiana, pp. 135 - 143.

PYE K. and KRINSLEY D.,(1984). Petrographic examinationof sedimentary rocks in the SEM using backscattered detectors. J. Sediment. Petrol., **54**, pp.877-888.

RAISWELL R., BUCKLEY F., BERNER R.A and ANDERSON T. F.,(1988). Degree of pyritization of iron as a paleoenvironmental indicator of bottom-water oxygenation. J. Sediment. Petrol., **58**, pp. 812 - 819.

RATSEY J.,(1973). Shear Strength Characteristics of Certain Colliery Discards with Respect to Coal Rank. MSc. Thesis, University of Durham.

REYNOLDS R.C.,Jr.,(1989). Principles and techniques of quantitative analysis of clay minerals by X-ray diffraction methods. In: Workshop on Quantitative Analysis. International Clay Conf., Denver Colorado.

REYNOLDS R. C. jr. and HOWER J.,(1970). The nature of interlayering in mixed-layer illite-montmorillonites. Clays and Clay Minerals, **18**, pp. 25 - 36.

REYNOLDS S. and GORSLINE D. S.,(1991). Silt microfabric of detrital, deep sea mud(stone)s, California Continental Borderland, as shown by backscattered electron microscopy. In: Microstructures of Fine-grained Sediments from Mud to Shale. (Eds. R. H. Bryant et al.), Springer-Verlag, pp.203 - 211.

RIEKE H.H. and CHILINGARIAN G.V.,(1974). Compaction of Argillaceous Sediments. Developments in Sedimentology, **16**, Elsevier, pp. 424.

ROBERTSON B. and MERRIMAN R,J.,(1985). The distinction between Caledonian burial and regional metamorphism in metapelites from North Wales: an analysis of isocryst patterns. J. Geol. Soc. London, **142**, pp. 615-624.

ROOTARE H. M.,(1968). A short literature review of mercury porosimetry as a method of measuring pore-size distributions in porous materials, and a discussion of possible sources of errors in this method. Lab News, **24**, pp. 4A -4E.

RUSSELL D.J.,(1982). Controls on shale durability: the responce of two Ordovician shales in the slake durability test. Can. Geotech. J., **19**, pp. 1-13.

SARMAN R, and SHAKOOR A.,(1990). Prediction of volumetric increase of selected mudrocks. 6th International IAEG Congress. 1990 Balkema,Rotterdam.

SARMAN R., SHAKOOR A, and PALMER D,F.,(1994). A multiple regression approach to predict swelling in mudrocks. Bull. Assoc. Eng. Geol.. V. **XXXI**, No.1 pp. 107-121.

SASAKI T., KINOSHITA S. and ISHIJIMA Y.,(1981). A study on water-sensitivity of argillaceous rock. Proc. Int. Symp. on Weak Rock, Tokyo, pp. 149 - 154.

SCHULTZ L,G.,(1960). Quantitative X-Ray determinations of some aluminous clay minerals in rocks. In: Clays and Clay Minerals (Ed. A Swineford).New York, Pergamon Press, pp 216-224.

SCHULTZ L.G.,(1964). Quantitative intrpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. U.S. Geological Survey Professional Paper 391-C, pp.31.

SEEDSMAN R.,(1986). The behaviour of clay shales in water. Can. Geotech. J., **23**, pp. 18-22.

SHAKOOR A.,(1995). Slope stability considerations in differentially weathered mudrocks. In: Reviews in Engineering Geology, **X**, Geological Society of America, pp.131 - 138.

SHAKOOR A. and BROCK D.,(1987). Relationship between fissility, composition, and engineering properties of selected shales from Northeast Ohio. Bull. Assoc. Eng. Geol., **XXIV**, pp. 363-379.

SHAKOOR A. and SCHOLER C. F.,(1985). Comparison of aggregate pore characteristics as measured by mercury intrusion porosimeter and Iowa pore index tests. ACI Journal, **82-38**, pp.453 - 458.

SHAW H.F.,(1972). The preparation of orientated clay mineral specimens for X-ray diffraction analysis by a suction-onto-ceramic tile method. Clay Minerals, **9**, pp. 349 - 350.

SHAW H.F.,(1981). Mineralogy and petrology of the argillaceous sedimentary rocks of the U.K. Q. J. eng. Geol. London, **14**, pp. 277-290.

SHAW D.B. and WEAVER C.E.,(1965). The mineralogical composition of shales. J. Sediment. Petrol., **35**, pp. 213-222

SHAW H. F. and PRIMMER T. J.,(1991). Diagenesis of mudrocks from the Kimmeridge Clay formation of the Brea area, UK North Sea. Marine and Petroleum Geology, **8**, pp. 270 - 277.

SHEPARD F.P.,(1954). Nomenclature based on sand-silt-clay ratios. J. Sediment. Petrol., **24**, pp.151-158.

SHROCK R.R.,(1948). A classification of sedimentary rocks. J. Geol., **56**, pp. 118-129.

SMART B,G,D., ROWLANDS N, and ISAAC A,K.,(1982). Progress towards establishing relationships between the mineralogy and physical properties of Coal Measures rocks. Int. J. Rock Mech. Min. Sci. and Geomech. Abstr. V. **19**, pp. 81-89.

SMITH T,J.,(1978). Consolidation and other Geotechnical Properties of Shales with Respect to Age and Composition. Unpublished Ph.D. Thesis, University of Durham.

SPEARS D.A.,(1976). The fissility of some Carboniferous shales. Sedimentology, **23**, pp. 323-327.

SPEARS D.A.,(1980). Towards a classification of shales. J. geol. Soc. London, **137**, pp. 125-129.

SPEARS D.A. and TAYLOR R.K.,(1972). Influence of weathering on the composition and engineering properties of in situ Coal Measures rocks. Int. Jour. Roch Mech. and Mining Science, 9, pp. 729 - 756.

SPEARS D,A., TAYLOR R,K, and TILL R.,(1970). A mineralogical investigation of spoil heap at Yorkshire Main Colliery. Q. J. eng. Geol.London, **3**, pp. 239-252.

SPINK T.W. and NORBURY D.R.,(1993). The engineering description of weak rocks and overconsolidated soils. In: The Engineering Geology of Weak Rocks. (Eds. J.C. Cripps et al.). Eng. Geol. Spec. Publ. No. **8**, Balkema Rotterdam, pp. 289-301.

SPOTL C., HOUSEKNECHT D.W. and JAQUES R., (1993). Clay mineralogy and illite crystallinity of the Atoka formation, Arkoma basin, and Frontal Ouachita mountains. Clays and Clay Minerals, **41**, pp. 745 - 754.

SRODON J.,(1980). Precise identification of illite-smectite interstratifications by X-ray powder diffraction. Clays and Clay minerals, **28**, pp. 401-411.

SRODON J.,(1984). X-ray identification of illitic material. Clays and Clay Minerals. **32**, pp. 337-349.

SRODON J. and EBERL D.D., (1984). Illites. In: Micas (Ed. S.W Bailey). Reviews in Mineralogy. Min. Soc. Amer. **13** , pp. 495-544.

STACH E., MACKOWSKY M-TH., TEICHMULLER M., TEICHMULLER R., TAYLOR G. and CHANDRA D.,(1982). Stach's Textbook of Coal Petrology. Gebruder Borntraeger, Berlin, pp.535.

STAPEL E.E. and VERHOEF P. N. W.,(1989). The use of the methylene blue adsorption test in assessing the quality of basaltic tuff rock aggregate. Engineering Geology, 26, pp. 233 - 246.

STARKEY H.C., BLACKMON P.D. and HUFF P.L.,(1985). The routine mineralogical analysis of clay bearing samples. U.S. Geol. Surv. Bull., **1563**, pp. 32.

STEWARD H.E.,(1984). Links between geotechnical and engineering properties in weathered pyritic shales. Unpublished Ph.D. Thesis, Sheffield University.

STEWARD H.E and CRIPPS J.C.,(1983). Some engineering implications of chemical weathering of pyritic shale. Q.J. eng. Geol. London, **16**, pp. 281-289.

STOW D.A.V.,(1981). Fine-grained sediments:Terminology. Q. J. eng. Geol. London, **14**, pp. 243-244.

STROHM W.B., BRAGG G.H and ZIEGLER T.W.,(1978). Design and Construction of Compacted Shale Embankments. Federal Highway Administration, U.S. Department of Transportation, Report. No. M **0543**, Washington DC, pp.142.

SWAN A. R. H. and SANDILANDS M.,(1995). Introduction to Geological Data Analysis. Blackwell Science, pp.446.

TAYLOR R.K.,(1967). Methylene blue adsorption by fine grained sediments. J. Sediment. Petrol., **37**, pp. 1221 - 1230.

TAYLOR R.K.,(1984). Composition and engineering properties of British colliery discards, Mining Department, National Coal Board, Hobart House, London.

TAYLOR R.K.,(1985). Cation exchange capacity in clays and mudrocks by methylene blue. Journal of Chemical Technology and Biotechnology, **35A**, pp. 195 - 207.

TAYLOR R.K.,(1988). Coal Measures mudrocks: composition, classification and weathering processes. Q. J. eng. Geol. London, **21**,pp. 85-99.

TAYLOR R.K, and SMITH T.J.,(1986). The Engineering Geology of Clay Minerals: Swelling, Shrinking and Mudrock Breakdown. Clay Minerals, **21**, pp 235-260.

TAYLOR R.K, and SPEARS D.A.,(1970). The breakdown of British Coal Measure rocks. Int. J. Rock Mech. Min. Sci. **7**, pp 481-501.

TAYLOR R.K. and SPEARS D.A.,(1981). The laboratory investigation of mudrocks. Q. J. eng. Geol. Lond. **14**, pp. 291-309.

TEICHMULLER M.,(1987). Organic material and very low-grade metamorphism. In: Low Temperature Metamorphism. (Ed. M.Frey), Blackie, London, pp.114-226.

TEICHMULLER M., TEICHMULLER R and WEBER K.,(1979). Inkohlung und illit-kristallinitat (vergleichende untersuchungen im Mesozoikum und Palaozoikum von WestFalen). Fortschr. Geol. Rheinl. Westfal., **27**, pp. 201-276.

TERZAGHI K., (1943). Theoretical Soil Mechanics. New York, John Wiley and Sons.

TILL R. and SPEARS D.A.,(1969). The determination of quartz in sedimentary rocks using an X-ray diffraction method. Clays and Clay Minerals. **17**, pp. 323-327.

TORRE M. D., STERN W. B. and FREY M.,(1994). Determination of white K-mica polytype ratio: Comparison of different XRD methods. Clay Minerals, **29**, pp. 717 - 126.

TROSTEL L.J. and WYNNE D.J.,(1940). Determination of quartz (free silica) in refractory clays. J. Amer. Ceram. Soc., **23**, pp. 18-22.

TRUEMAN A.E. (Ed).,(1954). The coalfields of Great Britain. Edward Arnold, London, pp 396.

TUCKER M.E (Ed.).,(1991). Techniques in Sedimentology. Blackwell Scientific Publications. pp. 394.

TUCKER M.E.,(1994). Sedimentary Petrology: An introduction to the origin of sedimentary rocks 2nd. Ed. Blackwell Scientific Publications. pp. 260.

TWENHOFEL W.H.,(1937). Terminology of the fine grained mechanical sediments. Rept. Comm. on Sedimentation for 1936-37, National Res. Council, pp. 81-104.

TWENHOFEL W.H.,(1950). Principles of Sedimentation. 2nd. Ed. McGraw-Hill, New York, pp. 673.

UNDERWOOD L.B.,(1967). Classification and identification of shales. Proc. Amer. Soc. Civ. Engrs. J. Soil. Mech. Foundn. Div., **93**, pp. 97-116.

VAN OLPHEN H.,(1963). An introduction to Clay Colloid Chemistry. Interscience, pp.301.

VARLEY P,M.,(1990). Susceptibility of Coal Measures mudstones to slurrying during tunnelling. Q. J. eng. Geol. London, **23**, pp. 147-160.

VELDE B. and LANSON B.,(1993). Comparison of I/S transformation and maturity of organic matter at elevated temperatures. Clays and Clay Minerals, 41, pp. 178 - 183.

VENTER J.P.,(1981). Free-swell properties of some South African mudrocks. Proc. Int. Sym. on Weak Rock, Tokyo, Vol 1, pp. 243 - 252.

WARR L. N. and RICE H. N.,(1994). Interlaboratory standadization and calibration of clay mineral crystallinity and crystallite size data. J. metamorphic Geol., 12, pp. 141 - 152.

WEAVER C.E.,(1959). The clay petrology of sediments. Clays and Clay Minerals, 5, pp. 159-173.

WEAVER C.E.,(1960). Possible use of clay minerals in search for oil. Amer. Assoc. Petrol. Geol. Bull., 44, pp.1505-1518.

WEAVER C.E.,(1989). Clays, Muds, and Shales. Developments in Sedimentology, 44, Elsevier. pp. 819.

WEAVER C.E. and Associates.,(1984). Shale-slate Metamorphism in Southern Appalachians. Elsevier, pp. 239.

WEAVER C.E. and BECK K.C.,(1971). Clay water diagenesis during burial: how mud becomes gneiss. Geol. Soc. Amer. Spec. Paper 134, pp. 96.

WEAVER C.E. and BROCKSTRA B.R.,(1984). Illite-mica. In: Shale-Slate Metamorphism in Southern Appalachians. (Eds. Weaver and Associates). Elsevier, pp. 67-98.

WEBER K.,(1972). Note on the determination of illite crystallinity. Neues Jahrbuch fur Mineralogie Monatshefte, **6**, pp.267-276.

WEIR A. H., ORMEROD E. C. and EL-MANSEY I. M. I.,(1975). Clay mineralogy of sediments of the Western Nile Delta. Clay Minerals, **10**, pp.369 - 386.

WENTWORTH C.K.,(1922). A scale of grade and class terms for clastic sediments. J. Geol., **30**, pp.377-392.

WHITE S., SHAW A. and HUGGETT J.,(1984). The use of back-scattered electron imaging for the petrographic study of sandstones and shales. J. Sediment. Petrol., **54**, pp.487-494.

WHITEHOUSE U.G., JEFFREY L.M. and DEBBRECHT J.D.,(1960). Differential settling tendencies of clay minerals in saline waters. Clays and Clay Minerals, 7, pp. 1-79.

WOOD L.E. and DEO P.,(1975). A suggested system for classifying shale materials for embankments. Bull. Assoc. Eng. Geol., **XII**, pp.39-55.

YUMEI X., WEILIN Z. and XUEHAN W.,(1993). Application of the microscopic features of weak rocks in underground workings. In: The Engineering Geology of Weak Rocks, (Eds. Cripps et al.), Balkema, Rotterdam, pp. 95 - 99

ZHABINA N. N. and VOLKOV I. I.,(1978). A method of determination of various sulfur compounds in sea sediments and rocks. In: Environmental Biogeochemistry; Methods, Metals ans Assessment, Vol. 3, Ann Arbor Science Publishers, Ann Arbor, Michigan, pp. 735 - 745.