Byzantine and Ottoman Mineral Exploration and Smelting in Eastern Macedonia, Greece and their Implications for Regional Economies

Volume 2

Nerantzis X. Nerantzis

A Thesis Submitted for the degree of
Doctor of Philosophy

Department of Archaeology and Prehistory
University of Sheffield

June 2009

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CHAPTER 6

The investigation of the metallurgical remains

6.1 Introduction

This chapter presents the metallurgical assemblages that were sampled from the surveyed sites and the results of their analysis by a range of instrumental techniques. The overarching aim of this chapter is to consider the array of data derived from the study (i.e. typology, microstructural, chemical and mineralogical) and to gain insight into the technical aspects of the metallurgical practices represented by these assemblages. The results of this chapter coupled with the results presented in chapter five will constitute the principle evidence that will be used to develop a socially constructivist account of Byzantine and Ottoman metallurgical practices in chapter seven. Sampling of the metallurgical production sites focused primarily on slag remains as slags are excellent materials from which the archaeologist can gain insights in to past practices (Bachmann 1982; Tylecote 1987; Craddock 1995). The metallic components along with the predominantly silicate mineralogy testify to the range and type of conditions within the furnace and reflect the technological choices made by metalworkers (Lemonier 1992; Killick 2004; Schmidt 1997).

Sampling of metallurgical sites is a complex undertaking and it is a critical step in the construction of any assemblage. Guidelines for sampling archaeometallugical sites were established by Bachmann (1982) and more recently expanded upon by Bayley *et al* (2001). It is recognised that many sites are multi-period, and that technology can change rapidly within short periods giving rise to differing slag types. A critical consideration in sampling of archaeometallurgical sites is the need to avoid 'interesting' or unusual looking samples. Whilst the archaeologist's eye is often drawn to such specimens it is unlikely that they are representative of the majority of the slag and hence reflect the full rage of processes enacted at the site. With these thoughts in mind, the assemblage was constructed only after site survey and once a familiarity with each site and the extent and nature of slag deposits had been established. After preliminary examination of many slags in the field, initial hand examination of the samples was carried out to characterise slags from each site with the aim of establishing a typology which would assist in comparative work between the various sites.

These typological categories also formed the basis for subsequent investigation using instrumental analysis. For microstructural examination sample preparation was undertaken at the Fitch Laboratory of the British School at Athens with subsequent microscopic examination being performed at the Archaeometry Laboratory, N.C.S.R. 'Demokritos'. Optical microscopy was supplemented by Scanning Electron Microscopy (ESEM) along with EDAX analysis which was invaluable for the characterisation of individual phases. For this the Philips XL30 ESEM FEG with an Oxford Instruments Silicon drift detector was used at the Materials and Engineering Research Institute of Sheffield Hallam University. Bulk chemical analysis on some initial samples using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) at the Department of Analytical Chemistry, University of Thessaloniki proved difficult. Due to problems occurring during sample digestion, the results were discounted as unreliable and hence an alternative analytical method was used. Analytically verifiable results were finally achieved using ED-XRF. Mineralogical analyses were undertaken using X-ray Diffraction (XRD) analysis at the Department of Analytical Chemistry, University of Thessaloniki.

As indicated in chapters 4 and 5, samples from some of the surveyed sites had previously been examined by others. For example, from a comparison of slag typology from smelting sites of various dates on Thasos and eastern Macedonia, Photos (1987) was able to determine crucial characteristics of the bloomery process such as raw materials, temperature ranges and average furnace shape and size and concluded that the high percentage of compact slags from eastern Macedonia points to a high shaft furnace that produced fluid slag, tapped during the smelting cycle, whereas the more numerous porous examples from Thasos indicate a smaller type of furnace producing more viscous, non-tapped slag (Photos 1987). Also previous studies had shown that microanalysis on specific phases has been successful for tracing diagnostic elements of certain raw materials (Photos 1987; Photos *et al* 1986). The availability of these data and the need for comparable information to be obtained in this research to allow testing of previous conclusions had some influence on the techniques employed here. For example, the material under study was subjected to EDX analysis in an attempt to discern how certain elements are distributed among the silicate phases.

Overall, it was the central aim of the current analytical programme to produce and use this diverse range of new scientific data to establish various technical parameters, e.g. operating temperatures, furnace atmosphere etc, along with insights in to other aspects of technological choice and compare the conclusions with those from a more limited set of samples studied earlier. The ultimate intention of such undertakings is to use this scientific data to comment on the material conditions within which specific and meaningful practices were enacted by knowledgeable human agents.

6.2 The sampled material: slag, speiss, refractories

Three general types of metallurgical residue were identified in the field surveys namely slag, speiss and refractory ceramics. The sampling strategy followed the general guidelines provided by Bachmann (1982) in order to choose specimens representative of their deposits. Slag in the field was not entirely uniform in terms of outer appearance but there was a range of certain types, common across each site. Although the volume of material is quite substantial three major types that share common external features were recognized and samples for each one of these were taken. Whenever layering of slag in heaps was encountered various cuts through their stratigraphy were chosen to get samples from various layers. Therefore samples were taken from different locations and layers that represent short intervals of deposition close to the surface. The find spots of all slag samples have been plotted and are marked in red on each site's topographic plan (see chapter 5).

In total 120 representative slag samples were taken from the four surveyed smelting sites (30 samples/site). These samples formed the basic study element for the typology. Subsequent to hand examination ten samples from each site were chosen for further examination: Angistro (AGS01-AGS10), Katafyto (KAT01-KAT10), Vathytopos (VTH01-VTH10) and Makrychori (MAK01-MAK10). These samples were examined under the optical microscope, the SEM and were further analysed by ICP, XRF and XRD for a determination of their chemical composition in regards to major, minor and trace elements (Appendix I).

Speiss is a metallurgical waste-product of iron, copper or nickel arsenides or antimonides deriving from the smelting of complex ores. Speiss is brittle and magnetic and upon fracturing reveals a bright crystalline surface. Ferrous speiss is a mixture of arsenical iron and iron arsenides while base-metal speiss is a mixture of copper, nickel, iron and silver in form of asrenides or antimonides with some sulphur or lead (Thornton *et al* 2009). Although lead does not form intermetallic compounds with arsenic or antimony it often accompanies the speiss phase due to its geochemical association with many base metals and its low melting point. Most speiss can be argentiferous or auriferous and hence contain concentrations of precious metals at various levels. Speiss was found among the slag deposits at Makrychori and Angistro and for the needs of this study five samples were subjected to microscopic and compositional analysis.

Refractory ceramics were noted in certain contexts and were carefully sampled to provide information about ceramic paraphernalia of the metallurgical practice such as use of tuyères and furnace lining material. Refractory pieces associated with metallurgical processes were recovered from Angistro, Katafyto and Vathytopos. Complete tuyères from Angistro and Katafyto show extensive exposure to high temperatures with adhering slag and a vitrified surface. Furnace conglomerates of substantial size (45 cm in length) were recovered from Katafyto. Further information is given in section 6.10 and Appendix IV.

6.3 Choice of instrumental techniques

The methodology used for macroscopic identification was based on standard recording of certain characteristics and properties of slag such as size, weight, texture, porosity, inclusions and magnetism (Bachmann 1982). Information on these macroscopic features is included in Appendix I. Based on the above four main groups have been distinguished representing the most common types of slag found across the sampled sites. The four types recorded fall within the following groups: compact (ropey), semi-compact (drop-like), glassy and spongy (figures 6.1-6.4). Such a variation in slag morphology is due to different processes or certain stages of a process taking place on site.

Figure 6.1 Group A: Compact slag

Figure 6.2 Group B: Semi-compact slag

Figure 6.3 Group C: Glassy slag

Figure 6.4 Group D: Spongy slag

The distinctive mineral phases observed under the microscope were further examined with the use of the Scanning Electron Microscope. This technique has been proved very useful for an identification of the morphological characteristics of silicate phases in the microstructure while the data acquired from the EDX detector were used to determine the composition of individual phases and inclusions. As indicated earlier this allowed a comparison of current results with data from previous research by others acquired through microprobe analysis.

A Philips XL30 FEG-ESEM instrument with an EDX detector was used to study the samples' structure and elemental composition. The polished sections were mounted onto a carbon coated, double-sided sticky tape straight onto an ESEM stub and placed in the specimen chamber of the microscope. The samples were analysed using the following instrumental parameters. Accelerating voltage: 20kV, working distance: 10mm, specimen tilt: 0 degrees.

The electron micrographs for each sample are presented in Appendix I while the tables of all chemical data from EDX point analysis are provided in Appendix II. Each table represents one sample from which various areas or sites of interest were analysed. Results acquired from the EDX are discussed with reference to representative examples for each site. SEM analysis proved to be important for further clarifying microstructural detail. The presence of microporosity (see above) made microstructural analysis using optical microscopy very difficult. The greater depth of field possible with the SEM has allowed for better resolution of individual phases.

To complement existing analytical data the samples' mineralogy was determined using X-ray diffraction. This technique allows the determination of mineral phases present and can thus provide insight on a range of issues related to resource perception and technological choices. Quantitative data was produced from these analyses but the difficulty in acquiring suitable standards relevant to archaeological materials has meant that quantitative data cannot be evaluated for accuracy. For this reason relative abundance of minerals has been reported as qualitative data. The diffraction spectra for each sample are presented in Appendix I. The relative abundance of certain minerals within each sample is denoted by the use of (+) symbol. The major minerals represented are denoted by ++, minor minerals are denoted by + and traces are also indicated in the corresponding tables for each assemblage discussed below.

The technique chosen initially for examining the chemical characterisation of the slag samples was ICP-AES located at the Department of Analytical Chemistry in Aristotle University of Thessaloniki. The intention was to determine major, minor and trace elements and to use this quantitative information for a thorough assessment of the processes involved during slag formation. However, the standard digestion method using Hydrofluoric acid proved incapable of dissolving magnetite, and presumably accompanying spinel minerals. The implication of incomplete digestion is that the analyses have a significant and unsystematic error for most elements.

Having discounted results from the ICP as unreliable due to the inappropriate digestion method used, compositional analysis was undertaken using X-ray Fluorescence. The technique relies on energy of electron transition when a sample is subjected to an incident X-ray source. Since each element, contained in the specimen, has specific transition energies, measurement of these energies allows the identification of the element from which it emerged. Equally, the measurement of the peak intensity at that energy allows concentration of that element to be determined. Among the technique's advantages is the precision and analytical speed in addition to being reasonable at resolving peaks for different elements. The instrument used was a portable XRF (Niton XL3T-P) which uses a fundamental parameter calibration. The calibration has been checked against standard slags hence accuracy and precision has been determined. All the chemical composition data are included in Appendix III, Tables 1-2 while precision and accuracy from standards are given in Table 3.

6.4 Katafyto slag analysis

Slag recovered from Katafyto falls within three of the aforementioned (section 6.3) major groups. The largest group is that of semi-compact specimens which are 23 in total, compact slags are 4 and there are 3 spongy examples. Ten samples representing all groups were selected for further analysis based on their secure context and their co-presence with Byzantine pottery that have been used as relative chronological indicators as shown in chapter 5.

6.4.1 Microscopic examination

Based on the microscopic examination some preliminary conclusions on the technical characteristics of the smelting process could be drawn. Many slag pieces were micro-porous and this prevented samples from taking a good polish so as to reveal microstructures over extended distances. The voids caused by microporosity are substantial in some cases leaving islands of intact microstructure which hindered identification of certain phases. The semi-compact and porous samples from Katafyto consist of two major phases; a network of wüstite dendrites in a darker grey matrix. Magnetite crystals are frequent while laths of fayalite are a rare occurrence in these slags. Unlike Makrychori and Angistro these slags contain occasional metallic prills in some instances reaching 40 μm in size and display extensive microporosity (figure 6.5). In one compact specimen leucite which is alkali feldspar rich in potassium has been identified. The presence of that mineral may indicate a tall shaft furnace since it is supposed that potassium can be refluxed and concentrated in the final slag phase with sufficient upright draught (Sperl 1980).

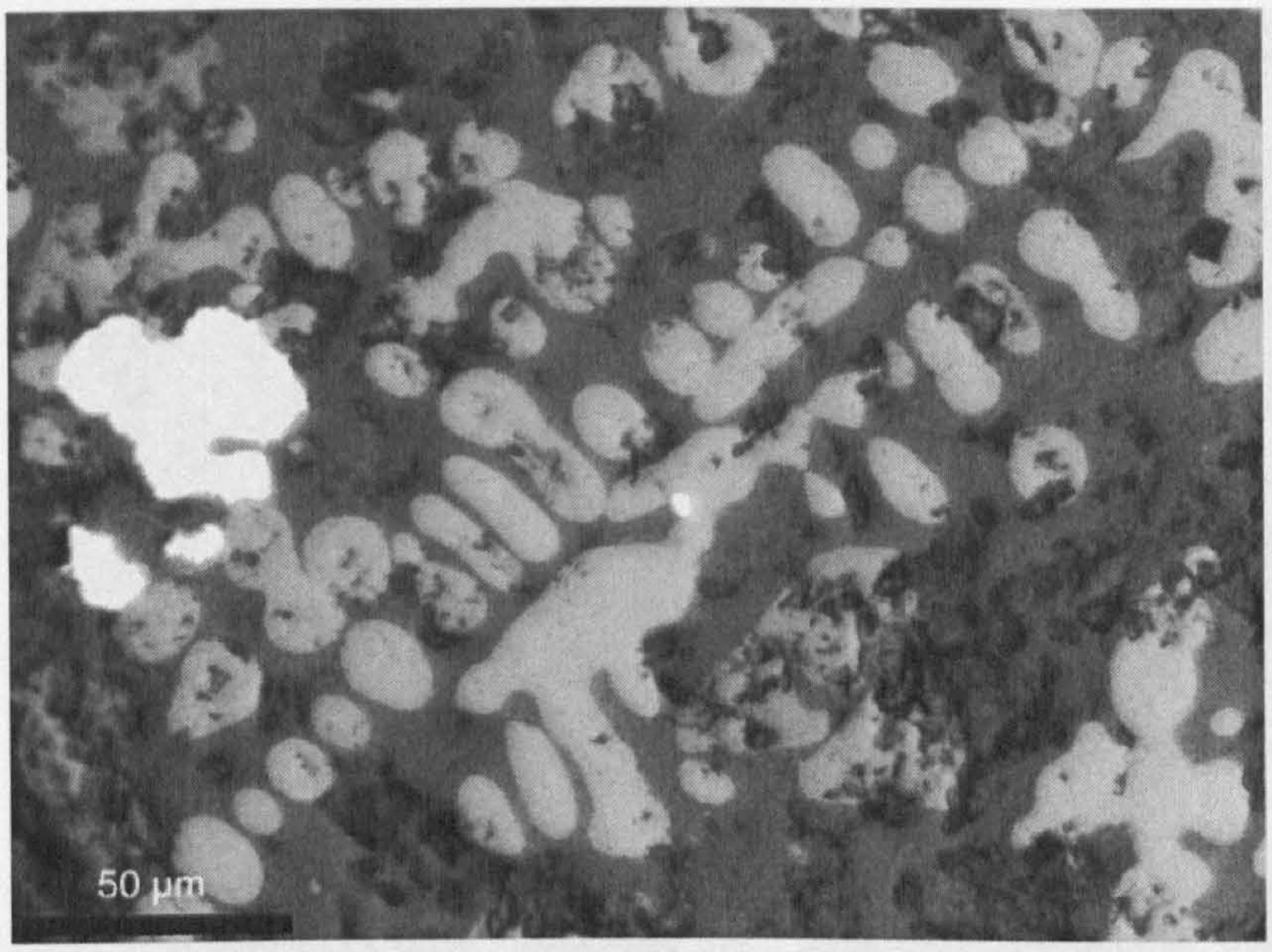

Figure 6.5 *KAT06*: Silicate matrix (mid grey), wüstite dendrites (light grey), metallic prills (white), microporosity evident as dark voids

6.4.2 Scanning electron microscopy and ED X-ray spectrometry

The mineral phases present in Katafyto samples are commonly wüstite, occasional magnetite and in some cases fayalite and spinels, a titanium rich oxide which can be distinguished by its pointed rhomboid morphology. Metallic inclusions are also present, commonly iron and more rarely speiss. The high levels of TiO_2 presumably deriving from the local ores used (Photos 1987), have been concentrated to form spinel crystals while infrequently Ti went into solution within the fayalitic matrix as shown by the EDX spectra. Appreciable amounts of vanadium were recorded in the spinel crystals rising in concentration proportionately with rising Ti contents (Figure 6.6). Low levels of Zr around 1-2% have also been noted mainly in the fayalite. Under higher magnifications achieved with the SEM microporosity was observed to transcend both matrix and individual phases.

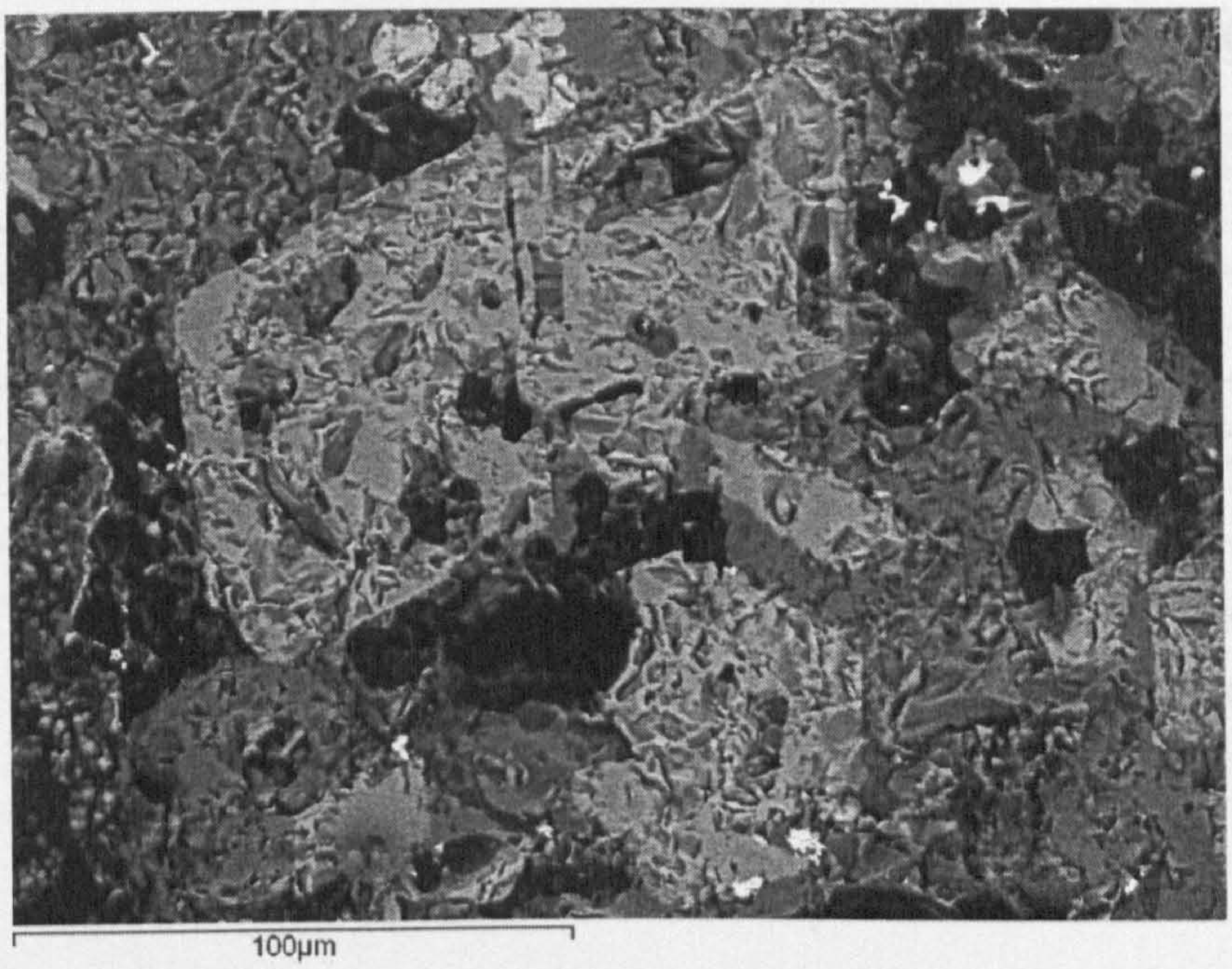

Figure 6.6 *KAT07*: silicate matrix (dark), spinel crystals (light grey) consisting of TiO_2: 16.44% and V_2O_5: 7.56% (SEM photomicrograph)

6.4.3 X-ray Diffraction analysis

All mineralogical information acquired from Katafyto samples converges to characterise an assemblage of typical bloomery slag. Magnetite appears to be the most common mineral found in nine out of ten samples in high concentrations. Wüstite is also frequent while fayalite present in less occasions a fact that was already established by optical and electron microscopy. Hematite, which is present in four specimens, might be a remnant of the ores being used. Quartz is also present within half of the samples. Minute quantities of lead (0.004%) were detected in four samples (KAT04-KAT07) by XRF whereas no individual phases which contain that metal were found by SEM-EDS. The traces of melanotekite detected by XRD in KAT06 and KAT07 are in agreement with the XRF data but traces of the same mineral in three more samples is contradicting XRF results which showed no lead. This is probably due to a sampling problem or the inhomogeneity of the material.

	Mt	Wu	Ht	Fa	Me	Mo	Qz	Cr	Kf	Di	Cc
KAT01	++			+	trace						
KAT02	++		trace		+		trace		+	+	+
KAT03	++	++			+	+	trace				
KAT04	++		+								
KAT05			trace				++	+			
KAT06	++	++			+	trace					
KAT07	++	+		+	trace						
KAT08	++		++				trace		+		Trace
KAT09	+	++		trace							
KAT10	+	++					trace				

Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Ht: Hematite-Fe_2O_3, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$, Qz: Quartz-$SiO_2$, Cr: Cristobalite-$SiO_2$, Kf: Alkali feldspar-$KAlSi_3O_8$, Di: Diopside-$Mg_{0.6}(Fe_{0.2}Al_{0.2})Ca(Si_{1.5}Al_{0.5})O_6$, Cc: Calcite-$CaCO_3$

6.4.4 Chemical composition determined by XRF

The major components present in Katafyto slag are FeO around 50% in average, SiO_2 around 20%, Al_2O_3 reaching 6% and CaO around 5% (see APPENDIX III, Tables 1 and 2). The presence of TiO_2 around 2% is characteristic for such residues as described above. Lower contents (<1%) of other elements and compounds such as Cl, MnO, Sr and S were also measured while K and P_2O_5 were not detected. Other metals such as Pb, W and Cu are present in very low contents in some of the samples while no As, Sb and Zn have been detected. With regards to minor elements V and Zr were measured in significant concentrations while three samples contained Ag ranging from 17.47 to 28.22 ppm. The presence of this precious metal derives from the ores being used on site but there is no confirmed evidence for its extraction. All compositional data testify to bloomery smelting residues formed through reduction of iron oxides while any entrapped silver contents ended up in the slag.

6.4.5 Other analytical work

Previous chemical analyses conducted on slag from Thasos and sites in northern Serres and Drama, namely A. Vrontou and Katafyto showed higher Ti contents of the former, ranging 4.96-17.80% and lower but appreciable amounts in Katafyto slag within the range of 2.15-3.70% (Photos 1987, 161). It has been shown through line scans and X-ray distribution maps that Ti is predominantly concentrated in the ulvospinel while the matrix is practically Ti-free (figure 6.7).

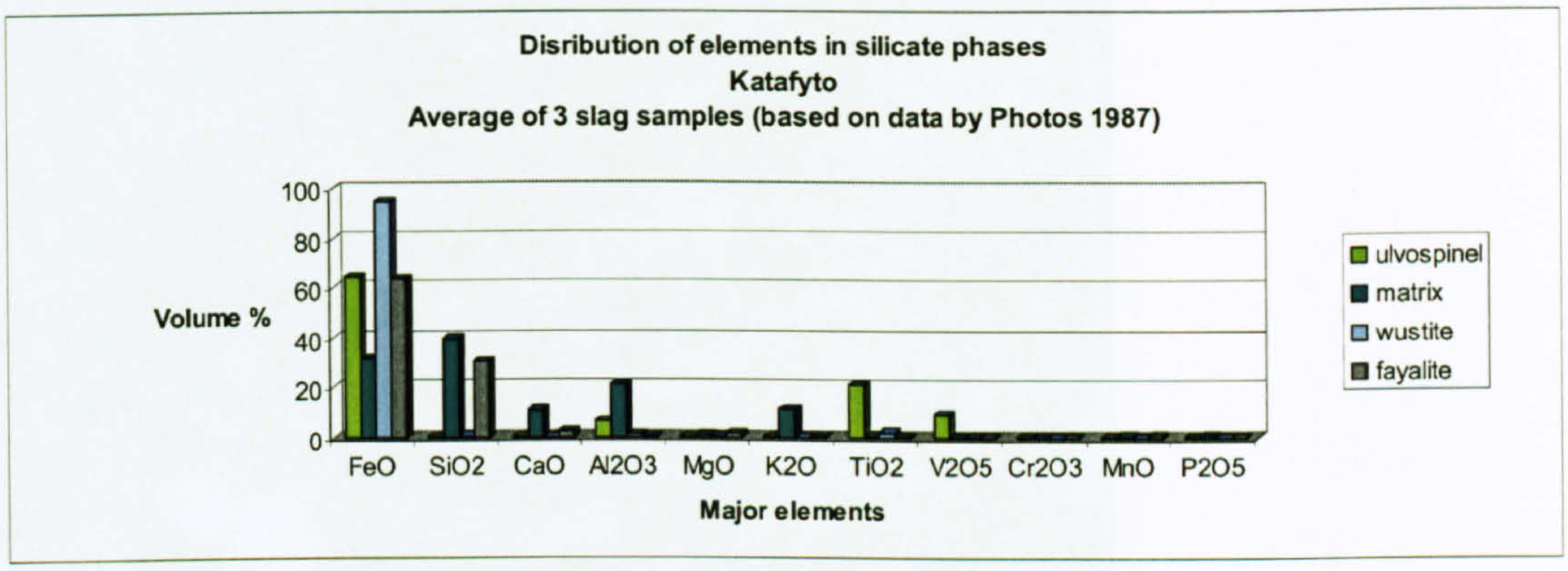

Figure 6.7 Silicate phases in Katafyto slag (based on analytical work by Photos 1987)

6.5 Vathytopos slag analysis

Slag from Vathytopos fall within three major groups as was the case with Katafyto slag. External similarities of the residues from these two sites point to potentially similar practice by which they had formed. Among the 30 samples recovered from the field there are 20 compact, 8 semi-compact and 2 spongy examples. Analysis concentrated on 10 samples, 6 of them compact, 2 semi-compact and 2 spongy, so representing the three main groups.

6.5.1 Microscopic examination

The dominant microstructural features of Vathytopos slag consists of a silicate matrix, networks of wüstite dendrites, and occasional metallic prills (figure 6.8). Magnetite has also been noted in a large number of specimens while fayalite is present but only occasionally. Spinels with typical rhomboid outlines have been located on numerous instances supporting further the similarities in consistency with Katafyto slag. Bright spots representing metallic inclusions, mainly iron oxides are frequent throughout most of the polished sections examined.

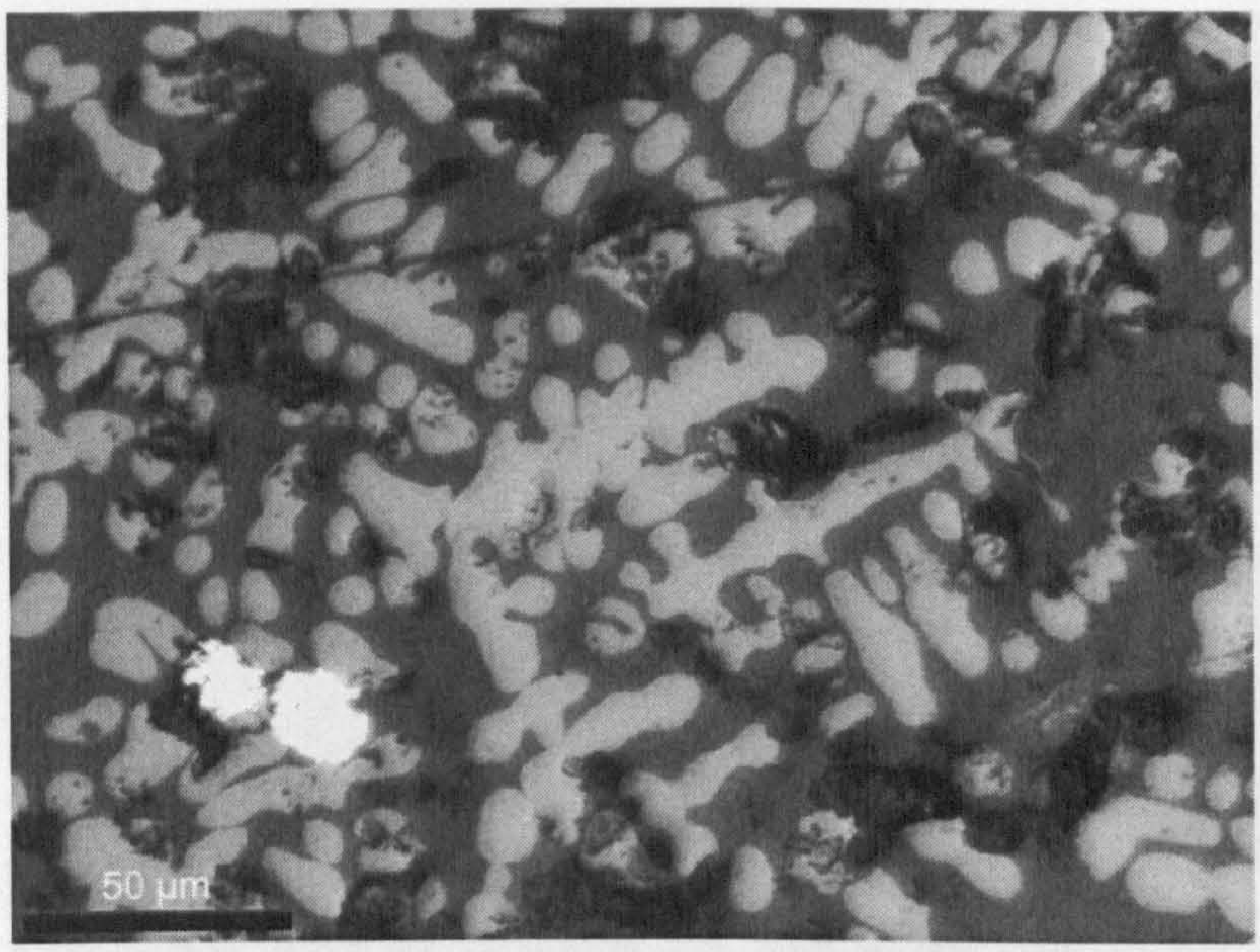

Figure 6.8 *VTH05*: Silicate matrix (mid grey), wüstite dendrites (light grey), metallic prills (white)

6.5.2 Scanning electron microscopy and ED X-ray spectrometry

The samples from Vathytopos show a typical ferrous slag composition with a high SiO_2 and FeO matrix, accompanied by lesser amounts of Al_2O_3 and CaO. A dendritic pattern of frequent wüstite associated with occasional fayalitic laths predominates. Occasional spinels are present, indicative of the similarity of the ores used at both sites, but generally lower in distribution than in Katafyto samples (Figure 6.9). The average Ti content is 2.60% only a bit lower than that noted in samples from Katafyto (3.40%). Differences in technology, i.e. in the details of a generally similar smelting process, between the two sites probably resulted in variations in the microstructures of slags formed from chemically uniform mineral sources. Inclusions rich in iron with both angular and amorphous outlines were recorded, the larger of which reaching almost pure iron composition about 90%. Zirconium is also present but only in minor contents not surpassing 2.5%.

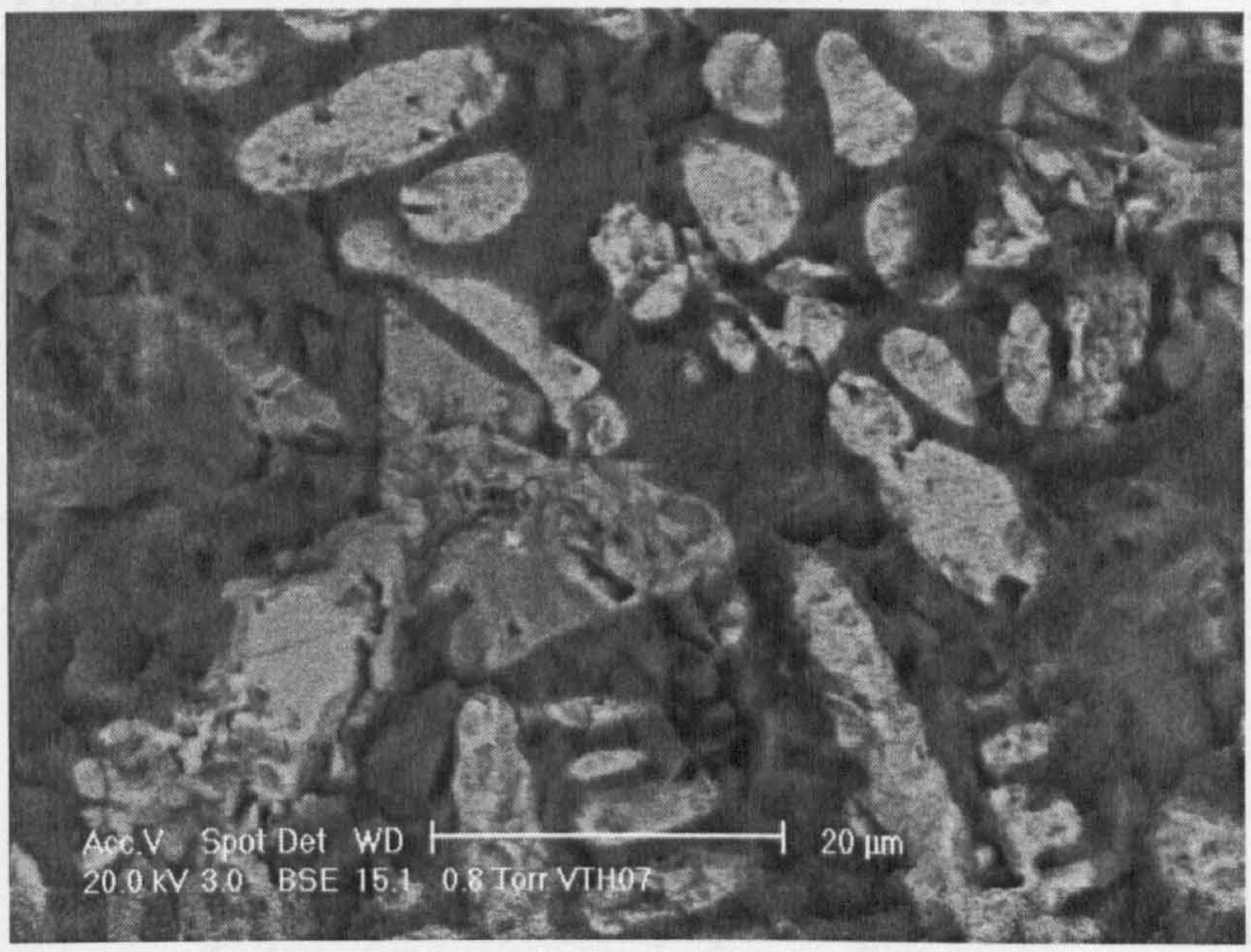

Figure 6.9 *VTH07*: silicate matrix (dark phase), dendrites of wüstite (white), rhomboid spinel crystal (light grey at the centre) consisting of TiO_2: 12.46% and V_2O_5: 5.39% (SEM photomicrograph)

6.5.3 X-ray Diffraction analysis

Vathytopos samples could generally be described as having a similar mineralogical composition with those from Katafyto. Magnetite could be found among all the specimens but wüstite is present in higher proportions. Fayalite occurs in low amounts. Those three specimens where fayalite is present also contain traces of melanotekite which again does not correspond to XRF results since no lead was detected. However the general mineralogical pattern for these slags is in agreement with microscopic examination results.

	Mt	**Wu**	**Fa**	**Me**	**Mo**	**Qz**
VTH01	+	++	trace	trace		
VTH02	+	++				trace
VTH03	+	++				
VTH04	++	++	+	trace		
VTH05	+	++				
VTH06	trace	++	+	trace		
VTH07	+	++			trace	++
VTH08	+	++			trace	
VTH09	+	++				
VTH10	+	++				

Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$, Qz: Quartz-$SiO_2$

6.5.4 Chemical composition determined by XRF

Major elements for Vathytopos slag include FeO which exceeds 60% in concentration for most samples, SiO_2 is present in concentrations around 20%, and lower contents of Al_2O_3 and CaO reaching around 6-8%. Considerable levels of TiO_2 were measured ranging from 1.5-3% suggesting that possibly similar iron ores as those in Katafyto have been utilised. Lower amounts of other elements have been detected such as MnO and Cl which are represented by less than 1%. Concentrations of trace elements show higher figures for V and Zr and also Bi, Cr and Ba. Four samples contain traces of Ag from 19.48 to 21.16 ppm a fact that shows the potential for silver extraction form available ores on site. However the overall composition of all the analysed samples corroborate to iron smelting practice by which no silver was recovered in metallic form but it remained in the forming slag.

6.5.5 Other analytical work

Photos (1987) also found appreciable contents of Ti in slag samples from Vathytopos with the Ti concentrated in the wüstite (figure 6.10). The importance of Ti contained in the analysed specimens lies on the fact that it acts as a potential tracer element for ore provenancing. Her experimental data on reducing iron sands from known locations to give rise to ulvospinel phases with similar composition to archaeological slag have enhanced the possibility of provenancing the ores that were exploited in the past (Photos 1987).

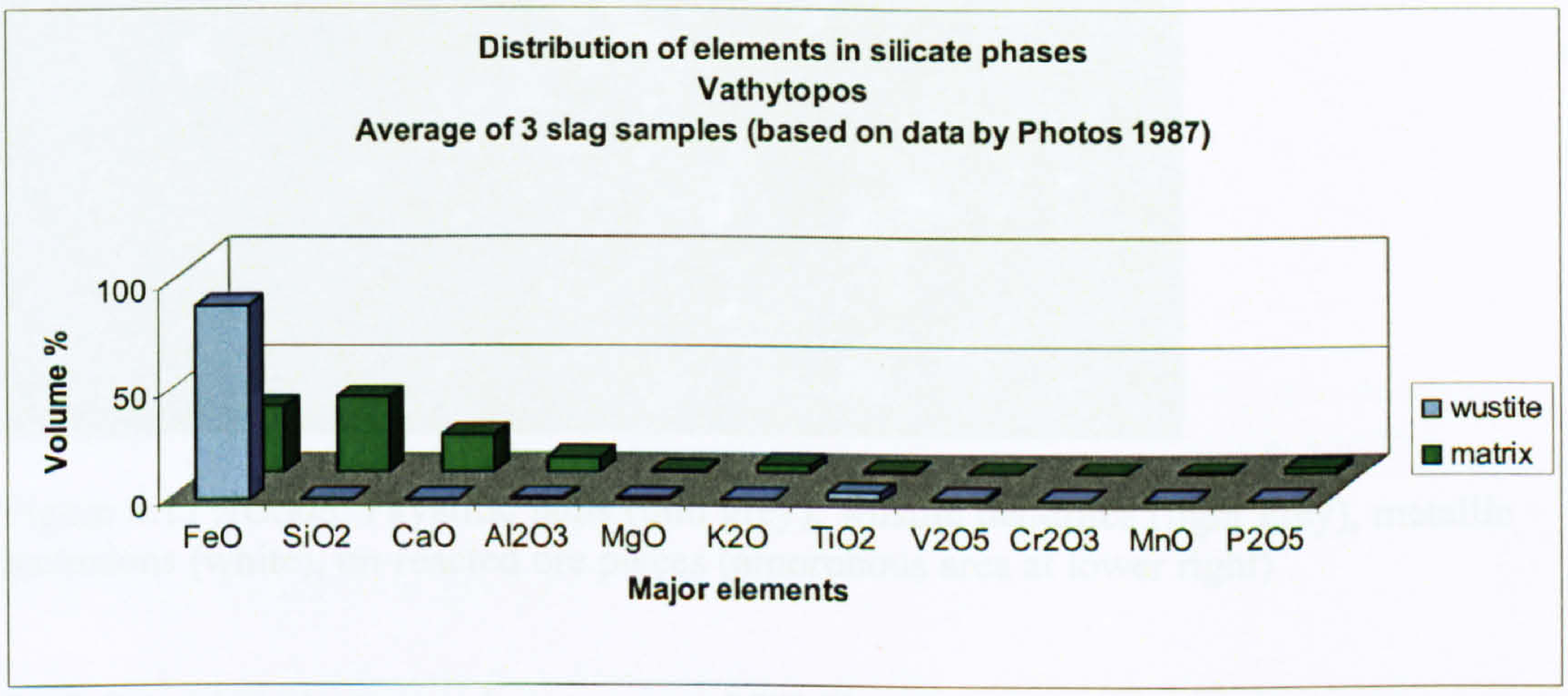

Figure 6.10 Silicate phases in Vathytopos slag (based on work by Photos 1987)

6.6 Angistro slag

The types of slag represented at the sampled deposit in Angistro are generally compact with a ropey texture indicative of tapping and also semi-compact and rarely spongy. Sampled material consists of 26 compact and 4 semi-compact specimens from which 10 have been further analysed.

6.6.1 Microscopic examination

Polished sections from Angistro reveal a microstructure with a predominance of wüstite dendrites, magnetite crystals and frequent fayalite laths in a vesicular silicate matrix (Figure 6.11). The predominance of fayalitic phases suggests silicate composition while significant iron oxides had been reduced to metallic iron hence wüstites are less dominant. Metallic inclusions are generally rare and in some cases there are pieces of un-reacted ore in clusters.

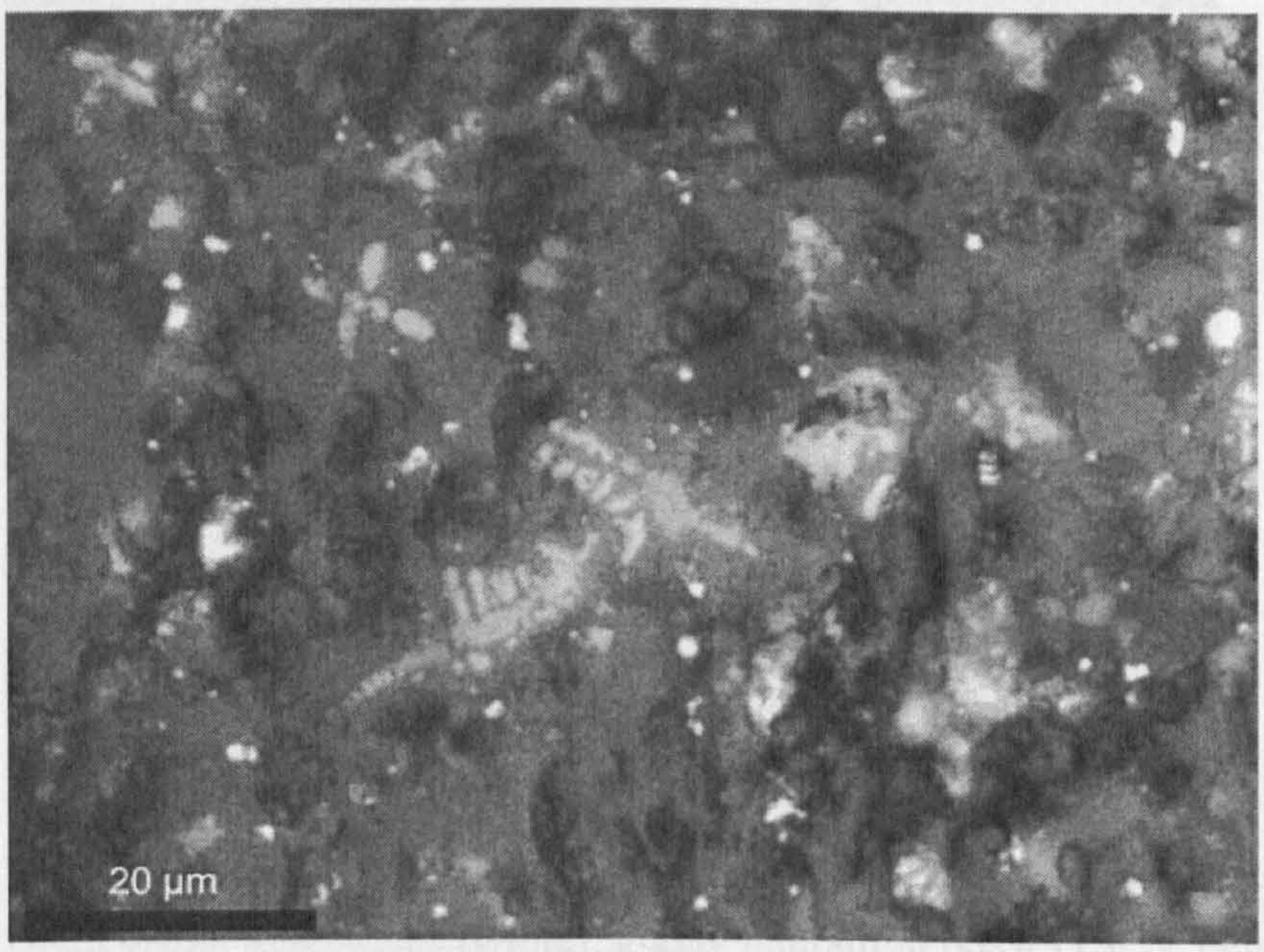

Figure 6.11 *AGS08*: Fayalitic laths (mid grey), wüstite dendrites (light grey), metallic inclusions (white), un-reacted ore pieces (amorphous area at lower right)

6.6.2 Scanning electron microscopy and ED X-ray spectrometry

Slags from Angistro are mainly of SiO_2-Al_3O_2-CaO composition with significant but lower FeO levels than slag from Katafyto and Vathytopos. There is excessive presence of fayalitic laths, rare inclusions of iron oxides and As/Sb-rich speiss. The notable presence of appreciable amounts of Pb and Cu could derive from some sort of collecting/lead washing operation for the extraction of gold during formation of such slag. Sample AGS08 is representative of the slags from Angistro and in some instances demonstrates the range of minerals present (figure 6.12). The angular white inclusions are iron rich phases, and some spheroid prills have a speiss composition. Occasional dark grey globular crystals consist of FeS a derivative of the

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sulphide ore that was readily available in the Angistro deposits (see section 4.4.6 in chapter 4).

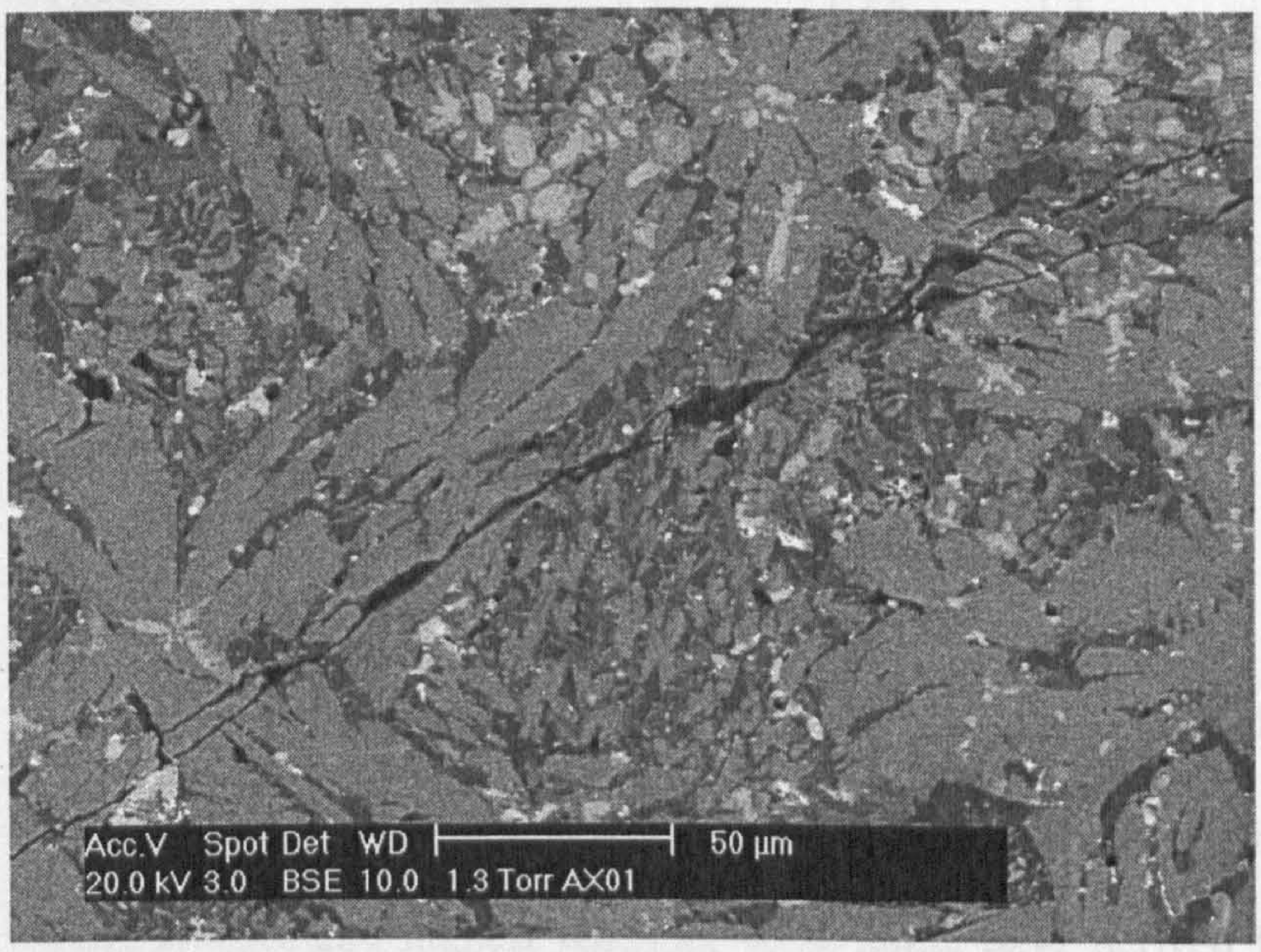


Figure 6.12 *AGS08*: large laths of fayalite (mid grey), decomposed wüstite dendrites (light grey), iron oxides (white), glassy interstitial phases (SEM photomicrograph)

6.6.3 X-ray Diffraction analysis

The major minerals found in Angistro slag are: magnetite, wüstite, fayalite and melanotekite. Magnetite (Fe_3O_4) is of frequent occurrence found in seven samples while fayalite is abundant among nine samples. Occasional wüstite was found in five specimens. The presence of melanotekite [$Pb_2Fe_2(Si_2O_7)O_2$] is of special importance since it was found as a major mineral in four out of ten samples. Quartz is represented as a major mineral in two samples.

	Mt	Wu	Fa	Me	Mo	Qz	Cr
AGS01	++		++	+	trace		
AGS02			trace			++	+
AGS03		trace	++	+			
AGS04		trace	++	++	+	+	
AGS05	+		+		trace	++	
AGS06	+		++	++	+		
AGS07	++	++	+	+	+		
AGS08	++	trace	++	+	trace		
AGS09	++		+	++	+		
AGS10	+	+	++	++	+		

Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$, Qz: Quartz-$SiO_2$, Cr: Cristobalite-$SiO_2$

6.6.4 Chemical composition determined by XRF

Compositional analysis on Angistro slag has revealed a picture of high temperature iron smelting practice. Considerably high levels of SiO2, with lowest values at 26% and highest reaching 45%, could have derived from successful iron reduction which led to highly siliceous slag. Likewise the increased contents around 10-12% CaO noted for all samples could have formed by interaction of the charge with furnace lining or might be the result of fluxing. The average FeO contents ranging 35-40% further support this picture. The presence of other metals in low amounts such as Pb, Sn, Cu and Zn are of some significance and As with Sb probably derive from speiss phases within the slag (section 6.8.4). Trace elements are generally in low concentrations while no precious metals were detected in these slags.

6.7 Makrychori slag

The samples taken from Makrychori form three major groups, one of which consists of glassy slag, absent from all the other investigated sites. In total the sampled material consists of 17 compact, 3 semi-compact and 10 glassy specimens out of which 10 samples were selected for instrumental analysis, 4 compact, 2 semi-compact and 4 glassy.

6.7.1 Microscopic examination

The microstructure of Makrychori slag is quite different compared to the other sites discussed mainly due to the presence of glassy phases noted in a number of samples. Most of the examined sections revealed extensive glassy phases and a homogeneous matrix with rare wüstite dendrites and fayalite laths indicating high silica contents, high viscosity and successful metal-slag separation. Magnetite crystals are common as well as amorphous inclusions with angular profiles (figure 6.13). Spheroid metallic prills are also present in lower amounts and microporosity is common.

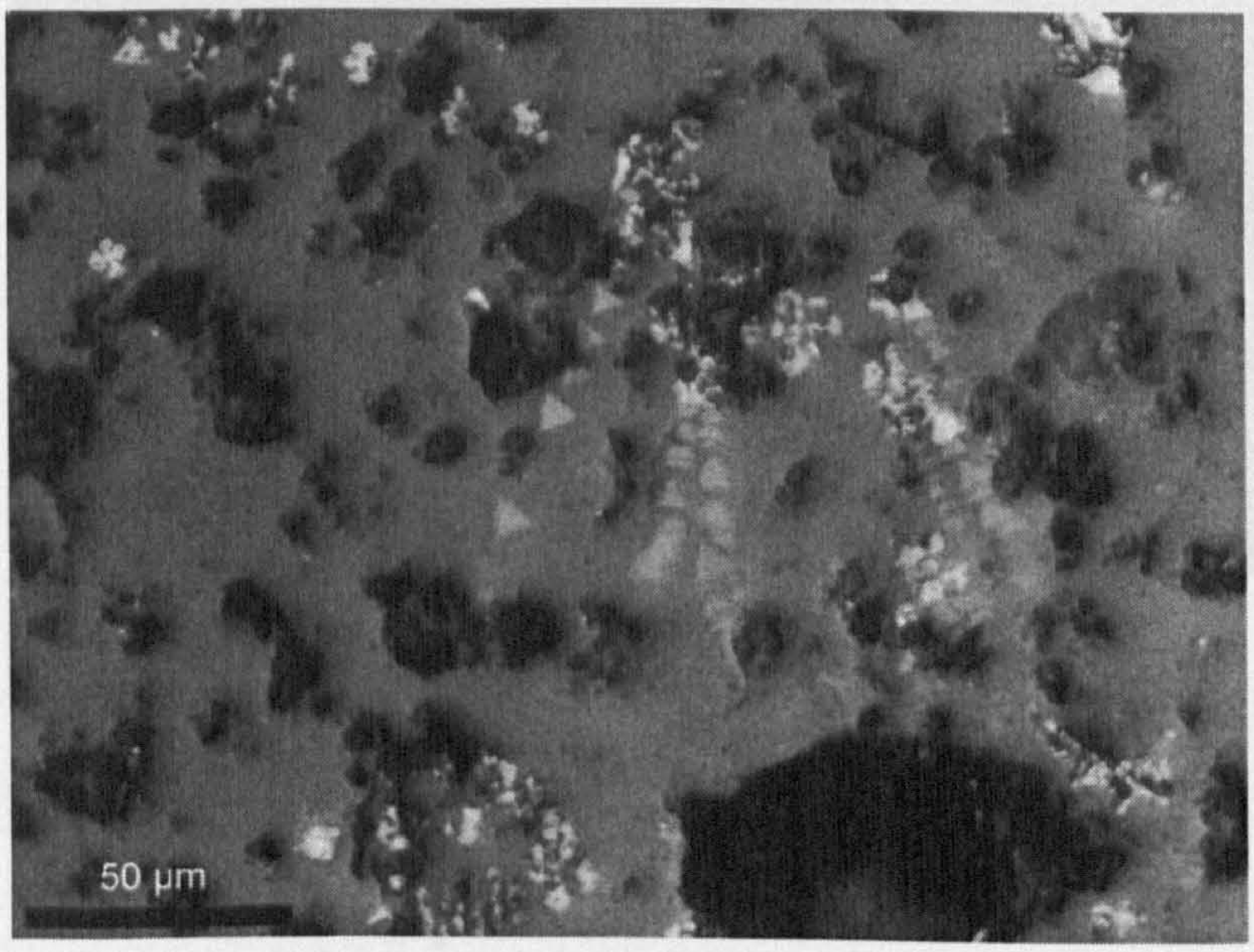


Figure 6.13 *MAK04*: Glassy matrix (grey), metallic angular inclusions (white)

6.7.2 Scanning electron microscopy and ED X-ray spectrometry

Samples from Makrychori consist of an iron silicate matrix (30-50%) with considerable levels of Al_2O_3 (8-20%) and CaO (5-14%). Analyses of large areas identified the presence of Mn sometimes up to 18%, compared with Fe at 12%. Small amorphous and globular inclusions rich in Pb represent individual inclusions and it is suggested here that they resulted from the addition of Pb within the charge at some stage of the smelting process because of the low levels of Pb in the regions' mineralogy. Other possible reasons for the presence of lead are discussed below. Speiss inclusions are also common featuring typical compositions with As around 10-17% and Sb between 24 and 32% (figure 6.14).

Figure 6.14 *MAK02*: glassy matrix (black) and spheroid speiss inclusion consisting of Fe: 6.72%, Pb: 22.2%, Cu: 1.43%, As: 10.74%, Sb: 24% (SEM photomicrograph)

Lead is widely distributed within the matrix and metallic phases but was not detected in the glassy phases suggesting at least moderately reducing atmospheres. The low amounts of FeO and scarce occurrence of wüstite in most samples indicates a well-practised technology by which iron was recovered in metallic form with small losses entering the slag. Further the presence of Pb could suggest that these slags derive from the smelting of auriferous iron ores in order to gain the precious metal through a lead washing operation similar to that described by Georgius Agricola (Book X in Hoover and Hoover 1950). Geologists who have conducted analyses on Fe-Mn ores and iron pyrite-arsenopyrite from the region report gold contents at 26 ppm and 38 ppm respectively (Vavelidis *et al* 1996) whilst Photos *et al* (1989, 186) report gold levels from Makrychori slag around 119 ppm.

6.7.3 X-ray Diffraction analysis

Samples from Makrychori are generally characterised by a broader diversity of minerals than that described for Angistro. Magnetite is rare detected in only three occasions and interestingly wüstite and fayalite are seemingly absent from a whole assemblage. The mineral suite is suggestive of CaO rich pyroxenes such as monticellite [$CaMgSiO_4$], diopside [$Mg_{0.6}(Fe_{0.2}Al_{0.2})Ca(Si_{1.5}Al_{0.5})O_6$], actinolite [$Ca_2(Mg,Fe^{+2})_5Si_8O_{22}(OH)_2$] and akermanite [$Ca_2Mg(Si_2O_7)$] which correlates well with the low Fe and high Ca values determined by XRF. The presence of quartz in six other samples reflects the high Si content of these slags and supports the idea of these slags deriving from higher temperatures than the normal range in a bloomery process. Equally, cristobalite (SiO_2) found in two samples suggests a similar scenario. Such high temperatures are further supported by the presence of minerals such as akermanite which only forms at elevated temperatures. Scorodite (iron arsenate) found in sample MAK07 derives from the corrosion of any speiss inclusions contained therein.

	Mt	**Ht**	**Sc**	**Mo**	**Qz**	**Cr**	**Kf**	**Pl**	**Ak**	**Di**	**Ac**	**Cc**	**Do**
MAK01	+			++									
MAK02					++								
MAK03	+			++	+								
MAK04		+			++		+						
MAK05		+			++	+					+	+	Trace
MAK06	trace				++			++		+			
MAK07		++	+	++					trace				
MAK08		trace			++	++			trace	+	+		
MAK09									++				
MAK20				++									

Mt: Magnetite-Fe_3O_4, Ht: Hematite-Fe_2O_3, Sc: Scorodite-$FeAsO_4(H_2O)_2$, Mo: Monticellite-$CaMgSiO_4$, Qz: Quartz-SiO_2, Cr: Cristobalite-SiO_2, Kf: Alkali feldspar-$KAlSi_3O_8$, Pl: Plagioclase-$NaAlSi_3O_8$, Ak: Akermanite-$Ca_2Mg(Si_2O_7)$, Di: Diopside-$Mg_{0.6}(Fe_{0.2}Al_{0.2})Ca(Si_{1.5}Al_{0.5})O_6$, Ac: Actinolite-$Ca_2(Mg,Fe^{+2})_5Si_8O_{22}(OH)_2$, Cc: Calcite-$CaCO_3$, Do: Dolomite-$CaMg(CO_3)_2$

6.7.4 Chemical composition determined by XRF

Chemical characterisation of slag from Makrychori has been crucial for a better understanding of the evidence since microscopic and mineralogical data have clearly separated these slags from those of the other investigated sites. FeO contents are considerably low ranging between 5 and 15% while SiO_2 concentration ranges between 40 and 68%. It is also interesting to note that Al_2O_3 contents are significantly higher than any other analysed slag in this study. The increased values of MnO 3-12% in relation to the low FeO values suggests efficient iron reduction of complex ores that contain manganese. The presence of As and Sb should denote speiss inclusions while Pb, Cu and Zn were probably introduced during smelting as discussed in section 6.8.4.

6.8 Discussion on slag analysis results

The most abundant type of slag found across all sites is of compact morphology, black in colour, relatively heavy and magnetic, with occasional flow patterns on the surface indicative of tapping, such slags are also characterised as ropey. The second category in abundance is the semi-compact class, also present on all sites, which includes brown-black, magnetic specimens with some porosity evident. The third group is smaller consisting of glassy slags which are only present at Makrychori and the fourth is made up of a few spongy slags found at Katafyto and Vathytopos. Figure 6.15 shows the various types of slag present in each site and their relative proportions while figure 6.16 shows the total abundance of each represented type in the assemblage.

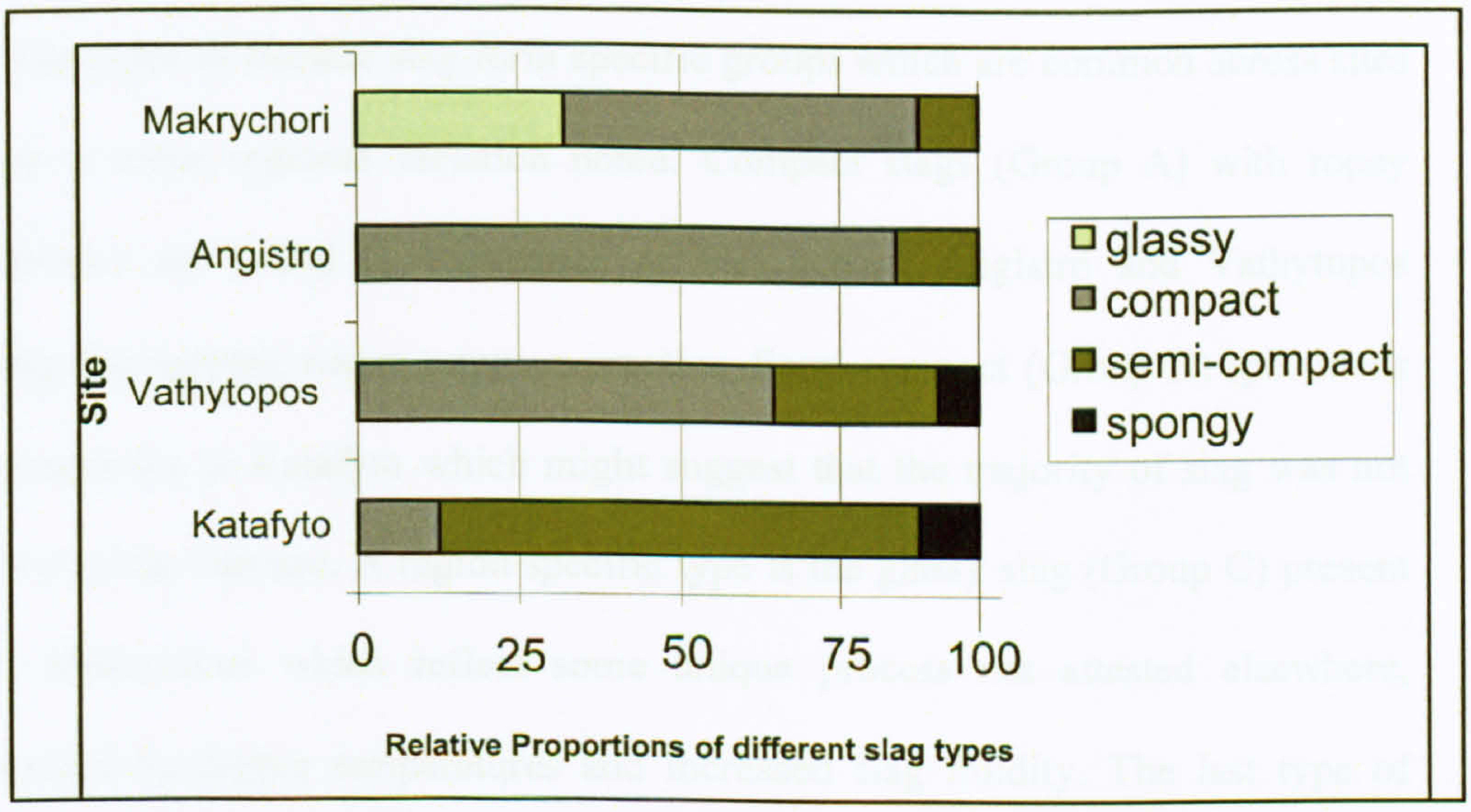


Figure 6.15 Chart showing the relative proportions of the four major slag types for each site

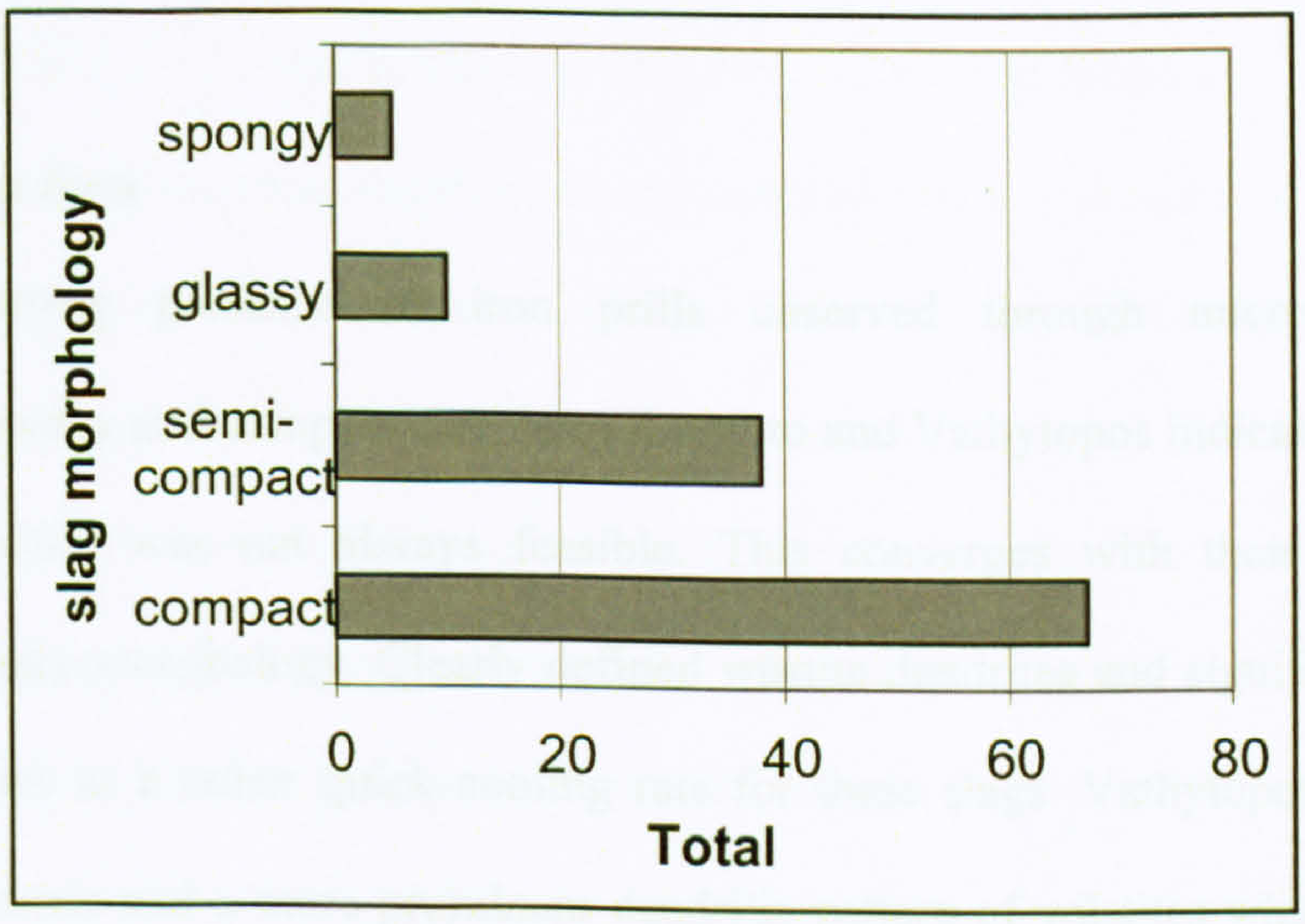


Figure 6.16 Chart showing the volume of each slag type

The results from the four sampled sites are in accordance with the morphological pattern for eastern Macedonia as described by Papastamataki (1985) and Photos (1987) with a predominance of compact and substantial amounts of semi-compact slag. Such a pattern is presumed to indicate the use of shaft furnaces with appropriate features to facilitate slag separation such as tapping hole and stoke. The predominance of compact slag is also considered to indicate capable furnace control with good recovery of metal (Bachmann 1982).

The types of furnace slag form specific groups which are common across sites but there is some regional variation noted. Compact slags (Group A) with ropey characteristics are found in abundance at Makrychori, Angistro and Vathytopos indicating that tapping was a common practice. Semi-compact (Group B) specimens are in abundance at Katafyto which might suggest that the majority of slag was not tapped out of the furnace. A region specific type is the glassy slag (Group C) present only in Makrychori which reflect some unique process not attested elsewhere, characterized by higher temperatures and increased slag fluidity. The last type of spongy slag (Group D) displays high porosity, lacks magnetism and probably derives from an interaction with fuel ash.

6.8.1 Microscopic data

The recurring presence of iron prills observed through microscopic examination in spongy and compact slag from Katafyto and Vathytopos indicates that metal-slag separation was not always feasible. This converges with their semi-compact and spongy morphology. Clearly defined wüstite dendrites and significantly large crystals point to a rather quick cooling rate for these slags. Vathytopos slags exhibit larger crystals and a more prominent dendritic pattern of wüstites which is a typical indication of rapid cooling. Further the abundance of metallic prills points to relatively unsuccessful gain in metal. Angistro slag is fayalitic with the presence of magnetite and occasional inclusions. These were shown to be mainly lead prills and speiss phases although iron oxides were also noted. Their overall texture is coarse and there are crystals of small sizes denoting slower cooling rates. Slags from Makrychori generally show a homogenous texture with numerous glassy phases and less microporosity compared to other sites. Wüstite is present but only rarely indicative of an operation by which most siliceous minerals remain in the slag and there is sufficient gain in metal compared to the other sites.

6.8.2 SEM-EDX analytical data

Previous work suggested that the major mineralogical phases present in eastern Macedonian slag are wüstite (FeO), spinel (Fe_2TiO_4) and a glassy crystalline matrix which is made up of kirschstenitic (Ca.FeO.SiO_2) composition and a K-Al-Fe silicate known as mellilite (Photos 1987; Vavelidis *et al* 1996). Such information provided by previous analytical work is being compared below to the current findings.

Slags from Katafyto reveal a typical ferrous microstructure with frequent wüstite and magnetite phases and occasional fayalites. Vathytopos specimens contain frequent wüstite and occasional fayalite with magnetite being less common. The presence of titanium noted in all the above samples derives from the local iron sands used and is distributed within the spinel phases. The characterization of individual phases helped discern an apparent overlap in major elements between these two sites. Although their morphology is somewhat different, the similarities in structure observed through the SEM could mean similarities in metallurgical practice.

For Angistro slag the presence of lead has been detected in numerous instances with an average concentration of 1.6%. Laths of fayalite appearing with pointed outlines predominate in a SiO_2 rich matrix (9.6%). Of equal importance are some regions with As reaching 0.35%, Zn around 0.7% and S on average 0.50% which could be indicators of the ores used at the site. Chiotis *et al* (1996) reported on the sulphide mineralization consisting of galena, pyrite, chalcopyrite and sphalerite with evident signs of mining in the region. The ore was likely dominated by arsenopyrite possibly intergrown with some pyrites which are common minerals in the mines of Angistro as has been shown by mineralogical data (Chiotis *et al* 1996).

The microstructure of Makrychori slags is characterized by widespread occurrence of a glassy phase with occasional fayalitic phases and rare wüstite. A common characteristic of these slags is the presence of Mn concentrated in the matrix at appreciable levels around 4%. In distinct phases such as metallic prills, lead could be found in higher concentrations (30%) associated with other metals such as Cu: 4%, As: 15%, Sb: 24%. Such compositions are typical for speiss and it could be concluded that collection of precious metals was taking place.

In addition to the data mentioned above a second group of slags, identified by specific mineralogical composition, at sites of the Lekani range in the Palaea Kavala region namely at Pyrgiskos, Dipotamos, Tria Karagatsia, Petropigi and Makrychori. Their main characteristic is the presence of Mn which is distributed among the wüstite phase. Other major phases include a Ca-rich olivine (kirschstenite) and a matrix which consists of either an Al-K silicate of mellilitic composition or a eutectic of mellilite and kirschstenite (Photos 1987, 192). Speiss pieces were also recovered from sites mentioned above, probably deriving from the smelting of complex ores, and speiss was also found within slag in the form of prills. Speiss acts as a precious metals collector due to its high contents of As and/or Sb which are close to Au and Ag in valance and are usually closely associated within a smelt.

6.8.3 XRD results

Although not providing quantitative data the results from the XRD have been useful for a characterisation of the minerals present in each specimen. Katafyto and Vathytopos slag are predominantly composed of magnetite and wüstite and also small quantities of fayalite and traces of other minerals such as melanotekite, monticellite and quartz. Traces of hematite were detected in Katafyto slag. The most common mineral in Angistro slag is fayalite followed by magnetite and melanotekite while wüstite appears only in traces. Quartz is abundant in two instances and traces of monticellite are common. Calcareous, siliceous and high-temperature in Makrychori residues suggest efficient smelting by producing free-running slag mainly composed of pyroxenes wherein insignificant quantities of metal became entrapped.

6.8.4 XRF results

The data acquired from this technique revealed a clear picture of the chemical composition based on concentrations of a series of major and minor elements (Fe, Mn, Ca, K, Si, Al, Na, Mg, Ti, Sb, Pb, Zr) as well as traces (Bi, Ni, Cr, V, Ag). Thus FeO contents were accurately determined to be around 5-10% for Makrychori, 10-30% for Angistro slag, 40-50% for Katafyto and 60-70% for Vathytopos slag. MnO for all samples is generally close to 0.5% with some increased values from Makrychori slag (2-6%) which is expected due to the Mn-rich ore deposits that characterise the region's geology (Spathi *et al* 1982). Compositional analyses provide a clear indication of the processes at particular sites and associated aspects of the technological choices associated with them.

Results of chemical characterization illustrate a clear-cut distinction of three major groupings for slag i.e. the high FeO-low CaO slag from Katafyto and Vathytopos, the moderate FeO-CaO levels indicative of fluxing in slag from Angistro and lastly the very low FeO and high CaO slag from Makrychori. The high melting points above 1300°C observed through ternary plots for slag from Makrychori as opposed to those for slag from Katafyto-Vathytopos which formed at considerably lower temperatures further support the hypothesis of two distinct types of processes being represented. Based on the above it could be argued that slag from Katafyto-Vathytopos and Angistro resulted from a bloomery process in low shaft furnaces while slags from Makrychori are derivatives of an indirect reduction process taking place in a blast furnace. The collection of precious metals might have been achieved by the following process: a charge consisting of Mn-rich iron ore with varying amounts of Pb, Zn, As, Ag and the addition of PbO/PbS. The products would have been Pb with Ag collecting in the bottom of the furnace, speiss floating on top of the Pb layer and slag floating on top of both. Slag would subsequently be discarded after tapping while speiss was either discarded or collected for reuse (Photos *et al* 1989).

Interestingly a series of metallic elements was detected in specimens from Angistro and Makrychori such as Sb, As, Pb signifying some sort of complex mineralogy as was suggested from the SEM data. Residual metals from gold or silver recovery operations might end up in slag and therefore such findings could indicate the presence of these activities on site. Most significantly low Cu, Sn and Zn contents, albeit at low levels, have been detected in all specimens from Angistro, representing rare occurrences which could hardly derive from the local ores. Mineralogical analyses (Spathi *et al* 1982) on ores from both sites did not detect Sn compounds and established the existence of only minor levels of Cu, which might be suggestive of intentional addition of these elements to smelts for specific operational needs (see Appendix V).

Important information on various aspects of the smelting process was derived from a comparison of the metallic elements and their concentrations and a consideration of the major siliceous and alkaline slag constituents. In more detail, comparative analysis of FeO with CaO or Al_2O_3-SiO_2 provides a clear marker of slag variation in terms of temperature and the melting point of each specimen. Plotting the samples based on their FeO-CaO concentrations revealed a picture of four roughly distinct clusters each representing one smelting site (figure 6.17). Vathytopos and Katafyto slag cluster in the high FeO-low CaO region with some evident overlap, those from Angistro group around moderate FeO-CaO values and Makrychori slag form an extended scatter in the very low FeO region. The same general pattern is evident through a comparison of the FeO-SiO_2 contents with Vathytopos-Katafyto showing a densely clustered group of low silica slags and Makrychori slag clustering more tightly towards the SiO_2 rich region, while Angistro slag concentrate in a tight group of moderate FeO-SiO_2 levels (figure 6.18).

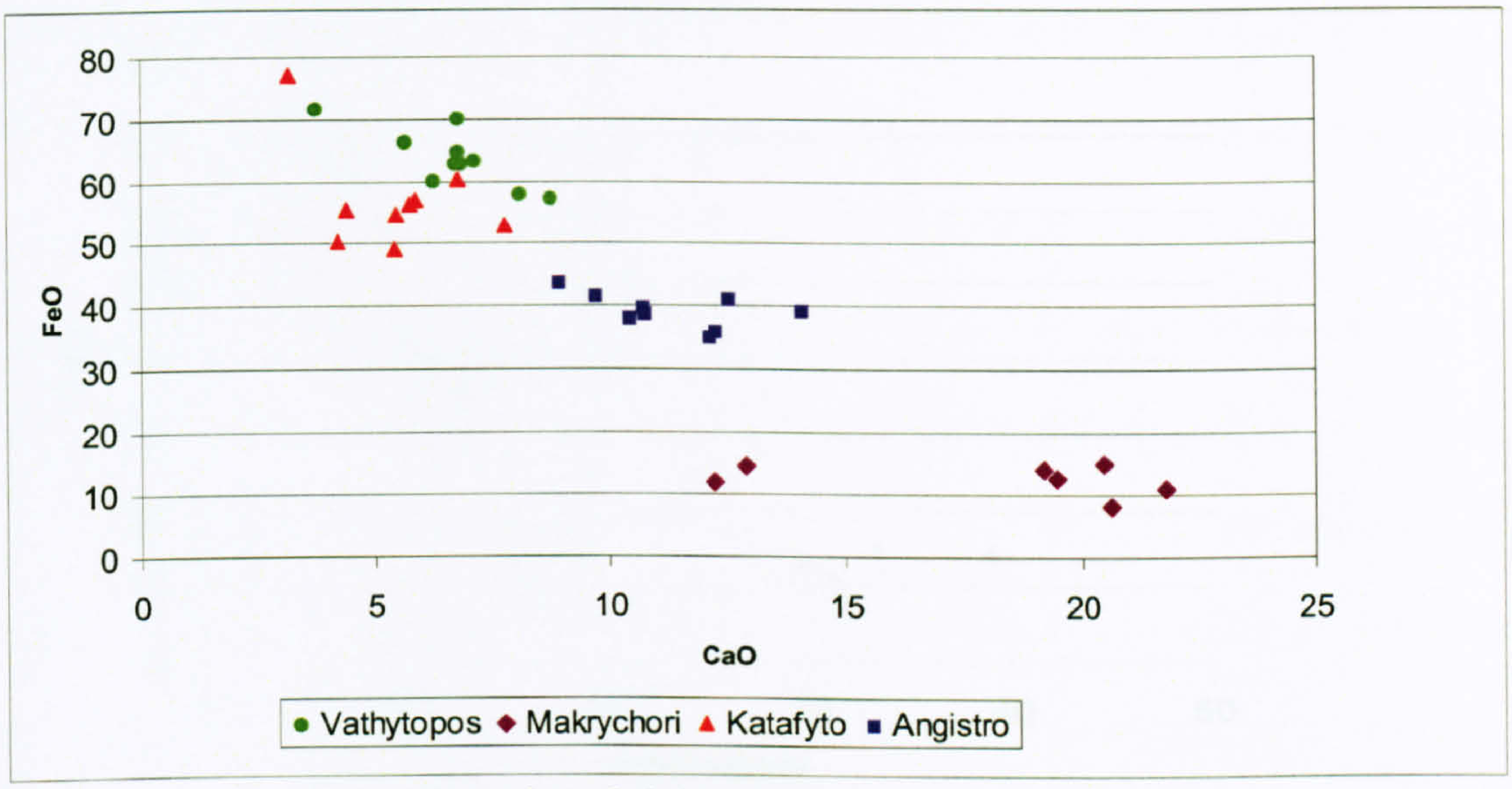


Figure 6.17 Plot of slag samples FeO-CaO correlation

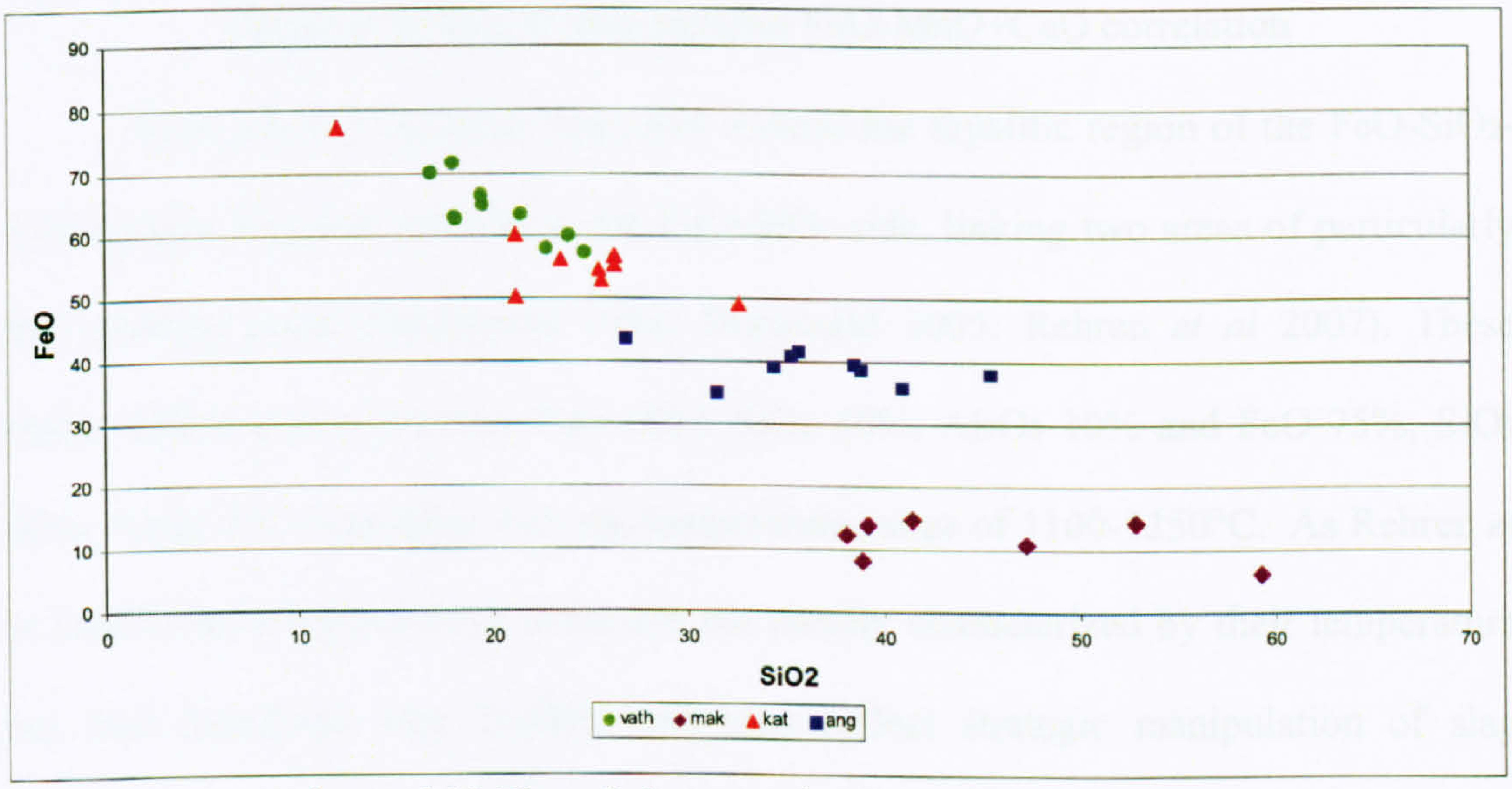


Figure 6.18 Plot of slag samples FeO-SiO_2 correlation

The clustering of samples into distinct groups was also observed through plotting on the FeO-Mn+CaO correlation. Katafyto and Vathytopos specimens cluster in the low Mn and CaO region (<10%), Angistro specimens form a tight group with Mn+CaO around 10% while those from Makrychori tend to concentrate in a >30% region. Even the two outliers of this group contain larger amounts of Mn supporting the suggestion that local Mn-rich ores had been used at this site (figure 6.19).

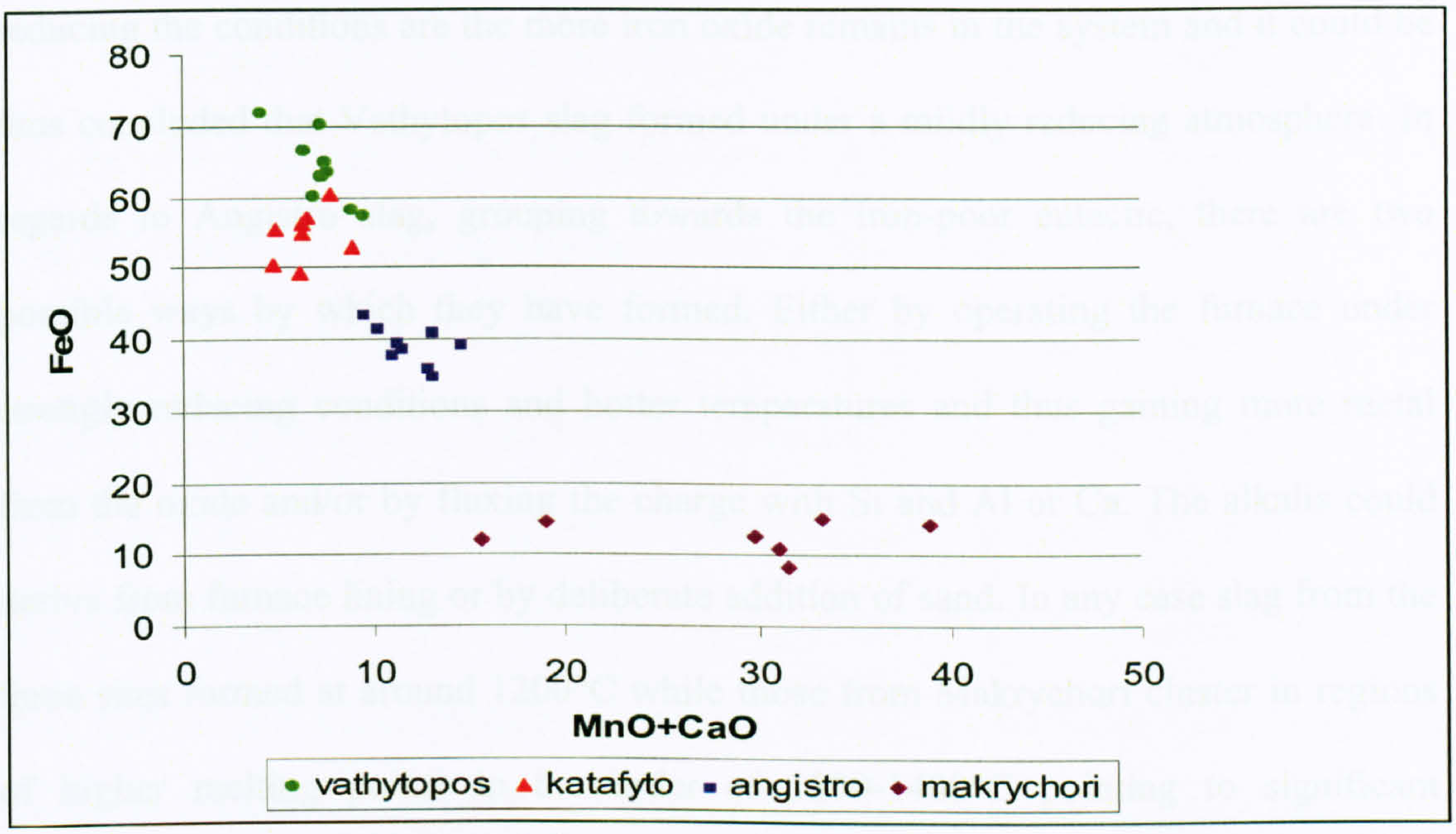


Figure 6.19 Plot of slag samples FeO-MnO+CaO correlation

Most ancient smelting slags plot around the fayalitic region of the FeO-SiO_2-Al_2O_3 phase diagram, parallel to the FeO-SiO_2 side, linking two areas of particularly low melting point (Bachmann 1982; Buchwald 2005; Rehren *et al* 2007). These points define a line between FeO 50%, SiO_2 40%, Al_2O_3 10% and FeO 75%, SiO_2 20%, Al_2O_3 5% coinciding with the temperature range of 1100-1250°C. As Rehren *et al* (2007) have argued these areas are not merely characterized by their temperature but also maximize slag fluidity, and may reflect strategic manipulation of slag composition to facilitate metal production. Plotting the analyzed samples in the FeO-SiO_2-Al_2O_3 system shows that slag from three sites fall within roughly distinct groupings along the line between the minima described above (figure 6.20). Interestingly, samples from Makrychori fall within a distinct group away from the fayalitic region and close to where cristobalite becomes a significant phase. This mineral was found by XRD as minor and trace in two samples (see below). Evidently the closely grouped slag from Vathytopos and Katafyto towards the iron-rich region is typical for a bloomery process by which under reducing conditions part of the iron oxide is reduced to iron metal and part remains as iron oxide. The less strongly reducing the conditions are the more iron oxide remains in the system and it could be thus concluded that Vathytopos slag formed under a mildly reducing atmosphere. In regards to Angistro slag, grouping towards the iron-poor eutectic, there are two possible ways by which they have formed. Either by operating the furnace under strongly reducing conditions and hotter temperatures and thus gaining more metal from the oxide and/or by fluxing the charge with Si and Al or Ca. The alkalis could derive from furnace lining or by deliberate addition of sand. In any case slag from the three sites formed at around 1200°C while those from Makrychori cluster in regions of higher melting points in the order of 1300-1400°C pointing to significant innovation in bellows technology and/or furnace design.

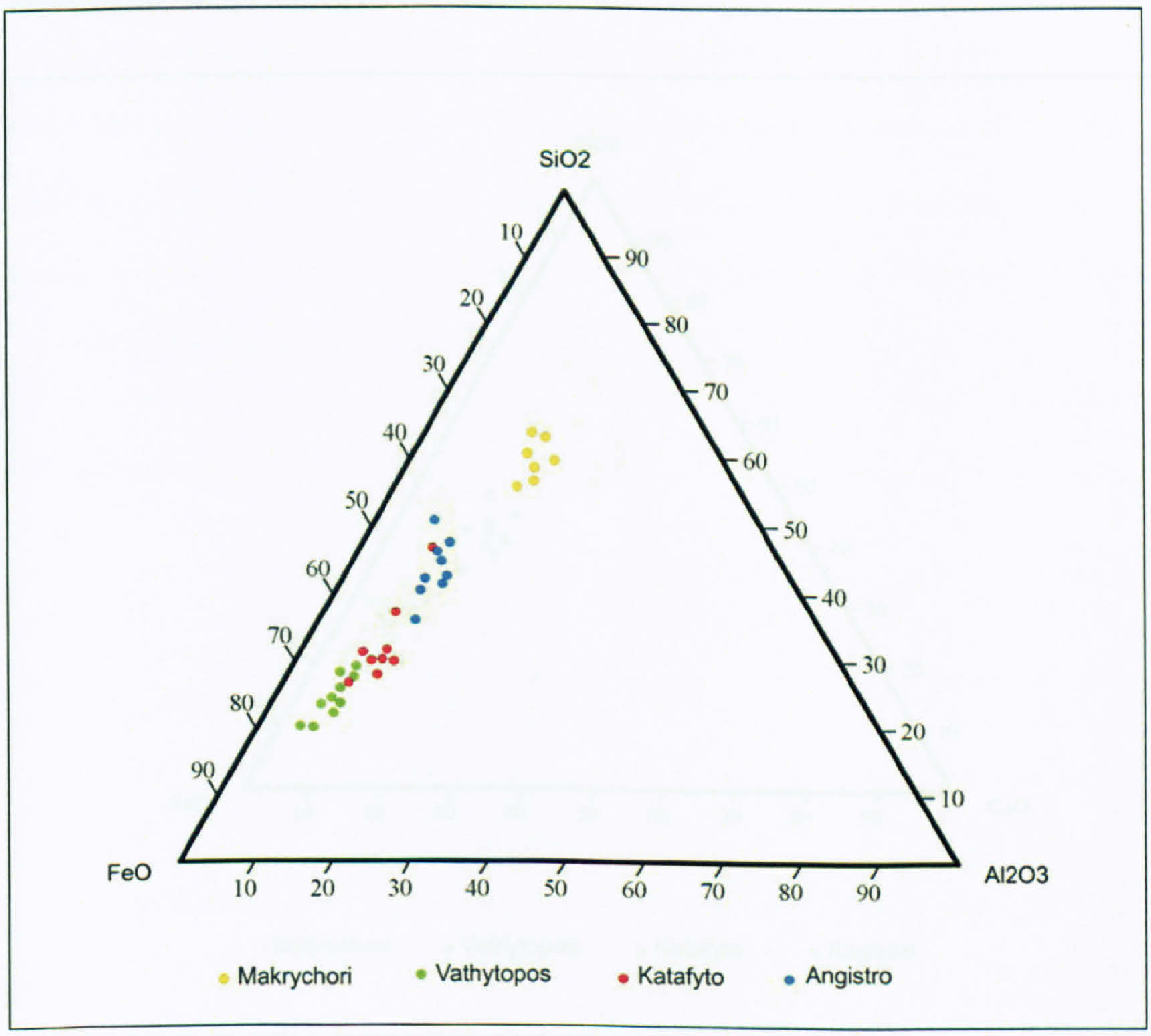


Figure 6.20 Plot of slag samples in the system $FeO-Al_2O_3-SiO_2$

To further investigate the possibility that smelters at Angistro added fluxes in the charge during smelting, the samples were plotted on the FeO-CaO-SiO_2 system (figure 6.21). Once again Angistro slag clustered together except for one outlier which falls in the low FeO region. It is highly possible that silica added through sand fluxing could explain such concentrations in combination with the smelting of a calcareous or very rich iron ore (Miller *et al* 2001; Veldhuijzen and Rehren 2006). It is however equally plausible that large tuyères protruding into the furnace were specifically designed to melt during the process, adding silica and stimulating in this way slag formation. Both cases manifest how decision making and certain choices taken by the smelters reflect upon the slag constituents and are therefore significant for a meaningful interpretation of the results.

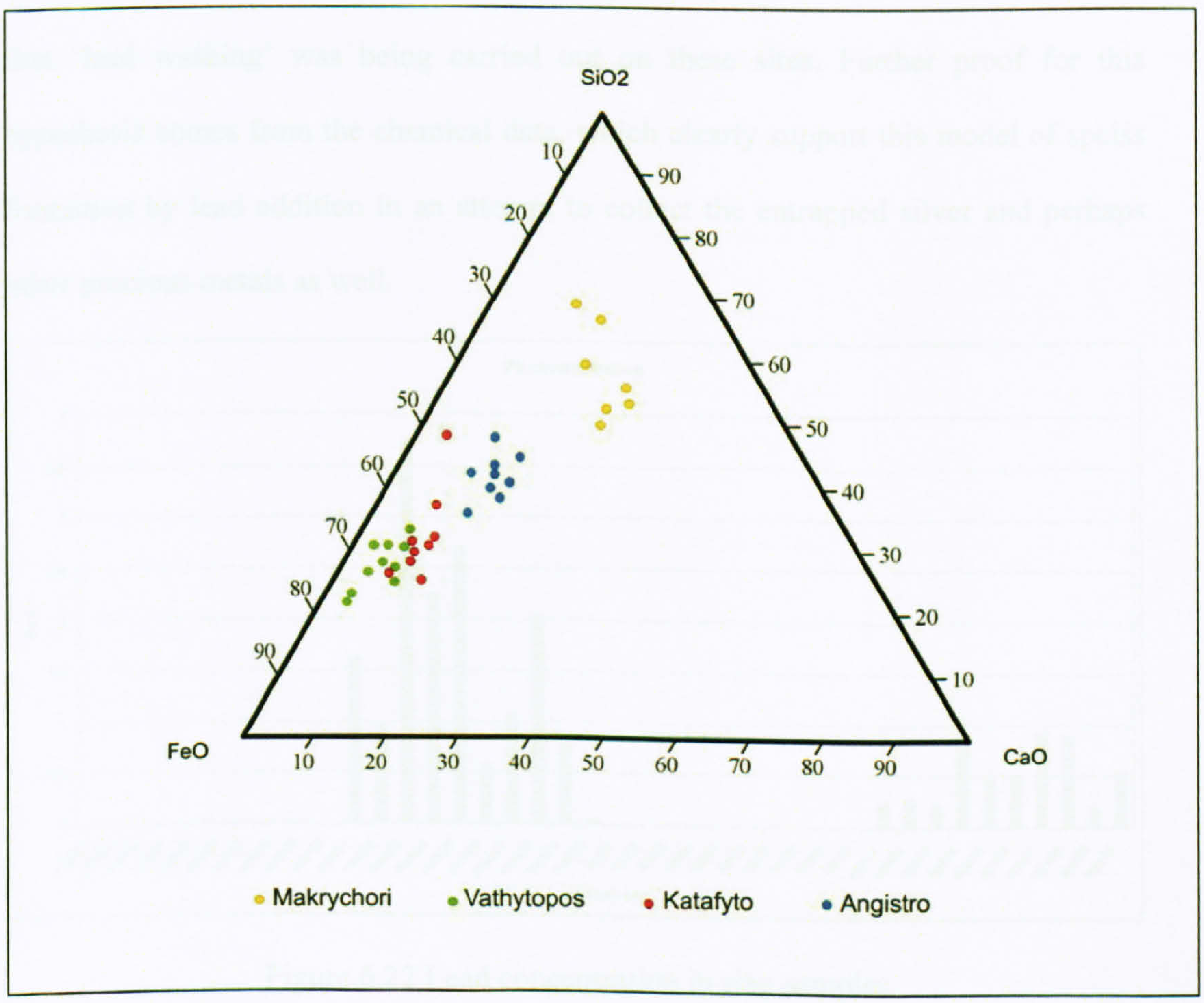


Figure 6.21 Plot of slag samples in the system FeO-CaO-SiO_2

The presence of lead at concentrations around 1-2% within the analyzed slag assemblage needs to be discussed separately as it affords solid information on distinct aspects of the process. All samples from Makrychori and Angistro contain some quantities of lead whilst only negligible levels of that metal are noted for slag from Katafyto and Vathytopos (figure 6.22). More specifically lead within slag from Makrychori ranges between 0.04 and 3.71% with an average of 1.57%. The specimens from Angistro generally contain lower lead concentrations from 0.19 to 0.93% with an average of 0.51%. As has been discussed previously, it is here suggested that the addition of lead was carried out during smelting to collect precious metals; the enriched lead would then be refined through cupellation. Significantly, no evidence of cupellation has been identified at any of the investigated sites (see chapter seven). The point analysis of certain phases by SEM provided some initial indications that 'lead washing' was being carried out on these sites. Further proof for this hypothesis comes from the chemical data, which clearly support this model of speiss formation by lead addition in an attempt to collect the entrapped silver and perhaps other precious metals as well.

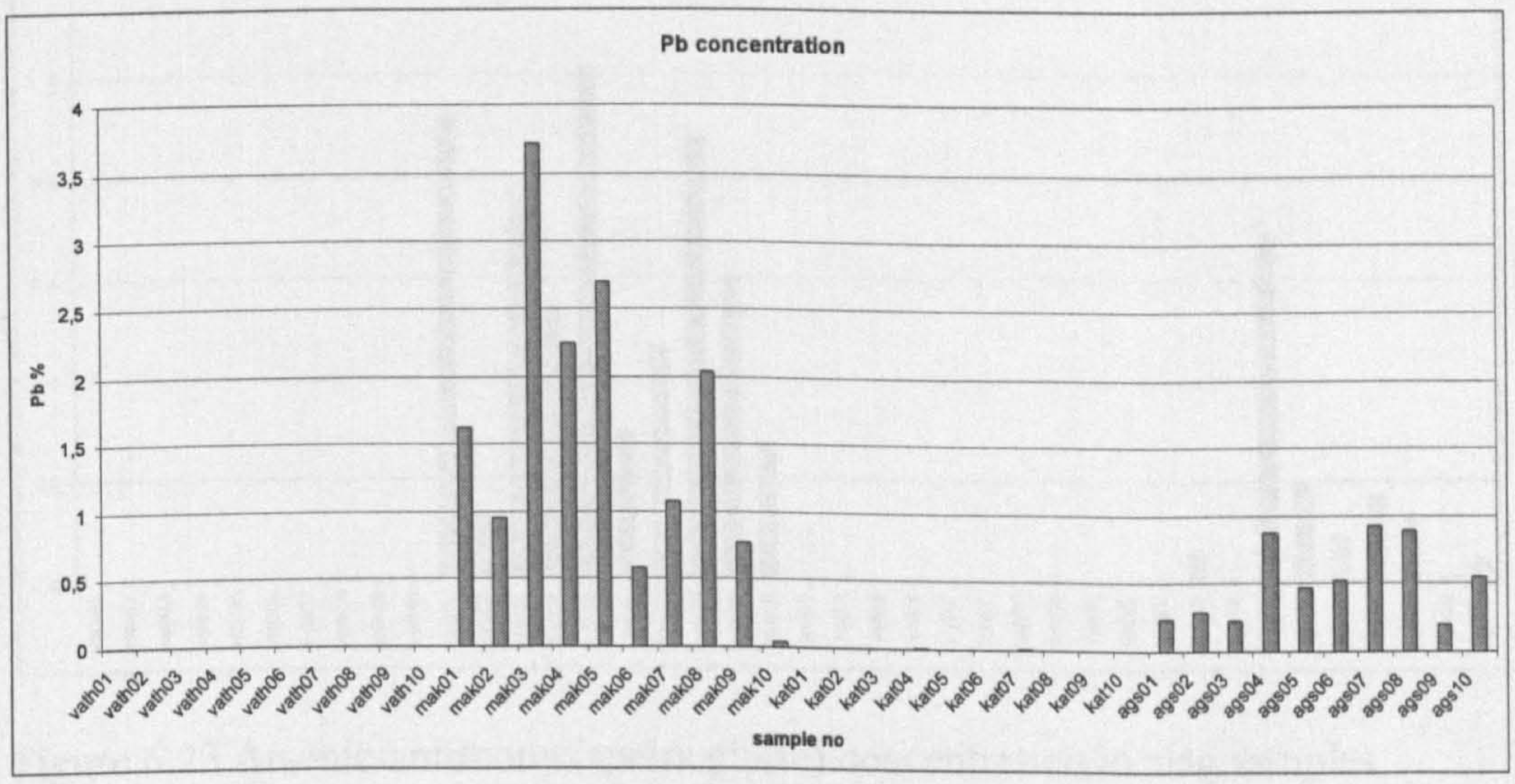


Figure 6.22 Lead concentration in slag samples

Speiss phases have been initially investigated by use of SEM analysis while the compositional data provided by XRF proved effective in terms of discerning the actual percentages of speiss within the bulk chemical composition of each sample. Such data are crucial for understanding the technical parameters of smelting auriferous or argentiferous ores by which precious metals were being extracted. The potential of such ores to yield gold or silver is reflected in speiss phases forming within the slag. Higher levels of such metals in the ore lead to proportionately higher levels in the slag. A straightforward method to discern speiss levels within slag involves measuring the levels of As and Sb which are the main constituents of these inter-metallic compounds. As might have been expected, such phases are only present in slag deriving from Angistro and Makrychori, sites that yielded substantial speiss plates just via field survey (figure 6.23). Concentrations of both metals are higher in Makrychori slag than in Angistro slag but the latter shows how As occurs in greater quantity than Sb probably owing to the region's asrenopyrite ore deposits.

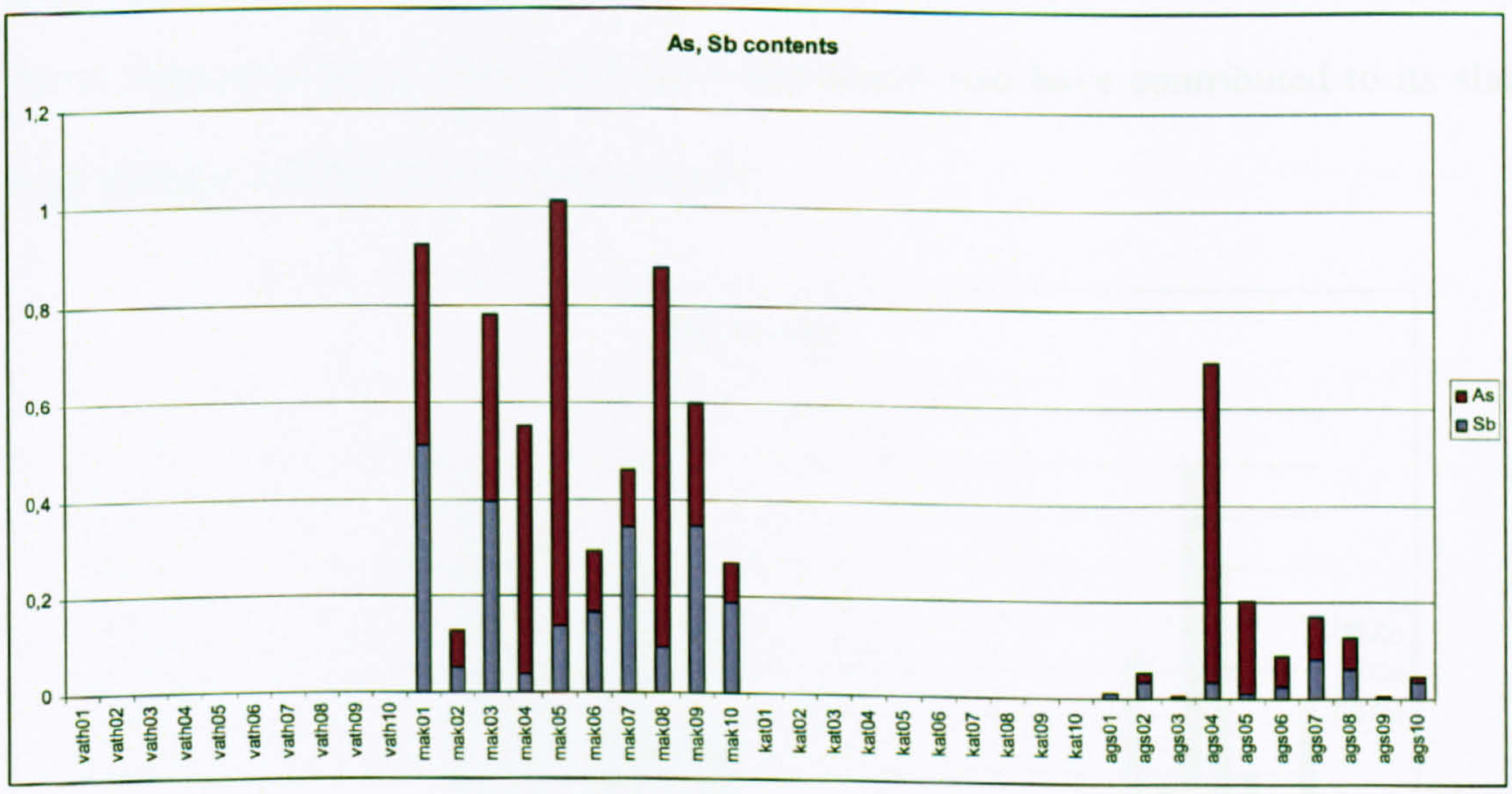


Figure 6.23 Arsenic-antimony (speiss phase) concentration in slag samples

Important data relating to smelting practice and further choices of a technical nature to address problems encountered during the process come from a careful examination of other metals present in the slag. Most interestingly Cu, Sn and Zn contents are present at significant levels that reflect certain practices. The presence of such elements within ferrous slag should be considered in regards to a method of incorporating such material into the smelt for specific reasons. For instance re-melting of old scrap metal, in particular bronze or other copper alloys, has been standard practice in traditional metallurgical operations when precious metals were to be extracted. The results from Angistro slag revealed relatively low –but still significant- levels of tin and copper, on average 0.026% and 0.019% respectively, but a proportionately higher Zn content, 0.32 on average (figure 6.24). Such figures might suggest the re-melting of brass and possibly also bronze alloys to collect any precious metals contained in the smelted ores. In addition, a correlation of lead-tin in Angistro slag coincides accurately with pewter composition which could be indicative of re-melting this alloy for the same reasons described above (figure 6.25). For Makrychori the re-melting of brass rather than tin-bonze could also have contributed to its slag compositions which show low tin contents.

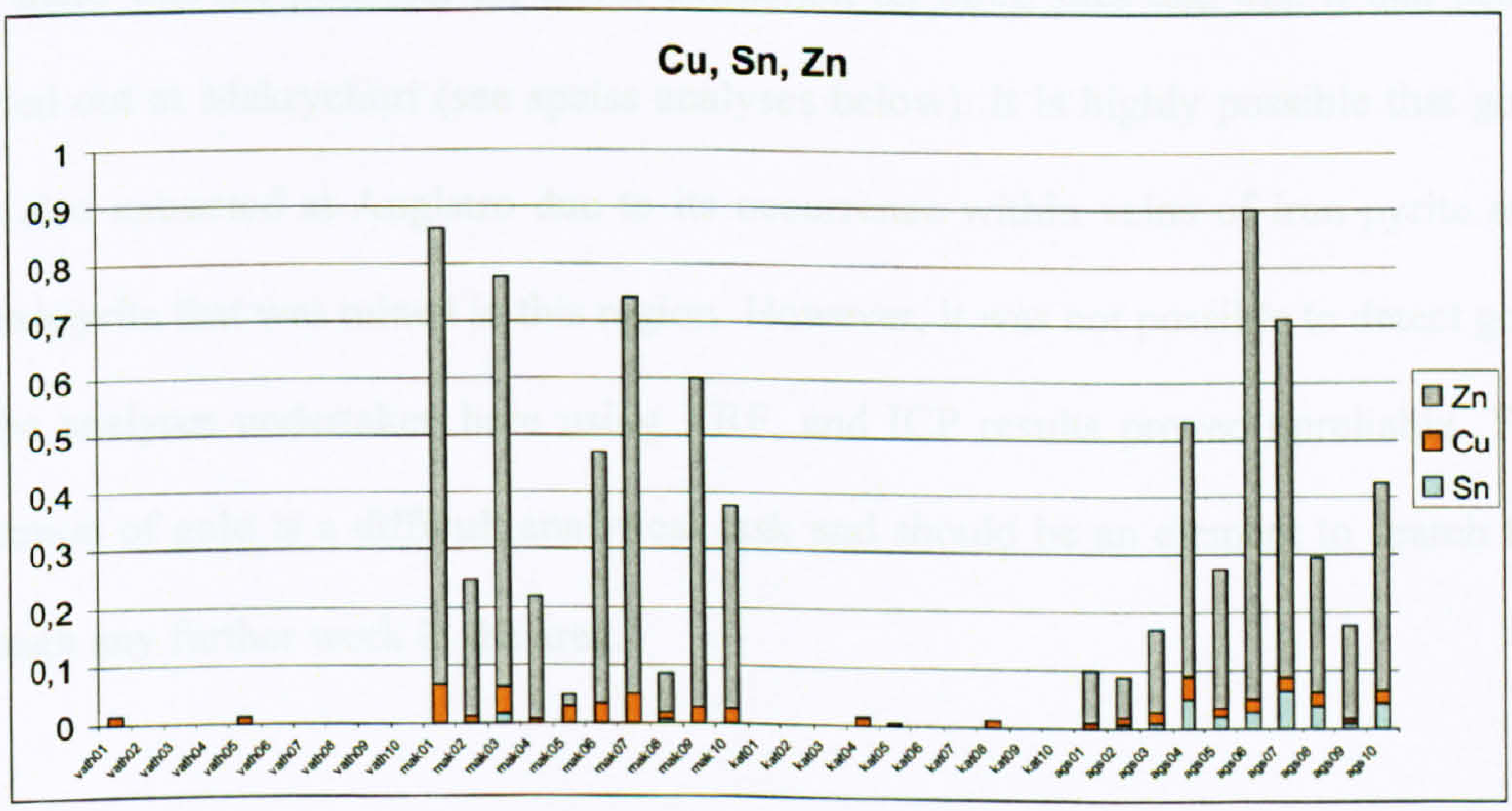


Figure 6.24 Copper, tin and zinc concentration in slag samples

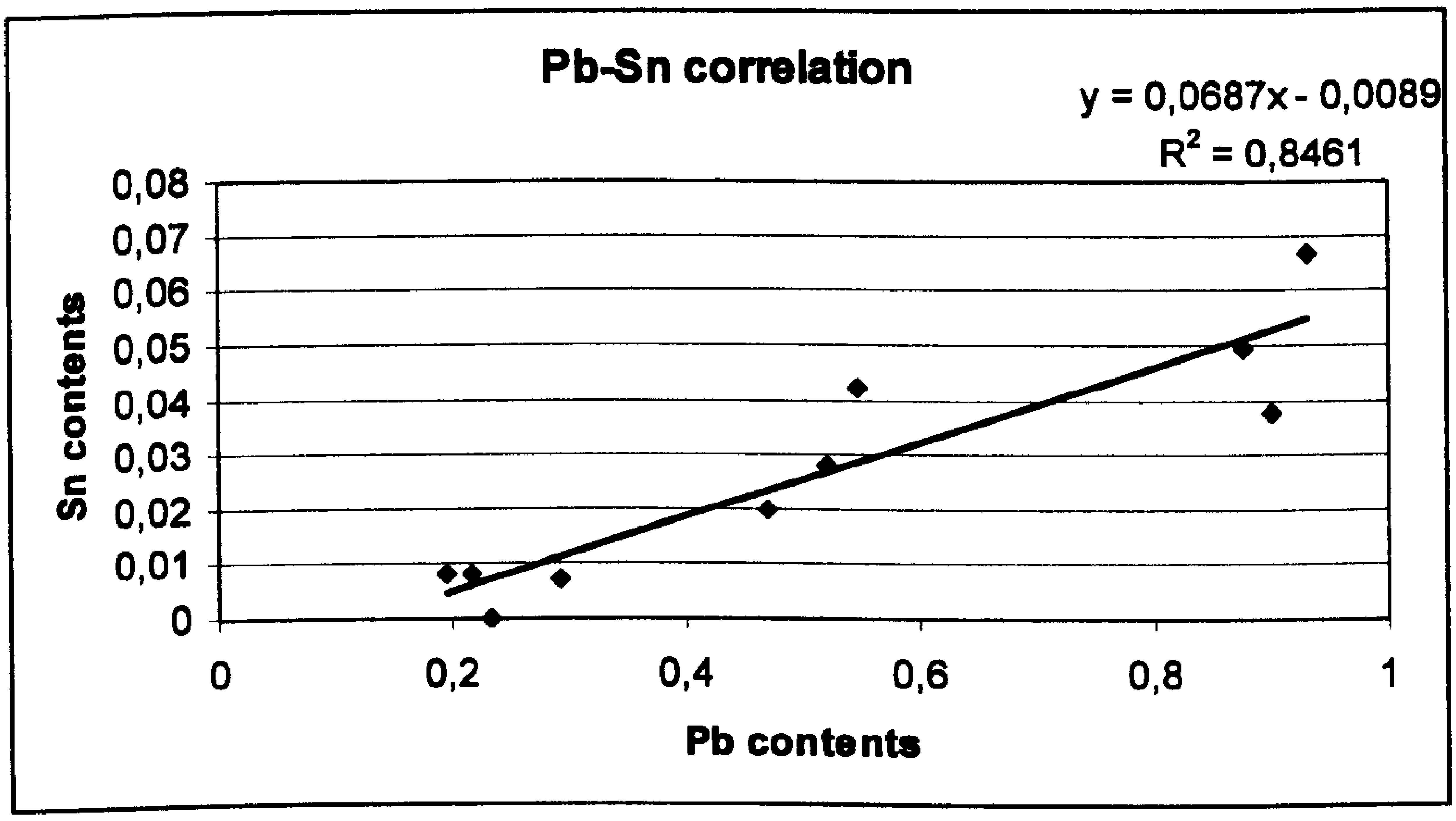


Figure 6.25 Lead and tin correlation in Angistro slag suggesting the melting of scrap pewter in the charge

Most importantly silver was found in concentrations up to 57 ppm in Makrychori slag but no traces of the metal were detected for Angistro (see Appendix III). Low amounts of silver around 20 ppm were also detected in slag from Katafyto and Vathytopos but the absence of any other conclusive evidence, such as appropriate levels of copper, tin and/or lead, suggests that smelters were unaware of its presence or incapable of recovering the metal. It could be safely concluded along these lines that there was the potential for silver extraction on three sites and that it had being carried out at Makrychori (see speiss analyses below). It is highly possible that gold was also extracted at Angistro due to its occurrence within veins of iron-pyrite and arsenopyrite that was mined in this region. However, it was not possible to detect gold in the analyses undertaken here using XRF, and ICP results proved unreliable. The detection of gold is a difficult analytical task and should be an element to search for through any further work in the area.

6.9 Characterisation of speiss

Speiss fragments were found amongst the metallurgical debris at Angistro and Makrychori. Large plates around 20-30 cm in diameter and up to 3 cm thick and smaller ones around 5 cm in length were noted at the major concentration of Patraki NW of Angistro village. Speiss at Makrychori can be found within the heaps and paths around the village but pieces generally smaller in size (5-10 cm diameter). Only a few speiss specimens were obtained due to their scarcity and also because this material tends to be uniform. The sampled material was one specimen from Angistro and five from Makrychori, all were roughly 6 cm in length and weighed almost 150-250 g on average. Their density is around 7.5 g/cm and they are covered by an oxidized crust resembling corroded iron. Photographs of the material as found on the field and sectioned are presented in Appendix IV.

6.9.1 Optical microscopy

All samples were sectioned, and after grinding and polishing were examined under the optical microscope. Preliminary investigation revealed two major phases dominant in the microstructure of specimens from both sites. The primary phase is dendritic, very rich in iron and antimony and is surrounded either by the second phase rich in arsenic and low in iron or by a eutectic of both phases (figures 6.26 and 6.27).

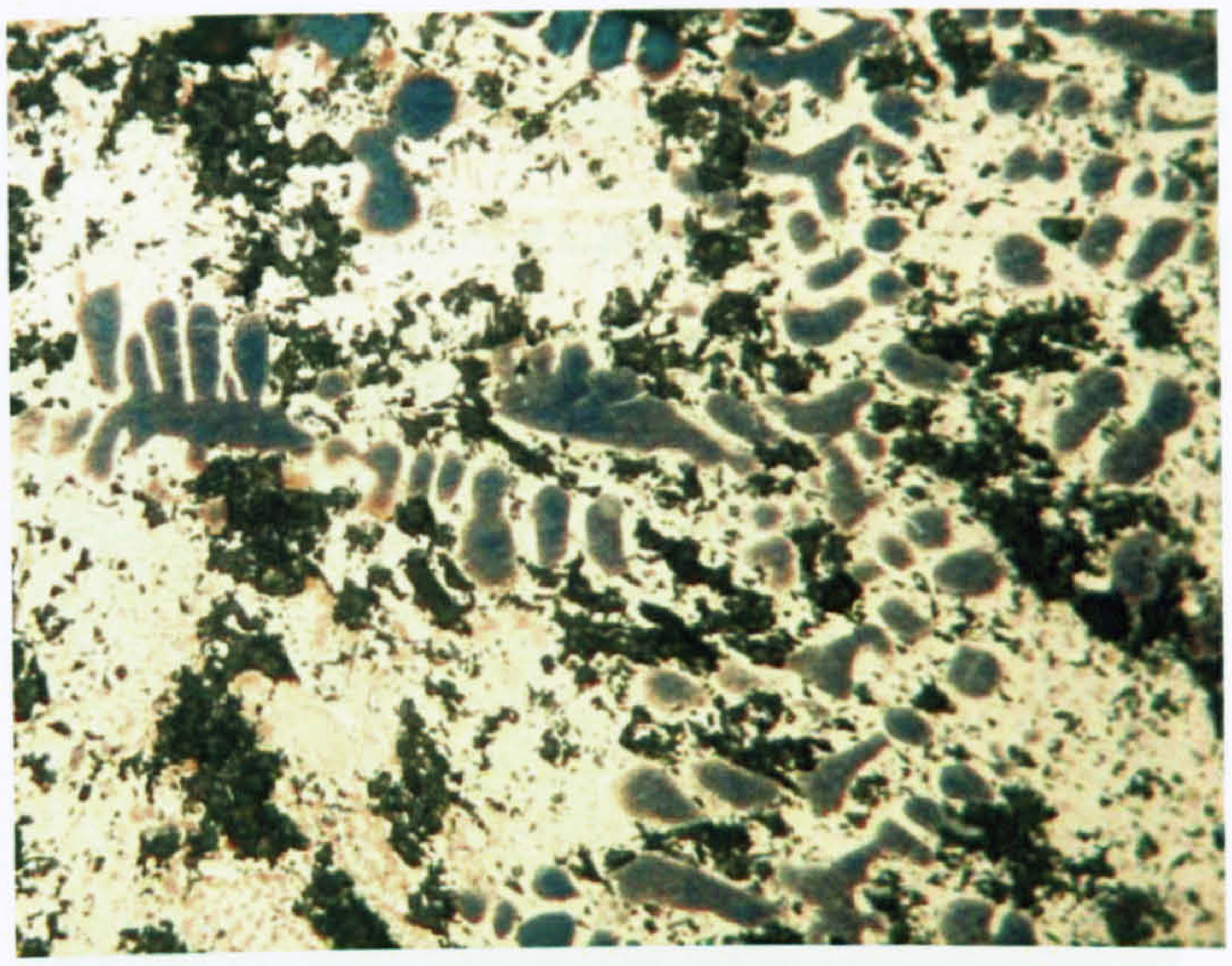


Figure 6.26 *MAK.SP10*: Photomicrograph of polished section. Dendritic FeAs in FeSbAs matrix

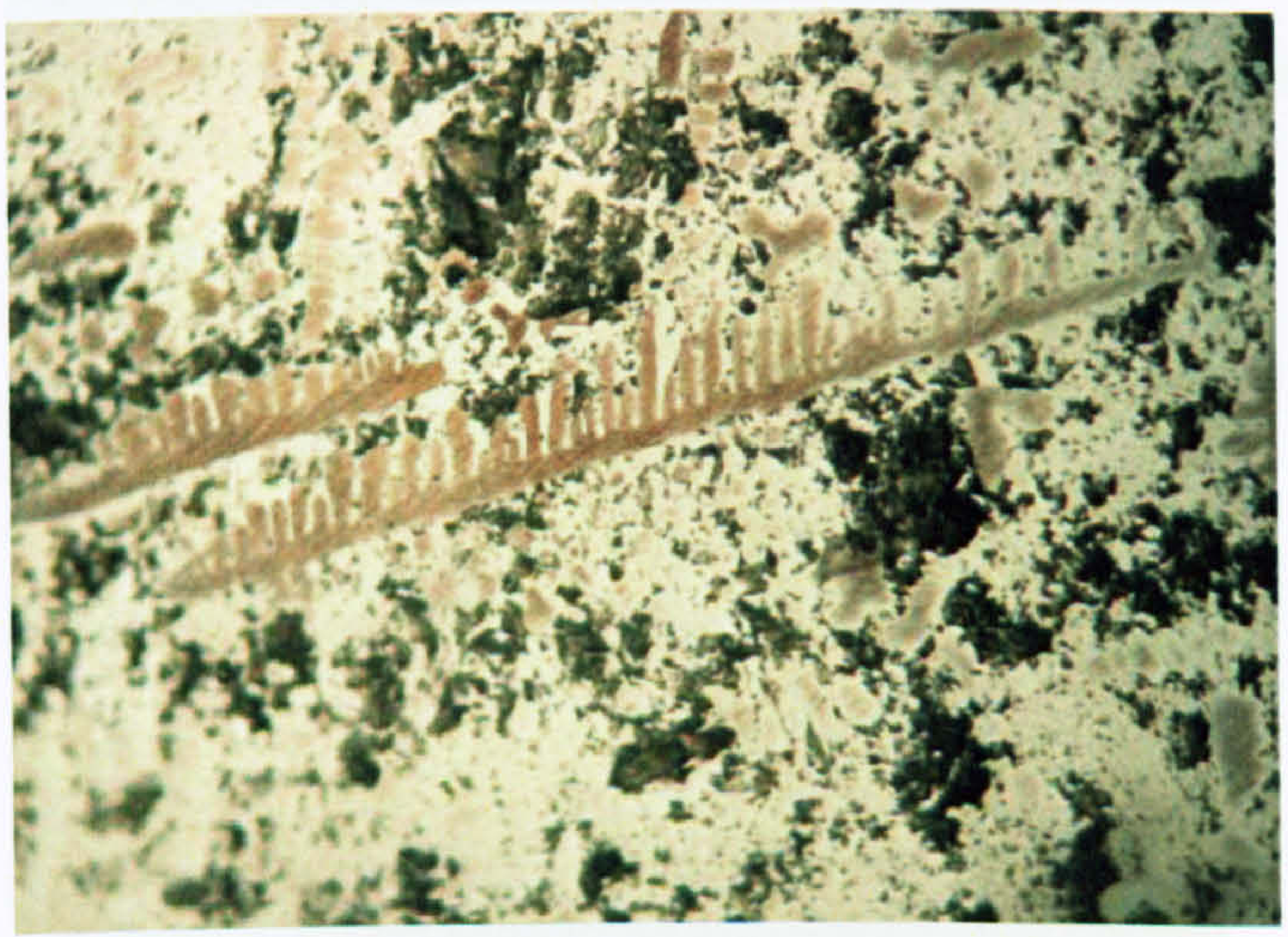


Figure 6.27 *MAK.SP35*: Photomicrograph of polished section. Dendritic FeAs in FeSbAs matrix

6.9.2 SEM-EDX analysis

The speiss examined with the SEM produced important results on microstructure and chemical composition on certain phases. The iron rich phase appears in form of a dendritic network with large clearly defined grey-black dendrites (figure 6.28). Brighter spots of the microstructure represent a low-arsenic, high-antimony phase which was more common in MAK.SP36 (figure 6.29). Other regions where arsenic levels are higher than antimony show as slightly darker grey areas. The matrix is composed of a eutectic of high-arsenic and iron.

Figure 6.28 *MAK.SP35*: dark grey dendrites represent the iron rich phase (SEM photomicrograph)

Figure 6.29 *MAK.SP36*: iron-rich dendrites (dark), low-As/ high-Sb phase (light grey) (SEM photomicrograph)

6.9.3 Compositional analysis

Chemical analyses to determine the bulk composition of speiss and the distribution of major elements within distinct metallic phases were undertaken to provide additional data. Results from the XRF show Fe contents ranging between 34-49% and As in substantially high values in the order of 20-35% (table 6.1). Sb was found in contents around 4% for all the Makrychori samples and only rising slightly higher (6%) for the Angistro sample. The presence of Cu ranges close to 1% while other metals such as Sn, Pb, Mn, Ti and Zn exist in low concentrations without major fluctuations in quantity. It is important to note that silver was found in all but one of the analyzed samples. The finding of low silver contents in the speiss is of crucial importance as it provides undisputable evidence for de-silvering on at least one of these sites. The current data are generally in accordance with results from previous analyses as described above. Photos *et al* (1989) on their analysis of speiss from sites in Palaea Kavala established the presence of silver contents ranging from as low as 1.2 ppm to 70 ppm. Analysis of a cast cannon ball of Ottoman date found in one of these sites showed a composition similar to that of speiss. It was therefore suggested that the speiss was used as raw material for the production of ammunition but no model of widespread practice could be constructed solely on one find. Based on low silver contents noted in speiss from Corta Lago (Ag<0.02%) and Los Arenillas, Rio Tinto (Ag: 1%, 0.27%, 0.07%) Craddock *et al* (1987) argued that the speiss from Los Arenillas had been de-silvered. However Kassianidou (1998) provided results on a crucible from Rio Tinto which had been used for the processing of silver-rich lead and not for the roasting and de-silvering of speiss. Given that such slagged crucibles with lead-rich prills were not found on the sites under study whilst Pb concentrations are significantly low and thus a de-silvering operation could still be a plausible explanation for speiss occurrence in Angistro and Makrychori.

Sample no.	Fe	As	Sb	Cu	Sn	Pb	Mn	Ti	Zn	Ni (ppm)	Ag (ppm)
MAK.SP03	49.09	22.45	4.41	0.50	0.33	0.16	0.00	0.07	0.01	989.23	152.94
MAK.SP08	35.76	35.09	4.97	1.17	0.03	0.32	0.00	0.06	0.02	1269.24	108.01
MAK.SP10	34.42	30.77	4.36	1.14	0.04	0.27	0.00	0.09	0.02	855.11	96.88
MAK.SP35	38.79	33.51	4.51	0.89	0.03	0.20	0.03	0.09	0.02	1441.87	86.34
MAK.SP36	34.81	19.34	6.38	0.97	0.00	0.37	0.00	0.11	0.02	1444.90	86.27
AGS.SP01	35.28	20.23	6.76	1.03	0.02	0.48	0.00	0.12	0.03	698.73	0.00

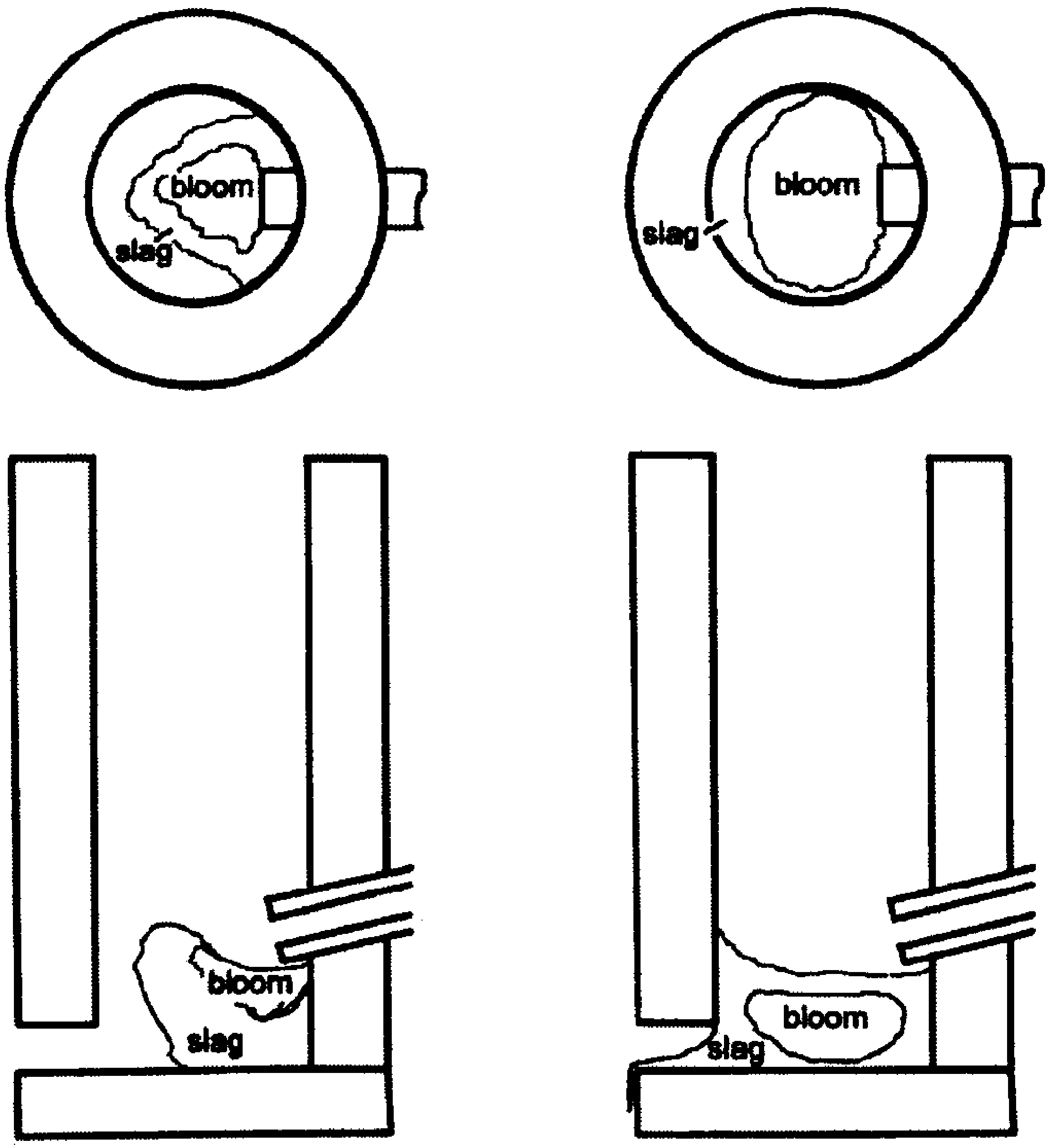
Table 6.1 Chemical composition of speiss

6.10 Refractory materials

The metallurgical refractory ceramics recovered were tuyères and furnace conglomerates. Two major fabric types were identified, a fine sorted reddish matrix tempered with ground quartz and a coarse orange matrix tempered with a variety of aggregate material including quartz. Two well preserved tuyères were recovered from Angistro and Makrychori and three conglomerates from Katafyto. These latter are vitrified on one side and oxidized on the other while one bears an embedded tuyère (figure 6.30). Photographs and basic descriptions of the refractory ceramics are included in Appendix IV.

Furnace conglomerates with entrapped tuyères point to small, bowl-shaped hearth furnaces no larger than 1m in diameter. In most of these furnace fragments from Katafyto the tuyères had been blocked by slag, caused by inadequate bellows operation leading to continuous rebuilding. These refractories are important since they provide information on actual practice in terms of furnace design, blowing rates and bloom formation. Since slag adherence blocked most of the tuyères found, it could be suggested that the furnace burden burned down in a narrow cone that funnels all material directly in front of the tuyère (Sauder and Williams 2002). This was either caused due to inappropriate furnace design whereby slag is not tapped out and the bloom forms very close to the tuyère, causing disruption of air inflow, or it has to do with low air rates due to insufficient blowing. Bloomery experiments have shown that with higher blowing rates the reduced iron particles do not have to pass directly in front of the tuyère on their way to the slag bath below (Crew 1991). If the blast of air is increased to reach 1.2-1.5 l/min/cm² the hot zone expands downwards, the bloom forms much lower and is thus protected by the slag bath, which leaves the air passage open (Sauder and Williams 2002). Examples of furnaces run on low and high rates are shown in figure 6.31.

Figure 6.30 *K.CON.01*: Furnace conglomerate with entrapped tuyère and vitrification on internal surface from Katafyto



Blast of 0.4 - 0.8 l/min/cm^2 Blast of 1.2 – 1.5 l/min/cm^2

Figure 6.31 Schematic representations of bloomery furnaces operating at varying blowing rates (after Sauder and Williams 2002)

6.11 Comparison of results

The combined approach adopted for slag characterisation has avoided over dependency on any single analytical technique for this current thesis. However, since different samples have been used it can be expected that there will be some contradictory as well as complementary results. What follows is an attempt to develop an interpretation from these data sets whilst explaining any apparent contradictions in the analytical data. The compositional data acquired with XRF and the phase analyses from SEM-EDS are generally is good agreement, especially for major and minor elements. Whilst detection limits for XRF are in the region of 10-50 ppm for most elements the SEM-EDS is determined to have a detection limit of about 0.25% for most elements reported in this study.

Silica contents are significant in slag as detected by the XRF and, based on SEM findings are distributed mainly among the matrix. FeO contents are generally higher for Katafyto and Vathytopos slag (average 60%), moderate for Angistro (average 30%) and lower for Makrychori (average 10%). Their distribution is mainly within the magnetites, wüstites and fayalites. The presence of Mn in Makrychori slag demonstrates how the chemical techniques are in accordance since the bulk composition of this element roughly coincides with phase analysis. To take an example, for MAK01 the XRF detected MnO at 19.74% while the SEM at 19.39% on matrix analysis. Of course these results are somewhat variable yet the broad correlation clearly demonstrates the agreement of such analyses.

A comparison of XRF with SEM-EDX data was used to resolve how lead is distributed within the slag. For example, the bulk composition of Makrychori slag showed overall low concentrations at around 2% while the metallic prills analysed by EDX in MAK02 were found to contain Pb in concentrations reaching 22% and 35%. From the SEM-EDX results it is also apparent that speiss phases are often associated with low levels of lead and copper suggesting that they have possibly formed during base-metal smelting through an intermediate stage of refining precious metals. Finally significant information on unreacted ore minerals was provided by XRD which detected traces of hematite which the other techniques used could not measure. The absence of evidence for wüstite and fayalite in Makrychori slag using XRD, when all other methods testify to their occurrence is the only discrepancy noted. This however could be easily explained by the insensitivity of the XRD technique.

Having tested the credibility of results acquired through the described analytical methodology the next step involved their comparison with existing results on similar material from the study region. Atomic absorption spectroscopy analyses conducted during the 1980's in IGME laboratories revealed high levels of precious metals in speiss and slag from Palaea Kavala and other regions of eastern Macedonia (Photos 1987, 197). However the lack of any information on sampling methodology, dating and descriptions of process relations meant that such data cannot be directly cross checked against the dated Byzantine material. Though the current results are in agreement with the region's compositional groupings, which could suggest that similar ore sources had been used to produce the undated (possibly ancient) and the current samples, a comparison was attempted so that further technological issues could be resolved.

Slag and speiss fragments from Petropigi and other sites fall within homogeneous typological groups suggesting a uniformity of metallurgical practices at most sites in Palaea Kavala but mineralogical and experimental data produced by Photos (1987) showed differences in minor elements within the three major phases of all examined groups. Experimental smelts conducted by the same author, working at temperatures around 1250°C, provided free-running slag with similar mineralogy to the archaeological examples. However the As-rich bloom produced through the course of Photos' experiments was a result of solid state diffusion of As and Fe since the bloom was never molten upon reduction. Speiss on the other hand was molten and thus the two distinct phases formed upon solidification. It is therefore highly likely that the Mn-rich ores of Palaea Kavala which also contain high As and Sb levels (see Appendix V, Table 6.1) have been the ore source of the speiss but could not have been used for bloomery practices, due to embrittlement caused by the presence of Mn. The ore introduced in a blast furnace would have produced combined As-Fe entering the speiss and slag while the precious metal contents would have been easily extracted.

Based on the above Photos (1987, 204) concluded that the Palaea Kavala iron ores, rich in precious metals were not utilised primarily for iron but for their Ag contents. What followed in the process was the addition of lead to collect silver since smelters could not have known the properties of speiss. Experimentally smelted ore from Petropigi produced Pb-free slag, while slag found on the field contained appreciable amounts of Pb suggesting that it was added during the process (1987, 205). After Pb was tapped, slag and speiss were discarded or re-melted, and the final stage of cupellation of the metal would produce litharge and metallic Ag-Au.

Previous chemical analyses on slag from Angistro, Katafyto, Vathytopos and Makrychori have been undertaken in the 1970s and 1980s. Although the earliest data by Papastamataki (1975; 1985) using AAS were not supplemented by archaeological information such as stratigraphy, context and approximate date they are valuable for comparison with more recent data acquired from stratified samples of known contexts. The chemical analyses by Photos (1987) with the use of XRF and SEM microprobe were concentrated on major elements as well as silicate phases by use of the microprobe analyzer and have added valuable information on distribution of elements within the major phases. The general pattern for most sites is typical for iron bloomery slags with predominance in FeO contents, significant SiO_2 contents, CaO below 20% and variable low amounts of other metals. Higher SiO and CaO contents could have resulted from deliberate addition of fluxes to lower the melting point and enhance slag fluidity and the sintering of Fe as it is reduced from FeO. Moreover CaO and alkalis like K_2O might have alternatively derived from lime in the furnace lining. The high percentages of FeO occasionally exceeding 40% show that considerable amounts of iron were lost in the slag during the smelting process.

For the needs of this current project an attempt was made to correlate the elemental composition of slag from Angistro, Drama and Kavala, measured by previous research (Papastamataki 1985) in order to produce comparable data with the dated sampled material. Average figures were calculated for 5 samples from Angistro, 5 samples from various locations in Drama and 6 samples from sites in Kavala. The highest FeO (52.94%) and lowest CaO (6.04%) contents noted in slag from Drama indicate an inefficient smelting during which iron was hardly retrieved in metallic form. Average FeO (42.88%) and CaO (11.29%) contents in Angistro slag hint to a typical smelting process where iron was retrieved from the local ores without significant losses in the slag. A superiority of technology in the sites of Kavala is underlined by the low FeO (28.27%) contents and the considerably high SiO_2 (28.72%) and CaO (16.58%) amounts (figure 6.32). Such compositions prove that most gangue minerals were incorporated in the slag due to higher temperatures and most of the FeO contents were reduced to metallic iron. Thus smelters in Kavala were successful at reaching high furnace temperatures in excess of 1300°C which allowed for low viscosity, free-running slag formation.

When the data from these earlier projects are seen in comparison with the current results derived from the dated Byzantine samples they display a compatible correlation and an overall tendency of agreement. Using the average chemical composition of the 40 analysed samples as shown in figure 6.33 it was possible to compare the newly acquired data with the previous ones. For elements and compounds such as CaO and Al_2O_3 concentrations are almost equal in value while As and TiO_2 contents are also in good agreement. There are however some discrepancies noted with regards to absolute figures in volume particularly in major slag constituents such as FeO and SiO_2. For Makrychori in particular FeO values are lower than any in other previously analysed slags while SiO_2 concentration greatly surpasses the average value estimated for sites in Kavala. Bearing in mind that the early projects focused on ancient metallurgical centers, the aforementioned compositions most likely reflect the conditions of ancient smelting processes. Looking at the data in conjunction it could be suggested that such difference has emerged through variation in practice or unequal development. Although gain in metal has been highly successful during Antiquity it seems that efficiency increases significantly when moving into medieval and Late Byzantine times.

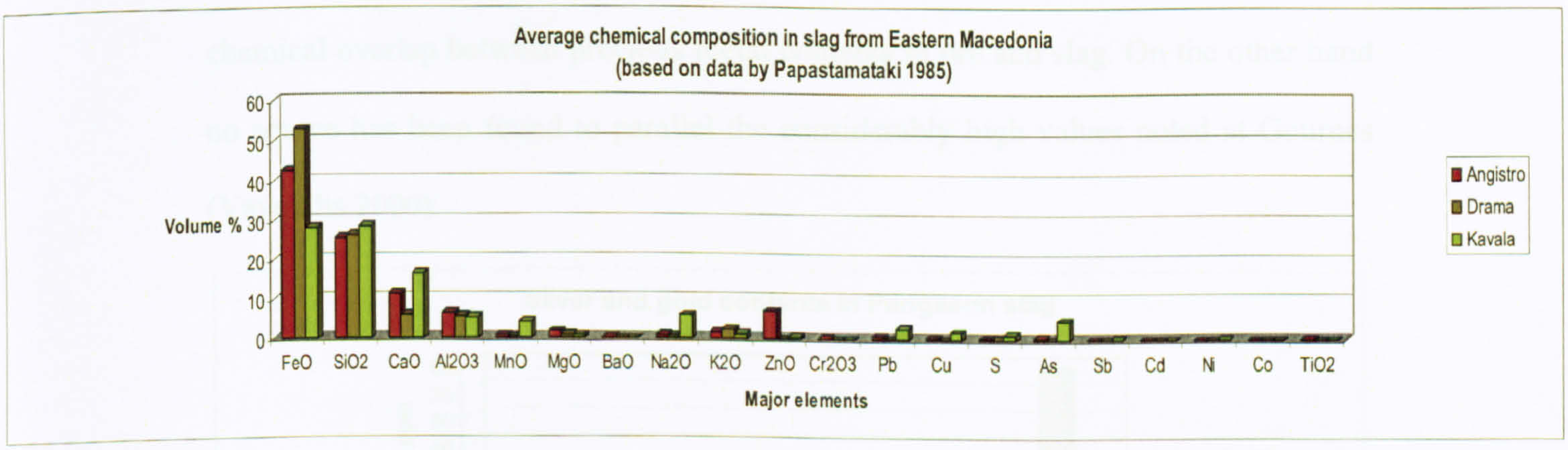


Figure 6.32 Chemical composition of eastern Macedonian slag (adapted from data by Papastamataki 1985)

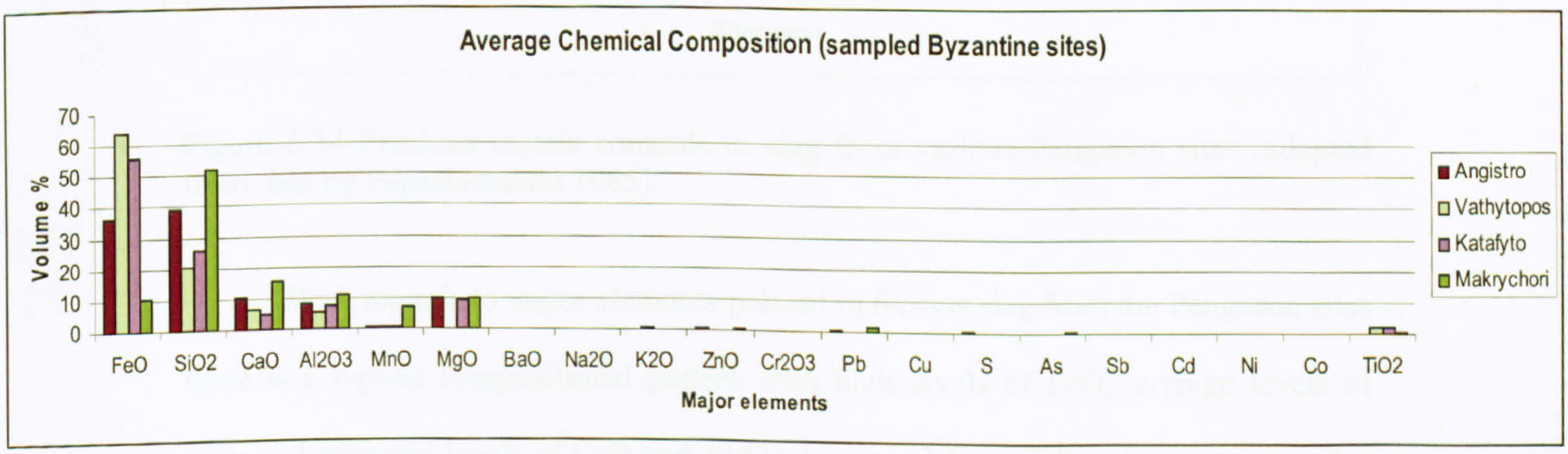


Figure 6.33 Chemical composition of Byzantine slag (current study)

Analyses on slag from various sites of Mt. Pangaeon provided by Papastamataki (1985) are useful for an average estimation of their Au and Ag contents, which might indicate the various ores being used in each site (Appendix V, Table 6.2). Thus the highest values for precious metals come from slag at Gournes with 104 ppm Ag and 10 ppm Au, followed by slag from Valtouda with 46 ppm Ag and 4.25 ppm Au as shown in figure 6.34 (Appendix V, Table 6.3). Significant amounts are also contained in slag from Livadia (15 ppm Ag, 8 ppm Au) where a double smelting furnace of Ottoman date was investigated by excavation during the 1980s. Livadia had probably access to the rich ores at Asimotrypes as shown by a chemical overlap between precious metal contents in ore and slag. On the other hand no source has been found to parallel the considerably high values noted at Gournes (Vavelidis 2000).

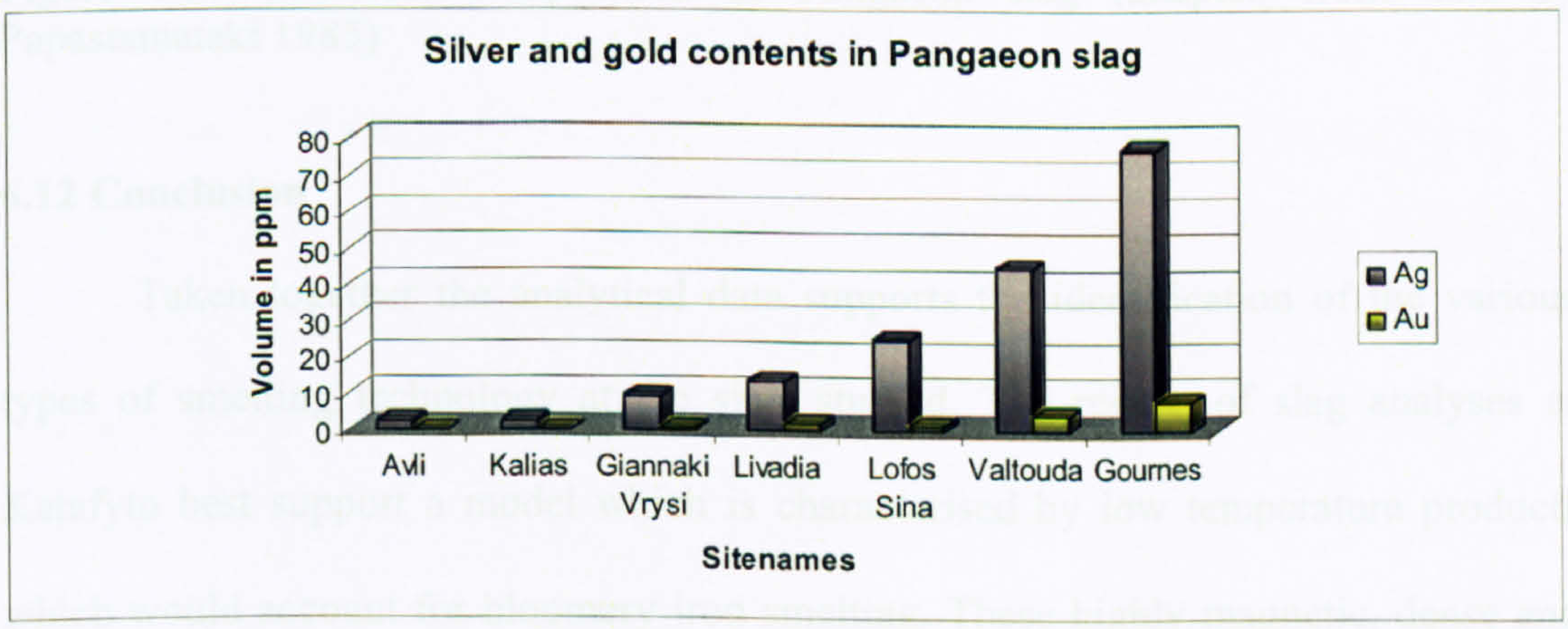


Figure 6.34 Precious metals contents in slag from various Pangaeon sites (adapted from data by Papastamataki 1985)

With regards to major elements present in ferrous slag from the Pangaeon sites there is a typical compositional pattern with high levels of FeO, average levels of SiO_2 and expected levels of CaO and Al_2O_3. Increased As and Sb values were noted at Livadia, Valtouda and Gournes which might suggest that extraction of precious metals was attempted through a speiss formation stage (figure 6.35). It should also be noted that the Pb values between 2.5-4.0 % could not have derived for the local ores and probably represent deliberate additions during separation of the precious metals from the melt. The examined ores yielded an average of 0.06 % Pb and thus higher figures could have formed via impurities in the ores and hence point to deliberate addition.

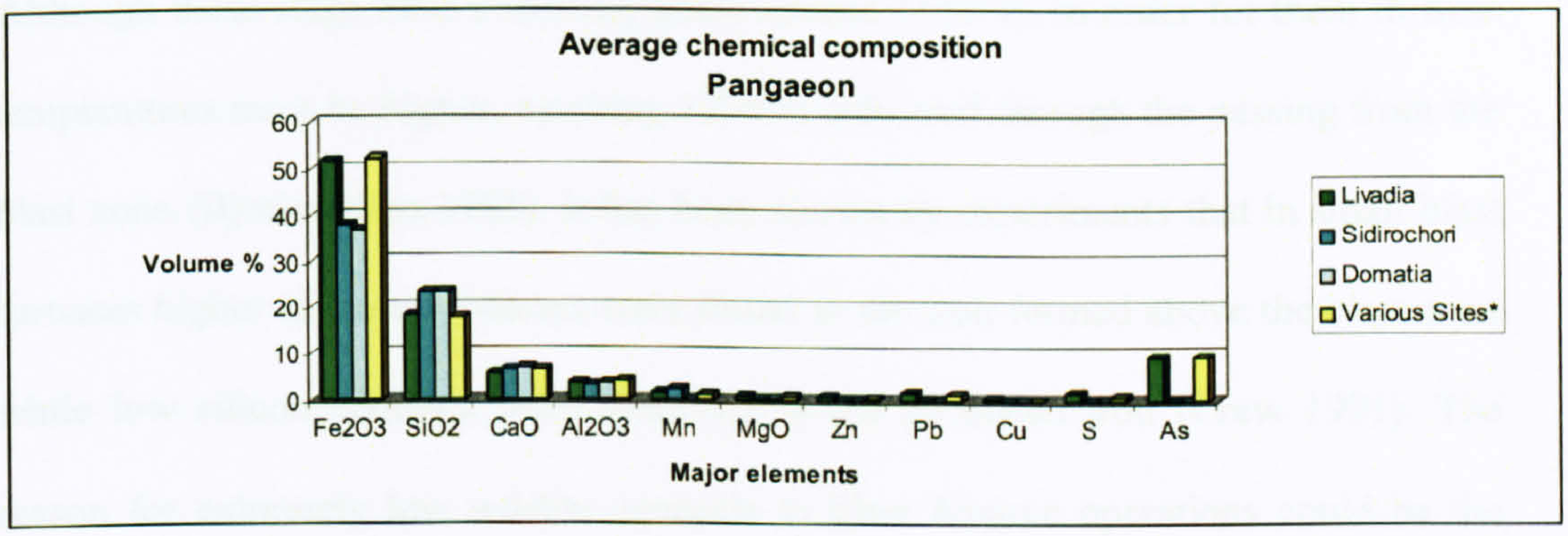


Figure 6.35 Chemical composition of Pangaeon slag (adapted from data by Papastamataki 1985)

6.12 Conclusion

Taken together the analytical data supports the identification of the various types of smelting technology at the sites studied. The results of slag analyses at Katafyto best support a model which is characterised by low temperature products which would account for bloomery iron smelting. These highly magnetic, dense and rich in FeO slags are typical derivatives of such bloomery operations where the absence of a blast zone within the furnace does not facilitate considerable temperature rise for a liquid slag to be formed. Likewise the Angistro slag with widespread fayalites and iron contents around 40% denote a bloomery process. The furnaces for bloomery smelting were small structures with a tapping arch and a shaft whence charging was done and would need a few persons to maintain. Therefore practice remains reflect labour associations which are crucial for an understanding of the technology involved. Examples of similar workshops from the southern Balkans have been recorded in the relevant literature that has been lucidly reviewed in chapter 4.

Whereas iron-rich slags are indicative of bloomery smelting the highly alkaline slag from Makrychori suggests indirect production of iron mostly using a technology which is reliant on increased draught to facilitate higher temperatures. Although these slags have a melting point around 1150°C, in order for them to flow temperatures must be higher, reaching 1250°C achieved through the passing from the blast zone (Bjorkenstam 1985). It has been shown by experiments that in small blast furnaces higher siliceous contents were found in the iron formed above the blast zone while low silicon contents were observed in the produced iron (Crew 1991). The reason for extremely low wüstite contents in blast furnace operations could be the silicon reduction of slag wüstite. The presence of alkalis is also important as such compounds accelerate the reduction of FeO and SiO_2. Clay from the refractory furnace material contributes to the formation of iron either always or just in initial smelts. As a furnace is used the lining becomes slagged and makes less contribution. Both characteristics of blast furnace slag i.e. low wüstite contents and high contents of alkalis have been found in Makrychori slag and could therefore be characterised as such.

The higher melting points would suggest the use of high shaft furnaces which need more workers to maintain. Such information has important implications on the organization of production which should have been large-scale and would require constant operation of such furnaces once the smelt was initiated. Such reactions could ideally take place in a blast furnace, but not necessarily a modern one of large proportions. Even small charcoal fired furnaces from which molten slag is drawn off have to operate at high temperature in the blast zone.

The distinctive processes represented i.e. bloomery in Katafyto-Vathytopos and Angistro, indirect iron smelting in Makrychori and also silver collection, might suggest that this technological variation meets the chronological framework proposed in chapter 5. Although silver collection is suggested for Makrychori, evidence for the final stage of this process i.e. cupellation is absent and could be thus presumed that such a process took place at a central place where direct political control would be exercised. Such practice coincides with administrative systems of control over resources possibly of imperial structure such as the Byzantine and Ottoman.

Having considered all the important parameters of slag formation and characterized the metallurgical remains it is possible to reconstruct the organization of production on the four sites albeit from a fragmented understanding of the various production processes. Problems solving and certain actions taken towards furnace operation have materialized in the residues and once interpreted could provide crucial information on the whole process of smelting. For instance a large number of blocked tuyères in Katafyto suggests that smelting was at times problematic. At the edge of the tuyère where excess of O_2 causes a highly oxidising atmosphere and the liquid slag is floating on the forming bloom, separation between the two was often unsuccessful. Further due to the failure to raise the temperature to necessary levels, the slag formed was viscous and did not flow freely. Presumably, if attempts to repair or effectively maintain the tuyères failed, then the entire furnace would have to be reconstructed but the evidence for such practice is non-conclusive. The large conglomerates with entrapped blocked tuyères and excessive clay lining from the dump heap could be interpreted as residues from unsuccessful attempts to separate slag from the sintering bloom and might also reflect incidents of furnace repair (see chapter 5 photos for Katafyto). All evidence converge to small groups of smelters consisting of no more than four to eight people which could work on a seasonal basis at the site.

Although the location of Vathytopos by the remains of a watermill would suggest application of highly productive technology whereby bellows operate by water power, no solid evidence for this is reflected in the slag. It is more probable that the water wheel was used to drive a hammer for the smithing of blooms which has been a common practice at various *samokovia* in Bulgaria and eastern Thrace (see chapter 4). The evidence suggests small-scale operations for short term durations and the analysis concurs with a bloomery workshop similar to that at Katafyto. Such findings would suggest that labour was organised on a similar scale involving eight to ten persons to operate the furnace and the bellows arrangements.

The characteristics of Angistro slag (i.e. moderate FeO, slightly alkaline) indicate successful gain in metal. Most of the associated residues such as tuyères and conglomerates hint to somehow slightly larger furnaces than those at Katafyto and Vathytopos. Clearly extended groups of workers would have been in need for such a large smelting site where discrete units of production are scattered around the village. The sampled site produced highly alkaline and siliceous slag with low FeO contents which have been interpreted as belonging to blast furnace operations. The high CaO contents in all analysed samples leaves little doubt that deliberate addition of fluxes was practiced. Since they derive from surface contexts they should possibly be the products of later exploitation phases. Additionally the absence of similar refractory ceramics from other sites could be indicative of different technology when seen in conjunction with the more alkaline slag as products of higher temperature smelts.

This chapter has achieved to demonstrate the difference between workshops whilst highlighting uniformity within sites. Even slags with different morphologies are similar chemically and it could be argued that a range of activities are site specific. Slags from Katafyto and Vathytopos are hard to distinguish chemically but the main morphological characteristics of slag are uniform. Bloomery iron smelting was practiced on both these sites a fact corroborated by microscopic, compositional and mineralogical results. Angistro and Makrychori are clearly different since the contents of precious metals in the slag and speiss with low silver values testify to collection by use of lead with an intermediary speiss forming phase. This data taken together with site survey will form a powerful corpus of material from which to discuss technological change in the periods examined.

CHAPTER 7

Technical acts and social transformation

7.1 Introduction

This thesis has coupled the study of relevant historical data with site prospection and survey and in turn united this with the investigation of material residues from metallurgical activities. The aim of this combined approach was to achieve an extended understanding of how communities were transformed in light of social and political change and how such recursive relations materialised in the arena of metal production in northern Greece during the early modern, late Byzantine-Ottoman state periods i.e. the 14th and 18th centuries. Both the material nature of the evidence used in this study and its technological origin allows this study to stand apart from the many traditional historical approaches to this period which have limited their analyses to abstract or conceptual models of political and economic domination based on historical records and often devised in opposition to contemporary western models of governance (Anderson 1991; Jenkins 1991; Turner 1998). It is then a point worth emphasising that this study seeks to understand social transformation and technological change in terms of the actual *practices* undertaken by communities in this period. It is for these reasons that specific aspects of the data such as spatial organisation, chemical analyses, and inferred technical processes, will be utilised, such aspects are not normally considered in typical accounts of this important period of European history.

Based on published evidence and the findings derived in this study, it appears that technological change in eastern Macedonia between the 14th and 18th centuries and the concomitant social transformations do not follow a simplistic development of increasingly efficient technical processes supplanting less efficient ones themselves accompanied by the industrialisation (urbanisation) of local communities. This itself contrasts with conventional models of western development/industrialisation (Anderson 1991; Hobsbawm 1962) although such models have recently been opened to critical analysis (Cassela and Symonds 2005). Put simply, the transformations witnessed in northern Greece stand as an alternative to the often vaunted case of western industrialisation (Finch 1951; Kirby *et al* 1990; Rossi 1997). The reasons for this are, predictably, complex but prior to a more detailed discussion, it is worthwhile highlighting here the need for any such analysis to recognise not just the material and technical contingencies which come to bear on such transformations but how memory, in the form of enduring beliefs and ideology, also structure the understandings of how change is realised.

In Byzantine terms change is understood within a culturally specific communal belief system, what Turner (1997) describes as the Social Myth, deriving from the inherited classical paradigm. Since the empire represents a valid continuity of the Romano-Hellenic world the social myth of antiquity as a total ideology and the institutions which repose upon it had been reinvented or modified with the advent of Christianity. The Byzantine emperor as a reflection of God or the embodiment of the Social Myth was obliged to execute state affairs and express perfect justice, law and piety for all his people (Turner 1997). In such terms change is realised in a transcendental context within which all Orthodox theology is being expressed and lived. The here and now are projected to eternal dimensions, transformation or social change is seen to progress according to cyclic events of cosmic essence (i.e. birth-death-resurrection). Any technological or economic action is therefore encapsulated within broader symbolic constructs of this theological exegesis of Byzantine cosmology.

This chapter aims to synthesise the diverse data presented in previous chapters and to suggest how this can be understood in terms of social transformation for this period and in turn to question some of the assumptions in our accepted histories. Key themes that are developed are the relationships that exist amongst technical know-how (Tylecote 1987; Craddock 1995), social identity (Knapp 1998; Douglass 1998), practice and the organisation of labour (Day and Doonan 2007). It should be clear that specific bodies of data already presented directly address some of these themes yet they remain to be united in a synthetic study.

7.2 Communities as agents of social organisation

Technology is unavoidably involved in many areas of production and consumption (i.e. food) whist also sharing common technical operations with agriculture and animal husbandry and often providing the material basis for such operations. Expressed another way the diverse *chaînes opératoires* in which a community is engaged are entangled at numerous stages, at times this may be continuously at others intermittently (Dobres 2000; Bourdieu 1990). This is a crucial point for emphasising the anthropological basis of technological practices (even technical processes), as Sillar (2000, 68) has stressed "it is by looking at the interconnections between many different *chaînes opératoires* that we will demonstrate the 'socialness' of technical processes by revealing how technology is deeply embedded within people's cultural knowledge".

The theory of agency has underlined the importance of historical contingency in the search for motives and meanings in human action and its role in the many unintended consequences that unfold in ongoing social processes (Giddens 1993; Bourdieu 1990; Barrett 1994, 2001; Shanks and Tilley 1987). Above all, it has highlighted the central importance of choice and the need to understand the many conditions within which 'choices' are constructed by knowledgeable social agents. There are numerous archaeological and ethnographic examples which document how specific social choices (particular techniques) are made and whole communities come to rely on specific actions, even though many others are potentially available (Lemonnier 1992). It is argued here that the opportunity for choice is always present even in contexts which are often seen as either 'economically' or geologically determined i.e. resource acquisition and procurement of raw materials (Gosselain 1994), in short how humans interact with the material world always carries with it the opportunity for alternative action and as such specific choices must be acknowledged as being culturally informed.

Therefore when approaching technological choices and materials acquisition in the context of medieval mining in northern Greece, the influence of political and ecclesiastic ideology on technical actions cannot, and indeed should not, be excluded. The 'imperial' state, institutionalised church authority, secular elites, large estate owners or powerful individuals often organized and coordinated long-distance exchange, whilst sustaining craftsmen under their 'protection' and controlling access to resources required in technical operations and simultaneously moderating the circulation and consumption of commodities and finished products (Haldon 2000; Harris 2003; Lefort 2002). So embedded were such institutions in every stage of craft from resource acquisition to consumption of finished goods that it becomes impossible to attempt any understanding of craft working without acknowledging the role of these social institutions. Clearly then any history which sets out to understand the transformation of production in this period, or any other, is destined to produce a dubious account if it limits itself to the 'commonsense' factors such as economy, efficiency and 'technological progression' to explain change.

A multitude of active agents have contributed to social transformation in the area under study since administrative control and economic practice have shifted from a centralised scheme during early Byzantine times (5th-6th centuries) towards gradual decentralisation of the later stages (13th-15th centuries). Historical documentation and material remains reveal a complex picture whereby village communities become increasingly important for active contribution to generating wealth at a regional level often aiming to sustain their populations (Vakalopoulos 1973; Angold 2001). Such an organisation of communities to better utilize available resources i.e. arable and pasture land, mineral deposits or communication routes for the trade of finished or semi-finished commodities could be understood in the light of transformations at a social level (Hardesty 1988; Herbert 1998).

The rural community has been taken as the basic unit of investigation in order to move beyond traditional perceptions of settlement sites as primary foci for societal organization and appreciate the current results regarding economic strategies within the specific surveyed regions. Local communities considered their survival fitting to a diversity of environmental settings as described in chapter 2 while the idea that metals production was entwined in broader subsistence schemes has been developed in chapters 3 and 4. Such a regional approach adopted here was proved enhanced against studies which overly focused on particular modes of practice at the expense of seeing how these were integrated in to wider schemes of subsistence (Knapp 1998; Douglass 1998; Canuto and Yeager 2000) although envisioning such an approach in the current field of study which has received such little attention is perhaps someway off.

The investigated sites reported in chapter 5 display various degrees of organisation and technological complexity which seem to broadly change through time. Analysis of the residues has revealed that those deriving from small-scale sites of the Late Byzantine period have formed under mildly reducing conditions. The technological means available could be characterised by low labour investment while optimisation of the process for increased output is not evident. When Ottoman administration replaced Byzantine authority the region witnessed certain changes in the social level which can be traced in the archaeological record in terms of demography, religion and architecture. Although technological transformation would presumably follow an evolutionary route towards optimisation or efficiency the evidence from a number of smelting sites shows a different picture. At sites such as Makrychori and Angistro increased output has been attempted by reforms in metallurgical practice i.e. more reducing conditions, the use of better fluxes and probably more efficient furnace design. However a growing number of smaller scale production sites (Nikisiani, Vrontou) that have come to light during survey show a parallel low yield, less 'efficient' technology. It could be concluded along these lines that technological transformation has been considerably variable and did not supplant previous traditional modes of production which existed in remote settings.

It does not therefore seem possible to identify a marked technological hiatus between the efficient installations of the centrally administered Angistro and Makrychori and the contemporary open hearth furnaces of the marginal sites. Their fundamental difference lies on the fact that the central sites were part of an entrepreneurial productive system organized on a vast scale, closely linked to the circulation of products on the market, whereas the technologically simple and scattered in the territory aimed to meet local demands (Cortese and Francovich 1995).

The investigated evidence for mineral processing revealed how the technical means employed in small and middling-scale production sites reflect a general lack of concerns with optimisation strategies. In most cases the individuals engaged in mining or smelting of ores utilised a low temperature smelting technique by which the overall output in metals could sustain communities of a moderate size. In effect the overwhelming volumes of slag noted in particular at Makrychori and Angistro could be derivatives from the latest stages of Ottoman or even industrialised modern exploitations by which labour constraints diminished and preoccupations with profit might have ensued increased output. Technological transformation can thus be understood as an outcome of social re-organisation where the conditions have been favourable.

7.3 Landscape, time and labour

Issues of space, landscape and temporality are not only central in any interpretation of the experienced past (Ingold 1993) but rather need to be incorporated in to an understanding of landscape. By regarding space and consequently landscape as inhabited, experienced, lived, narrated and commemorated (Bourdieu 1977; Tilley 1994; Dornan 2002) we can situate our studies better to reveal the complex of inter-personal and social networks that operated in the past (Knapp 1998). In effect, the concept of industrial landscapes is relevant to approaching such cases where alterations of the environment and socially embedded transformation of the material world are involved. Critically, such understandings of the development of landscapes and, crucially, the *practices* of the communities that dwell in them, provides us with a means by which we can develop understandings of how community identities emerge in different places and how they transform through time.

As Ingold (1993) has illustrated, the concept of landscape should not be understood as a representation of the natural and built settings where human action takes place, rather a 'dwelling perspective' that sets out from the premise of people's perceptual engagement with the world. Slag concentrations could be appreciated differently by those related in metallurgical activity, or other groups with different interests. They could be seen as waste products, polluting the 'natural' environment, or as a potential resource for re-smelting to gain any entrapped metals or indeed durable construction materials for other purposes. A layering of variable meanings and evaluations, economic concerns or interests is therefore attached through time on such landscapes.

To further promote an understanding of how communities engage with the world, anthropologists introduced the notion of temporality seen in opposition to chronology and history (Kubler 1962; Gell 1992). When seen as the passage of events either in temporal succession or as isolated happenings temporality and history seem to merge in the experience of those actively engaged with the process of life. Ingold (1993, 158) introduces the taskscape as a concept entwined in landscape which lies in rhythmic interrelation or patterns of resonance such as focal points in the lifespan of dwelling and the various cycles associated with 'work' and other forms of 'living'. The taskscape is an entire ensemble of tasks (organism-material interactions) which acknowledges their rhythmic spatial and temporal distributions (Ingold 1993, 159). Through living and acting in a socially structured landscape, conceptualising and measuring the temporal process becomes predetermined by societal parameters. For Durkheim (1976) the temporal ordering of events comes from society, corresponding to the 'periodical recurrence of rites, feasts and public ceremonies'. The temporality of landscape is a crucial notion for understanding the unfolding of human activities, their duration, resonance and rhythm as these have become incorporated as meaningful elements in the archaeological record (landscape) and retain value for communities as well as archaeologists (Bourdieu 1977; Cosgrove 1989; Tilley 1994).

The performance of activities for the production of metals through the application of pyrotechnology involves space, time, different raw materials, tools, procedures, specific knowledge of the local environment and skills together realised as labour. Through a comparison of units for measuring abstract notions, Ingold (1993) described the currency of labour being time, just as space is the currency of land and money the currency of value. Along these lines Sorokin and Merton (1937) illustrated the distinction between astronomical and social time becoming apparent through a comparison of recurring physical phenomena (i.e. planetary motions, the change of seasons) and performance of cultural events (i.e. rites, festivals) that mark specific moments in social interaction. Such a distinction may lead to conclusions that whereas labour is measured out in units of astronomical time, the temporality of the taskscape is essentially social. In other words time could be seen universally as a measurable dimension or a conventional construct appreciated and understood according to certain social conditions.

What is clear from the study undertaken here is that the period studied witnessed profound and dramatic transformation not just in how communities organised themselves but their understanding of how they related to the world, how the world could be exploited and what the consequences of such exploitation was. In Byzantine terms concepts of temporality were founded on ideas of eternity and perpetual motion towards the end of time marked by salvation (Ahrweiler 2000; Angold 2001). Such ideas had been present in ecclesiastical liturgy, imperial ceremonies, pedagogical philosophy and all other aspects of everyday activities.

Extended temporality was conceived as synchronous with the historical unfolding of events but influenced Byzantine attitudes towards ephemeral action of daily life as opposed to eternal afterlife anticipation. Therefore organising communal ventures by managing time and appropriating tasks had always been affected by notions of extended temporality and thus had a direct connection with broader theological issues.

Some relevant data gathered from the studied sites reflect conservative attitudes towards technological innovation which in turn combine with contemporary perceptions on time. It appears that ancient methods survived for considerable periods as far as ore acquisition is concerned particularly at sites of highland Vrontou where the iron sands were extensively utilised. Likewise the bloomeries recorded at Leukogia, Exochi and Katafyto show characteristics that in the 13th and 14th centuries might have seemed anachronistic and obsolete compared to European counterparts (for relevant examples see chapter 3). Even where technological transformations are apparent particularly at Makrychori and Angistro they occur with the application of existing, simple technical means rather than by a wholesale adoption of unfamiliar methods developed elsewhere. This is evidence that although transformations do occur they are not embedded in a thought system of linear development unfolding through the passage of time. Ideas of change through cyclic events were more persistent in this rural world of agrarian communities that were only partly involved with industrial practice.

7.4 Technical know-how

The physical making and use of material culture involves certain technical acts, which embedded within social value systems are being expressed through the knowledgeable practice of everyday technologies. A large number of sites where mining and smelting has been confirmed through this study underlines the fact that metal working constitutes a regular and frequent activity in the region which is present in many landscapes. Some commonly recurring external features characterising these sites could be understood in light of a shared tradition of technical know-how across eastern Macedonia. In most cases furnace material is not represented or survives in a severely fragmented state indicative of the ephemeral and probably haphazard nature of operations. Such findings suggest that the people involved made knowledgeable judgments on ore potential which had to be smelted through seasonal gatherings with shared labour constraints, in small furnaces that had to be destroyed leaving behind insignificant traces. Success would certainly rely on memory, performance and luck. In cases of failure which might have been frequent technical choices dictated by experience and experimentation would have served to counter specific problems inherent in material transformation activities.

It appears that workers in both upland and lowland sites had to compromise logistics or symbolic issues on remoteness opposed to proximity to settled areas and preconceptions regarding materiality and 'effective' technological action. Their knowledge about the environment, potential resources and the practical know-how to effectively manipulate material properties were founded upon technological traditions. Therefore prospecting for raw materials, mining and transportation methods did not change drastically over time once their effectiveness was judged acceptable for a given local community. The quality of ores was being tested by trial smelts while roasting and enrichment would have presumably taken place close to the mines. These early processing stages are difficult to trace archaeologically and therefore no signs of ore treatment prior to smelting has been determined close to the visited mines.

Smelting evidence from the field testifies to the use of primarily low furnaces operating with short tuyères not protruding considerably into the furnace superstructure. Ethnographic and archaeological examples have demonstrated how clay from vitrified tuyères partly contributed in slag formation while Schmidt (1997) has argued that in East African bloomeries the length of tuyères allowed preheating of the air leading to considerable temperature increase. The tuyère fragments found at Katafyto and Angistro are fragmentary and their average length was estimated around 8-10 cm but their considerable width (5.40 cm inner diameter) reveals technical information on bellows size and arrangement. Air input through such wide tubes might suggest the use of double bellows arrangements operated manually, similar to those described in medieval crafting manuals i.e. *On Divers Arts* by Theophilus (Hawthorne and Smith 1963). Such furnace characteristics would facilitate bloomery at moderate temperatures that would need small groups of smelters to maintain, consisting of up to perhaps eight individuals. Although common technological traditions in the region would not vary from site to site the larger workshops would arguably use more sophisticated techniques at least in the field of precious metals extraction from the available complex ores.

7.5 Site distribution

The sites investigated in this study display features which account for multiple processes defining a duality of organisation running along parallel but possibly discontinuous lines. Widespread production of iron has been noted across the study region in various environmental and geographical settings. These findings have questioned the argument being raised in numerous literary sources that precious metals have been of primary importance in this region. Iron which was in great abundance and a crucial resource for manufacturing tools and implements was evidently of great significance to the local agricultural communities.

Apart from factors affecting the presence of natural resources and the availability of technological know-how, other elements, tied to the demand for metal, contributed to the locations in this distribution pattern of smelting activity. Above all the demanding markets of Constantinople and Thessaloniki were important, and should in the first place have required considerable quantities of metal. A second major catalyst was probably the great development of Serres into an important urban centre of this region, which was making ever higher demands for iron by the 12th century onwards.

The small-scale bloomery workshops investigated tend to concentrate in upland settings (i.e. Magnesia, Ano Vrontou, Faia Petra) but there are also some examples situated on lower ground (i.e. Leukogia, Exochi, Kalithea). The sites in the uplands had direct access to crucial resources to facilitate smelting such as minerals and timber. Their obvious distance from settled areas might have sprung partly by geographic limitations determined by the presence of minerals but may equally have facilitated a clandestine atmosphere to develop around the nature of metalworking practice, at least in some contexts.

Quite differently the small-scale lowland sites lack immediate access to resources but would have countered this shortcoming by exchange. Being closer to settlements their production output would have hardly remained unnoticed. Such proximity is often presumed to offer opportunities for quicker transportation of finished products to consumer markets in rural towns or larger cities. Such presumptions though fail to recognise issues of self-sustaining communities aiming at autonomous strategies which integrate sustaining goals i.e. agriculture with secondary priorities (Brumfield and Earle 1987; Costin 1991; Knapp 1998).

With regards to the moderate (<500m² slag coverage) and large-scale (>500m² slag coverage) production sites, there is an apparent geographically determined distribution pattern. Those that produced iron at a middling scale (Katafyto and Vathytopos) are situated in upland environments, whilst the extensive ones (Angistro and Makrychori) where iron and precious metals extraction has been determined by instrumental analysis are located in lowland settings. It should be noted though that both Angistro and Makrychori had easy access to rich mining sites found in their vicinities. As far as precious metals are concerned, their conspicuous production is rarely reported in traditional models, which tend to emphasise the role of a central dominating power (i.e. imperial state) that exercised control over such practices. Relevant literary sources (Lemerle *et al* 1979; Lefort 1985) inform us that by late Byzantine times production of either base or precious metals diminished to restricted small-scale operations often decentralised, a fact that is reflected by data gathered from the field.

Some of the small-scale production sites that were dated by ceramic finds to the Byzantine period are generally part of this decentralised model. However the sites where Ottoman metallurgy is evidenced are both small and large-scale and contrary to what has been presumed they are either conspicuous, in lowland settings or in other cases clandestine in remote, mountainous areas. For instance the excavated furnace at Livadia on a highland location of Mt. Pangaeon has produced evidence for precious metals collection of restricted and clandestine nature that has possibly escaped central control. The analysed remains from Makrychori provide evidence of conspicuous extraction of precious metals but the later stages of cupellation are not represented and presumably took place elsewhere and hence under the control of different groups, although of course extended survey in the area may well shed light on this issue. Therefore the picture emerging through an assessment of the current results does not seem to follow chronologically presumed arguments of Ottoman control of production imposed on all metalworking sites.

Political control over resources and craftsmen, and the meticulous registering of produce have been conventionally taken for granted for most stratified societies of the past. Thus the surviving records compiled for taxation purposes have been often regarded as accurate indictors of surplus accumulation and economic expansion. Ethnographic work carried out by Halstead (1998) on farming in northern Greece has demonstrated that even by modern standards the central government failed to adequately assess the extent of agricultural practices, even despite agricultural land being open visible and impossible to hide. Often terracing, difficult topography and local informants could too easily mislead governing officials. Farmers were often reluctant to provide information on their practice (kinds of crop cultivated; compensation rights depending on crop type) in certain areas while despite the technological means available tracking of such processes by state officials has been unsuccessful. Such a realisation is of profound significance to the current study since metalworking in the past which often took place at remote, marginal locations was supposed to have been closely monitored by authorities. When such control nowadays is limited for easily accessed agricultural land it seems reasonable that in Byzantine or Ottoman times monitoring of marginal locations would have been considerably difficult if not impossible to maintain. Such case studies are absolutely invaluable for warning us against taking documents at face value.

Where then do the small-scale workshops fit in a model of state-owned and state-operated mines when at the same time the production and trade of metals are centrally controlled? Although the current study sets to approach such a question future fieldwork is necessary to shed more light on these issues. Nevertheless the existing strands of information discussed above suggest fluidity between state sanctioned and clandestine mineral processing and metal production in late Byzantine-Ottoman Macedonia. Such variation is proof that technological knowledge can move about and could therefore be seen as a subversive act for communities involved in such practices.

Historical information describes the marginal upland zone of eastern Macedonia as a vital source of mineral resources, crucial for the survival and security of the Byzantine state (Moutsopoulos 1997; Vakalopoulos 1973). Until recently it was thought that the development of the region's infrastructure has been the result of exclusively royal initiatives implemented by local officials. However recent studies have underlined an apparent site to site interdependence in modes of production, which presents a different picture, one where state control is present but only rarely (Inalcik 1973; Meyer 1997; Meyer *et al* 2000).

Regional politics and technical franchising of a local character played a greater role in the development of networks for procuring and processing raw materials, through a pattern that demonstrates the inadequacy of a monitoring centralised power. Such practice was probably widespread because central authority did not need to dominate contexts of production as long as they controlled contexts of consumption or exchange in urban markets. Therefore the question becomes not how did the state control resources but why were choices made to change the context in which power was exercised. This could be because of concerns with efficiency, martial threat, or other symbolic forms of domination. Further the presence of state control is more eminent especially where gold and/or silver assaying was exercised but the general practice for state-controlled enterprises involved undertaking and management by private contractors (Rozen 1993).

This feeling of marginality and isolation was at times beneficial due to a lack of state control as witnessed with the parallel and contrasting sites of Vrontou (small-scale) and Makrychori (large-scale) but more often too precarious due to external threats. Most of the rural regions of eastern Macedonia have been sporadically invaded by Slavic tribes through the 6th to the 10th centuries while the Ottoman conquest started by late 13th century. An element of insecurity has been characteristic of the region's communities and indeed individual groups within them. Although playing significant roles in local communities and being central to the maintenance of the demanding broader networks of consumption, it appears from the location and character of their settlements and the range of material culture that miners and smelters remained at the fringes of peasant society (Douglass 1998).

The peripheral location of investigated production sites and the lack of any high status material culture or elaborate architecture further emphasises their ephemeral nature. Their craft materialised in social relationships featured the insignia of a profane activity carried out at the precincts of settlements (Cortese and Francovich 1995; Danisman 2007). An evaluation of the 'structured' deposits of their workspaces and interpretation of the technical choices behind the performance of smelting can be understood in light of choices in other spheres of life. Relevant information derived from an appraisal of the geographic unfolding of metals production which involved distant mining locations, peripheral settlements and active fringe communities has been a constant theme developed in this thesis.

7.6 Practice

The embedded and corporeal nature of technologies and their enactment or what Mauss (1979) has termed the *techniques du corps* have two common themes, that of materiality and corporeality (Hamilakis *et al* 2002). One central aspect of materiality is that of practice or the enactment of certain steps towards a desired end result. Practice is structured by space, seen either as natural environment or architecture and unfolds through the passage of time. Bourdieu (1990) has highlighted how practice is central to constructing identities. This study has illustrated how differences in metallurgical practices can reflect specific schemes of labour organization and therefore the structuring of identities through a materialisation of relationships by common undertakings.

The actual practices represented on the four sampled sites could be evaluated in light of results from the field and the scientific data reported in chapter 6. The bloomery process evidenced at Angistro, Katafyto and Vathytopos involved reduction of the iron ores in a bowl-shaped or shaft furnace which facilitated liquefaction of the gangue constituents (around 1200°C) and formation of the bloom. During such processes the metallic iron mass enveloped in slag contains varying carbon contents ranging from wrought iron (less than 0.05% C) to steel (around 0.5% C) (Photos *et al* 1986). Subsequent forging would have removed all residual slag, an activity which is not represented on these sites and would have presumably taken place elsewhere. Forging evidence comes from the early Byzantine fortified settlement of Orini in Serres but no sampling was carried out on the site.

More complex practices are represented at Makrychori where the mineralogical and chemical data from sampled material point to higher temperature extractive methods presumably taking place in a blast zone of a high shaft furnace with the possible use of fluxing agents. An evaluation of the melting points for analysed slag indicate that reduction of the ores could have reached close to the melting point of iron (c. 1550°C) therefore leading to effective gain in metallic iron and free-running glassy slag. Further as has been argued in chapter 6 the numerous lead inclusions and appreciable silver contents detected in Makrychori slag could have resulted from refining practices for the gaining of the precious metal. Again only certain steps of the process are represented since no litharge or concrete evidence for cupellation being practiced on site has been found. This might reflect a fragmented production sequence whereby the stage of cupellation is taking place in a centrally controlled context away from primary extraction sites.

Further information concerning the raw materials and organising the different steps in ore treatment (i.e. roasting, pre-heating) and charcoal production is equally important to understand the dominant practice regimes on these sites. The ores available from the mining sites generally consist of hematite which has been the presumed primary mineral extracted for iron smelting in this region. However as has been suggested in the past alternative sources could have been utilised such as the plentiful magnetite sands found in stream beds and crevasses of the Vrontou region. According to Photos *et al* (1986) preliminary TL data ascertain that these sands were smelted in the late Byzantine period.

Based on the results discussed in chapter six the detection of titanium and vanadium in slag from Katafyto and Vathytopos is of special value as it provides solid information on the ores being used. Such residual elements that become incorporated in the slag during smelting are indicative of iron sands that had been possibly used as primary ores on these sites. Presuming that mixed practices involving small scale mining and collection of readily available magnetite sands gave rise to autonomous procurement of raw materials, local communities would seem to be willingly involved in metallurgical practice. In such situations the organisation of ore collection and processing would have been considerably different than underground mining for minerals hosted in hard rocks. Collection of such decomposed surface ores through water channelling and separation by floatation would require small groups of labourers and relatively low cost investments.

The presence of arsenic-rich minerals (scorodite) and speiss phases in Angistro slag has suggested that the local arsenopyrites have been utilised as major ore sources while in the case of Makrychori the high levels of manganese testify to the use of local ores. Clearly extraction of such ores was undertaken by underground mining which involved overwhelming numbers of labourers and higher expenditure. Further issues such as maintenance of deep shafts, effective drainage and ventilation would require capital investment that local communities would hardly shoulder. State officials and the landed aristocracy were most likely to have had the necessary capital to invest in mining contracts (Edmondson 1989) and were probably actively engaged in those wide-ranging production centres.

Recycling of scrap metal would have constantly supplied blacksmiths at times when mining diminished in output. Indirect information for fluxing with sands or other constituents to drive off gangue minerals was derived from slag mineralogy as in the case of Angistro. Finally the numerous slag accumulations investigated reveal certain patterns of deposition which were in accordance to contemporary attitudes towards discard of unwanted material and might reflect the lack of technical means for further processing or alternative usage.

7.6.1 Organisation of production: Seasonal and specialized practice

The lack of evidence for buildings of any sort close to the mining sites is probably indicative of the seasonal nature characterising the prevalent practice regimes or the lack of administrative infrastructure associated with such operations. It is highly possible that itinerant miners were staying in temporary shelters which left little trace in the archaeological record. On the other hand the location of the smelting centres at the edges of villages still inhabited today should not be understood as mere coincidence. Some of the older villages (16th century) close to the smelting sites investigated were very likely the homes to smelters who utilised all available resources for an optimisation of their personal and communal gain strategy. The 17th and 18th centuries are not represented by concrete architectural evidence but at the same time there is no information for considerable village desertions in the historical record. Some of the most recent villages reported as refugee's settlements came into existence in large numbers after the population exchanges of 1922 (Toynbee 1970). Although it is difficult to assign production sites to occupational areas in strict temporal terms, certain clues such as architecture could help towards that direction.

The years of Ottoman rule left behind a number of characteristic landmarks defined by religious architecture such as mosques and minarets which spread to rural contexts, often side by side to Christian monuments such as churches and monasteries. Thus most villages of northern Greece could be seen as palimpsests upon which religious geography could help at elucidating a chronology for various settlements. Looking at certain villages' churches and their foundation dates one should get an idea of their Christian past and the broad dates for settling around previously used mining regions. For Kato Nevrokopi where four smelting sites were located, ecclesiastical architecture and foundation dates converge to middle 19th century. Specifically Aghios Nikolaos at Katafyto 1813-1869, Taxiarches at Akrino 1848, Naos Koimiseos Theotokou, Dasoto 1870, Aghios Nikolaos, Perithorio 1835, Ag. Theodoron, Kato Vrontou 1835 point to late Ottoman times (Emmanouilidis 1981). During that period industrialization gradually transforms most of northern Greek countryside and the social organization of rural populations. It is important to note that within such conditions remains from small-scale activity reveal a haphazard organization scheme aiming to meet local demands whilst not affording and/or ignoring innovation towards industrial modes of production. Seasonal expeditions for mining and social gatherings for small-scale smelting of local ores became identity forging events which separates such communities from full-time specialist counterparts.

Apart from agriculture, which in the case of highland sites with altitudes above 800 m was piecemeal due to a lack of arable land, the choice to smelt local ores appeared as an economically viable alternative to stock-raising and was pursued on the basis of communal enterprises. Either seigneurial investments covered the expenses for resource mobilisation and labour organisation or alternatively partnerships of peasants provided the necessary capital and labour force. The latter case is elaborately demonstrated in 18th and 19th century Chalkidiki were the inhabitants of the Mademochoria formed an early partnership association for the working of mines and furnaces of their region (Rozen 1993). Finding labour among their local workforce to work seasonally would benefit the community towards effective resource exploitation and autonomy.

Population movement across the Balkans juxtaposed facets of existing communities' identities whilst allowing intermingling of cultural traits including religious practice and artistic expression as well as the exchange of technical knowledge and practice (Lefort 1993). The bearers of technological 'secrets' i.e. the guilds of craftsmen, enriched traditional operations with innovative methods in the fields of raw material acquisition and modification. Although specialization is reported in contemporary documents, often the same groups of people were responsible for the manufacture of certain categories of artefacts (Matsche 2002; Oikonomaki-Papadopoulou 2006). More efficient smelting furnaces and devices for the various stages of metal refining (ore washing, sorting and crushing, blowing devices) in conjunction with emergent regionalism and segmentation brought about an increasing reliance on local resources and small-scale production, aiming at self-sufficiency. The region under study displays a certain degree of integration amongst agricultural communities which sustained small populations of craftsmen such as blacksmiths, masons and potters working in close relation with other sectors of agrarian life mainly farming and stock breeding (Brumfield and Earle 1987; Costin 1991; Dobres and Hoffman 1994).

More specialized labour was centered on specific places of strategic interest for the state, such as mineral rich zones and smelting workshops where precious metals were being processed for the needs of the contracted imperial capital. Such places became regions of control, exercised through martial means as well as through a segregation of the operational process into spatially distinct areas with specific skills sets and technical knowledge i.e. specialization, characterizing each separate stage of production. In such cases the knowledge and practices of one stage are obscured from agents engaged in others with the cumulative result that the whole process becomes mystified. Only the combined result of a 'fragmented' *chaîne opératoire* constitutes a logical representation of the act of crafting in such cases (Clark 1995; Sillar 2000).

According to Costin (1991) control over production could maintain or even enhance political power; in the case of the examined workshops attached specialists enjoyed the protection of state officials which in turn displayed their wealth through luxury items of precious metals. Apart from silver, iron was also produced on a larger scale at Makrychori and Angistro and thus workforce specialization correlates with high demand of standardized goods for the needs of densely populated communities or uneven access to resources. It is important to note that the concentration of specialists at such sites is directly affected by geographical proximity to resources, market-places and politico-economic centres as well as the organization of trade and degree of settlement nucleation (Clark and Parry 1990; Costin 1991; Clark 1995). Further issues such as efficiency, scale and intensity should not be seen in connection to large facilities and profit oriented production but rather as social constructs. Risks and scheduling for instance determine the degree of intensity being recognized as full-time or part-time among which it is difficult to discern for the current sites.

7.7 Social Identity

Seeing technologies as meaningful acts of social engagement with the material world is of crucial importance if interactions between technicians and the materials they work are to allow us to evaluate wider frames of action and to gain insight into any historical contingencies and an awareness of the context of material transformation (Gosden 1994; Dobres 2000). As Dobres (2000, 126) has illustrated technological practice serves as a medium of expressing world views, values and social judgments whilst producing practical knowledge and material things but also personal and cultural understandings that can serve political ends. The unfolding of such processes allows people to construct and express personal views and also participate in social collectivities thereby forging their communal identities.

Approaching the dynamics behind technological practice situated in a context of congruence of meanings applied to resources might reveal a layering of relationships between contrasting identities of metalworkers from different backgrounds. Further the enforcement of political control over precious resources might have significantly contributed to contrasting identities amongst the labour force in mining regions. Of equal importance is the culturally defined belief system in which technological practices unfold, impacting on the way individuals perceive human labour and spiritual completion. The following sections focus on the major parameters affecting the structuring of such communal identities namely value attachment on resources, political organisation and control, and socio-cultural proscriptions in an attempt to interpret the material evidence derived from the study area.

7.7.1 Resource perception and the creation of value

Throughout the middle and late Byzantine periods state officials, the clergy and high-ranking landowners negotiated their access to arable land and associated labourers with the central authorities whilst craftsmen were occasionally established at their estates (Haldon 2000; Harris 2003; Lefort 2002). Following the events of 1204 and the fragmentation of power among regional rival states resource perception passes through a transformational process. On a regional scale local communities oriented their subsistence strategies towards efficient exploitation of local resources aiming at self-sufficiency and autonomy and in doing so negotiated certain social identities of distinct characteristics (Hardesty 1988; Herbert 1998).

For most of the 13th century Byzantine landowners relied on labour from local communities to extract metals from their land. Technological practice was enacted along traditional lines which have diachronically covered the needs of local communities for agricultural implements (Bryer 1986). Those peasants involved seasonally with metal production identified themselves as integral groups of their agricultural social background. Smelting debris from their workshops reflects a technology involving industrious skills but hardly any specialization in production which might suggest that these workers did not exhibit a special status to socially differentiate them from fellow peasants. An apparent overlap of status differentiation among such agrarian communities reflects an overlap or entanglement in rural practices engendering a common identity for farmers and miners. However some internal differentiation within groups of practitioners might occur based on variable levels of experience, skill or even luck during practice. A sharing of beliefs concerning the right time, space or pace for certain technical actions, and the historically defined values or proscriptions are likely to have contributed to the development of such identities. Yet experienced or elder workers would have possibly obtained special status within their groups.

With the gradual settling of Ottomans in Macedonia around 1380s a whole set of social relations becomes modified to the conditions formed by contact of indigenous communities with the newcomers. Quite unlike the situation of European expansion to the western hemisphere, which imposed colonial production regimes in the south American mining regions (Thomas 2007) the Ottoman conquest over Greece did not overrule existing technological practices. Contact however gave rise to syncretic technologies through meanings and values attached towards natural resources which could have been contradicting or negotiated. Since according to

Pfaffenberger (1993) the *meanings* that people ascribe to situations can vary from group to group within a culture we can speak of a variety of behavioural responses to a situation which can potentially override other considerations. The agricultural basis of Byzantine rural communities motivated attachment of value to mineral resources associated primarily with the production of tools for their fields. Iron was the prominent metal used for utilitarian objects and farming equipment such as hoes, shovels or plough shares and their production and consumption has been constantly widespread across the rural sector (Bryer 1986). The lack of sophisticated material culture and the rare use of ecclesiastical precious metalwork underlines further the attachment of value and meaning to iron minerals which facilitated farming and therefore the survival of such communities.

Iron mineral procurement and processing would have been crucial for the Ottoman expansive policy over Christian populations mainly for the production of effective weapons and ammunition for the guns industry (Pamuk 2000). Likewise prospecting for gold and silver to supply the mints and producers of luxury items was of special importance. Thus the incidental co-presence of martial forces and a newly imposed bureaucracy to support taxation purposes inarguably drove Ottoman society to attach economic and symbolic value on iron and silver minerals that were available in Macedonian mines (Rozen 1993; Vakalopoulos 1996). Such concerns are demonstrated by archaeological findings, as discussed in previous chapters, since the large output in iron from the large scale sites consists of innovative technological applications as is furnace operations at high temperatures noted at Makrychori.

Mineral procurement and the 'profitability' of any mining operation depended upon availability of indigenous labour which Ottoman officials dragged out from the subjugated communities. One major change in the makeup of the labour force is the presence of foreigners brought into the mines and smelting workshops but traditional skills of the local communities played a more prominent role (Rozen 1993). Therefore such socially imbued understanding of resources as 'valuable' became the catalyst for technological syncretism expressed through identity variation. Within such mixed communities a multiplicity of potential meanings attached to resource, layered within technological action would reflect a nexus of value induced identities at times contradicting or in some cases converging (Cusick 1998; Thomas 2007).

7.7.2 Political control

Results from the field and the laboratory indicated two models of practice which are equated with distinctive social organisation. The intensive and large-scale practices such as those in evidence at Angistro-Makrychori seem to be state-sanctioned based on the location, visibility and investment in extensive infrastructure i.e. watermills, road networks etc. Such operations no doubt employed greater numbers of people engaged whereas the small-scale process (Katafyto-Vathytopos) is most likely associated with localised community organisation and possibly clandestine practices and hence associated with smaller groups of workers. These parallel models can give rise to specific identities characterised by certain differences in practice methods although it is possible that individuals may at certain times be involved in both types of production either simultaneously or intermittently. Therefore it would seem plausible to envisage those larger groups being part of extensive networks through which commodities and knowledge could be exchanged over large areas (Canuto and Yeager 2000). Such large-scale endeavours would presumably involve numerous workers brought from various locations often alien groups which can give rise to cosmopolitan dimensions within community identities

(Anderson 1991; Munro 2002). Equally, such influx can serve to reinforce existing identities with the strongest expression of insular identities often evident at such boundaries or interfaces. Issues of competitiveness and mistrust are not irrelevant in this context since multicultural communities often lack local knowledge whilst trust among their members is often superficial.

With regard to socio-economic orientations such highly specialized communities would have been involved in mining and metallurgy full time for most of the year's duration. Being secluded from farming or herding their basic subsistence needs are provided for through exchange with other groups or a coordinating central power such as the state (Brumfield and Earle 1987). Disengaged from subsistence constraints such workers might have been forced to intense production in order to provide high yields to meet demands of the imperial treasury. In such conditions individuals would share a common sense of subjugation and control from central authorities, as they were probably working for most of the year, secluded from other sectors of economic subsistence. Additionally operating regulations would have been severely strict as far as gold and silver extraction is concerned. Within a context of adversities defined by social control the smelters became gradually accustomed with innovative techniques and in particular hydraulic energy to maximise efficiency in an attempt to react against their degraded social status (Cresswell 1993; Cowen 2000).

Within the regional level small-scale undertakings such as seasonal mining and smelting of ores were supplementing farming and pastoral activities which provided basic subsistence. Such populations succeeded at being autonomous concerning subsistence strategies by engaging with stock breeding and agriculture. As demonstrated by the archaeological record decentralised production at Katafyto and Vathytopos, aimed to meet local demands, was integrated in the economic base of the local communities and was thus intertwined with their socio-cultural identity. Iron smelting represented part of their seasonal economic supplement and would have been pursued at their own consent. Their communities engaged in mining and metallurgy only seasonally and probably did so at times of the year when being disengaged from constraining subsistence activities primarily agriculture and pastoralism. In such situations the economy of rural communities becomes organised towards autonomy with little political control from a central authority.

These smaller groups would have operated in restricted networks but their agents would share local knowledge which allowed them to develop ideas of trust. Such insular societies often form secretive relationships and strengthen their lateral trust by family or clan affiliation bonds expressed through clandestine production of metalwork (Knapp 1998). The investigated Byzantine sites yielded evidence for small-scale bloomery whilst those where Ottoman presence has been confirmed seem to include silver refining as well. Such a picture might represent variable concerns towards production and different levels of control supported by tangible evidence from this study.

This duality of Ottoman organisation has been clearly demonstrated in the study area whereby production of metals at Makrychori and Angistro involved large expenditure as opposed to Nikisiani and Vrontou where production had been organised locally. It was to the state's interest to have some knowledge of and control over production in gold and silver producing regions if some broad-term financial planning would appear at least to the extent that state expenditure was likely to be high to fund military campaigns. Further the high inflation throughout Europe around 1550 caused by the influx of American silver (Rozen 1993) led to redoubled efforts to maximize the output of precious metals from the Empire's own natural resources.

7.8 Future work

As outlined in the above discussion the multitude of metalworking sites present in eastern Macedonia display a potential for future research to elaborate on the various issues on technology, organisation and political control. The presence of extensive archaeological deposits relating to diverse aspects of the production process and the evidence for great chronological depth represents a significant resource on the socio-economic and cultural histories as well as the history of technology of this region and its place in wider European history. However the breadth of evidence and complex implications of a fully integrated social and technological history to be explored can hardly be exhausted within the confines of a thesis. Yet this study has succeeded in demonstrating how metalworking practice offers a contrasting line of investigation to agriculture and land tenure to study clandestine versus state-controlled production and to challenge our accepted knowledge of how political control was exercised in these periods.

A significant issue which this thesis has wrestled with is that of chronology and future work should concentrate on matters of accurately dating such metalworking activity in order to establish an accurate chronological framework. In this way social transformation and associated technological change could be clearly understood within their temporal context and reveal contrasting regional strategies. Absolute dates from charcoal entrapped in furnace material would clearly define a chronology for the various sites. Radiocarbon dating on charcoal or the application of thermoluminescene on fired clay lining would appear suitable for dating smelting activity. Further scientific analysis on metal refining residues could resolve issues of gold and silver extraction in Macedonia of the Byzantine-Ottoman periods. Future studies might for instance resolve whether lead in Makrychori slag was added as some kind of collector for precious metals or if it was part of the ore, an issue that has not been established. What is needed for the future is to meticulously excavate the everyday spaces of Byzantine miners and smelters and then contrast this with agricultural communities for which more information is available. By understanding the materialisation of such entanglements, coherent conclusions could be drawn concerning the social and technical intertwined dimensions of life in regional rural communities. Such a task might be attempted as a localised regional approach by firstly establishing chronology of metalworking sites and then a targeting on specific sites that display various scales of organisation and different processes.

One of the implications of this study has been to promote awareness amongst both the public and professionals concerning the importance of metallurgical landscapes by demonstrating their variety and archaeological significance through basic field recording. Their rapid deterioration due to significant disturbance for road building materials and general development calls for at least a basic strategic plan to assure their recording and protection. This study has demonstrated how limited funding is needed since simple reconnaissance techniques and a few test pits would suffice for the creation of an accurate record of the evidence. Sites on Cyprus that constitute landscapes of past metal extraction have now become scheduled monuments protected by state legislation (Given *et al* 2002; Given and Knapp 2003). English Heritage has also scheduled numerous early modern extraction and working sites as part of its Monument's Protection Plan (MPP). Such initiatives resulted from the realization that industrial landscapes constitute monuments of multiple dimensions worthy of preservation due to their historic, archaeological and scientific value. Strategic plans incorporating industrial sites in protection programmes are only lately gaining credibility mainly because technology is not been seen truly social. However such landscapes have been proven suitable for exposing the intersections between human knowledge, skill, gestures and broader social phenomena such as world views, value judgments and communal beliefs and therefore deserve imminent protection. So far, burdened by a wealth of archaeological resources and no doubt underfunded the Hellenic Ministry of Culture was not keen to recognise the archaeological value of these sites. It is hoped that this thesis may act to initiate such investigations and to recognise the wider value of 'technological' remains.

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APPENDIX I

Sample preparation for optical microscopy

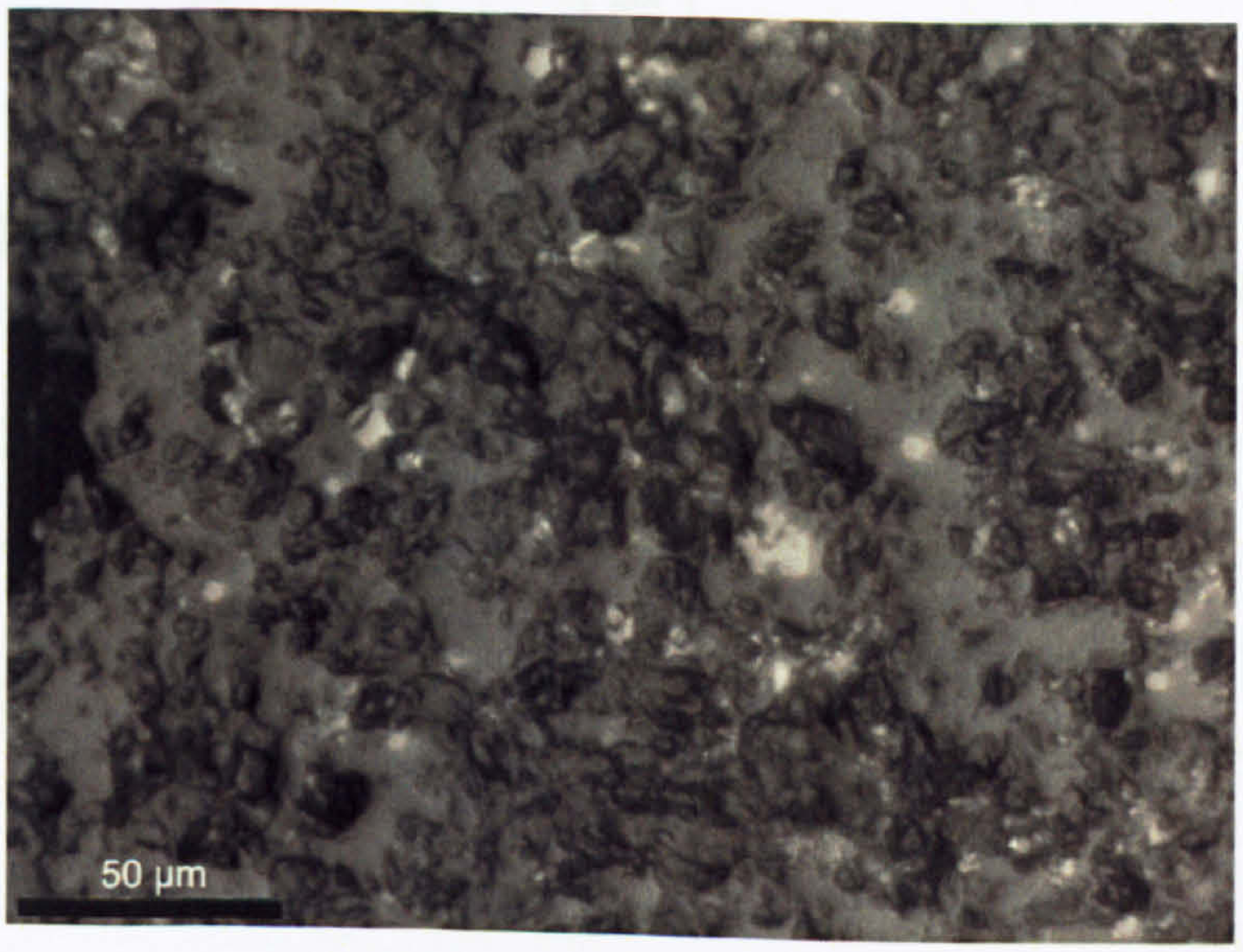
Samples were acquired from slag pieces by careful sawing on the vice. Sawing was attempted in such a way to avoid roughness of the exposed surfaces. After cutting the small specimens were mounted for examination under the metallographic microscope. Mounting was completed using Buhler Epoxy resin and hardener in a ratio of 1:5 and all samples were left for 24 hours to settle. When settling was complete the mounts were removed from the moulds. Grinding was undertaken using grinding papers in sequence of grit numbers. P220, P320, P400, P600 and a finish with fine sorted emery powder. Polishing followed on rotating polishing wheels with lapping fluid on cloths with diamond particles in sequence of 15 μm, 6 μm and 1 μm. After each polishing stage the sample was introduced to a bath of soap+ethanol+H_2O in the soni-cleaner and was washed with teepol and water before proceeding to the next stage.

Sample No. MAK01

Macroscopic features

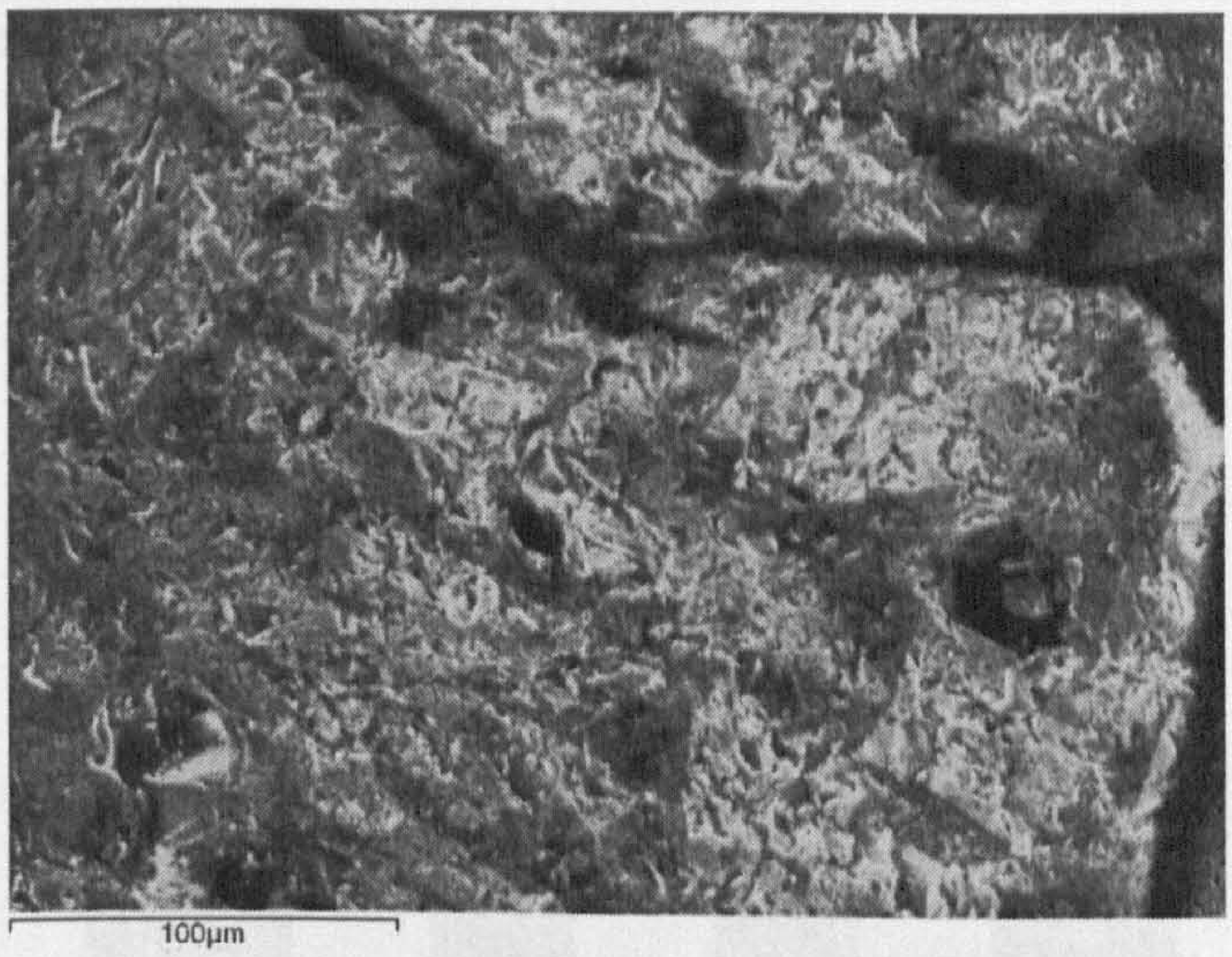
Size	4.50 cm
Weight	30.00 g
Colour	dark grey/black
Texture	spongy
Porosity	high
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



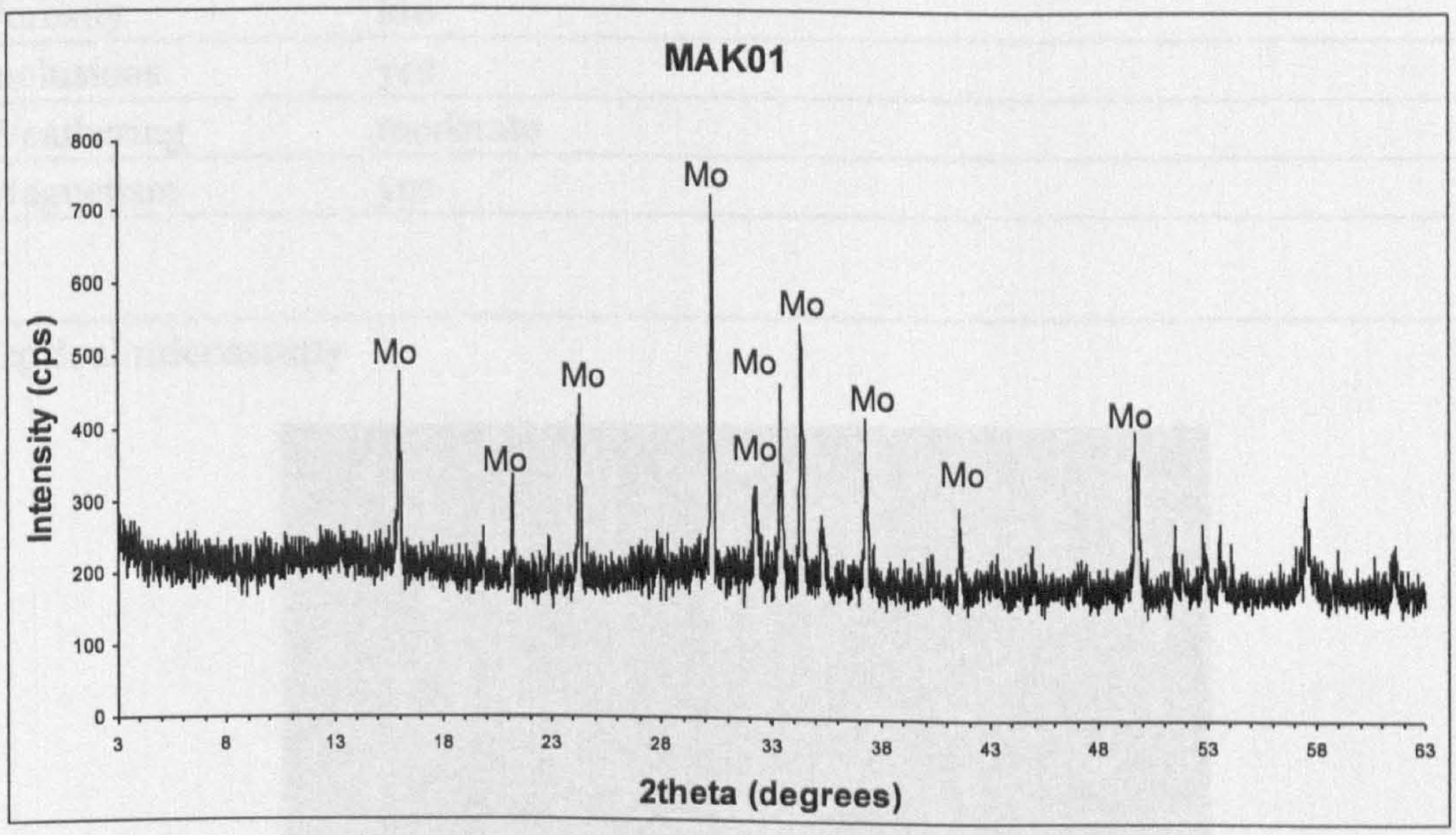
Vesicular matrix with glassy regions/Occasional metallic prills (x 400)

SEM image



Amorphous material of vesicular texture forming the matrix is dominant with frequent laths of fayalite in a slightly darker grey shade. Occasional round globules of darker colour appear as distinct glassy phases while no metallic prills are present.

XRD



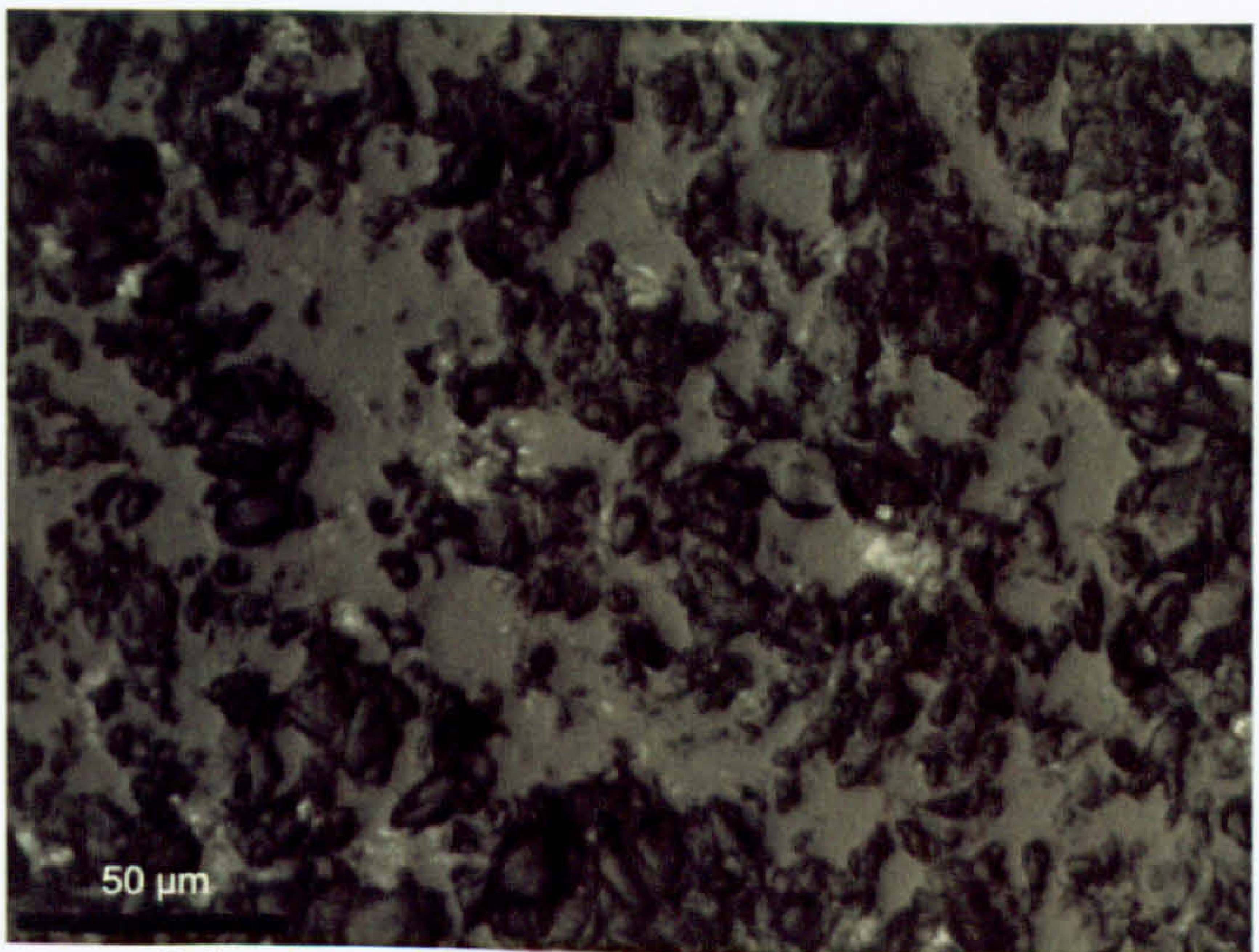
Intensity curve of sample:
Mo: Monticellite-$CaMgSiO_4$

Sample No. MAK02

Macroscopic features

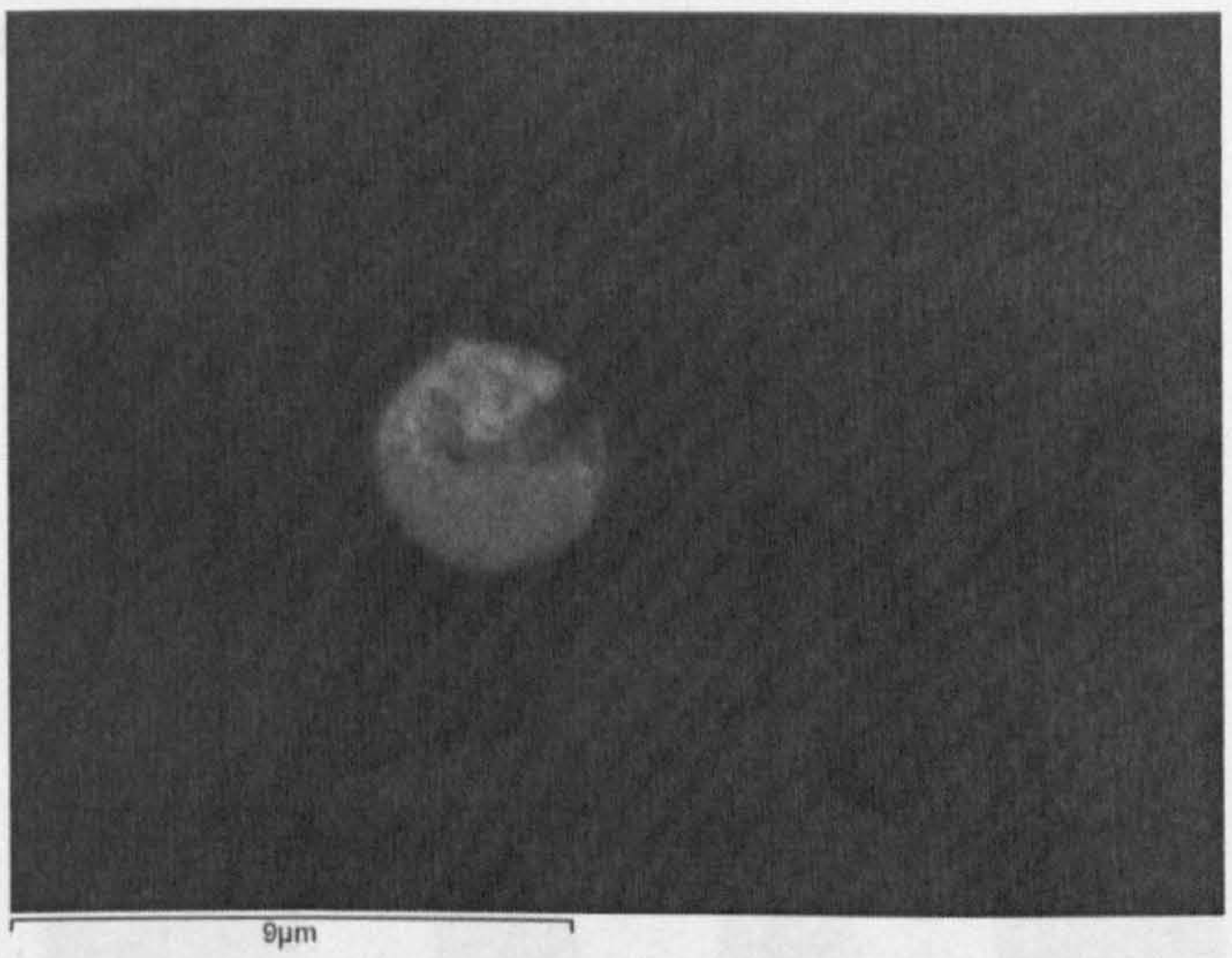
Size	2.50 cm
Weight	16.50 g
Colour	dark grey/black
Texture	ropey (conchoidal)
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



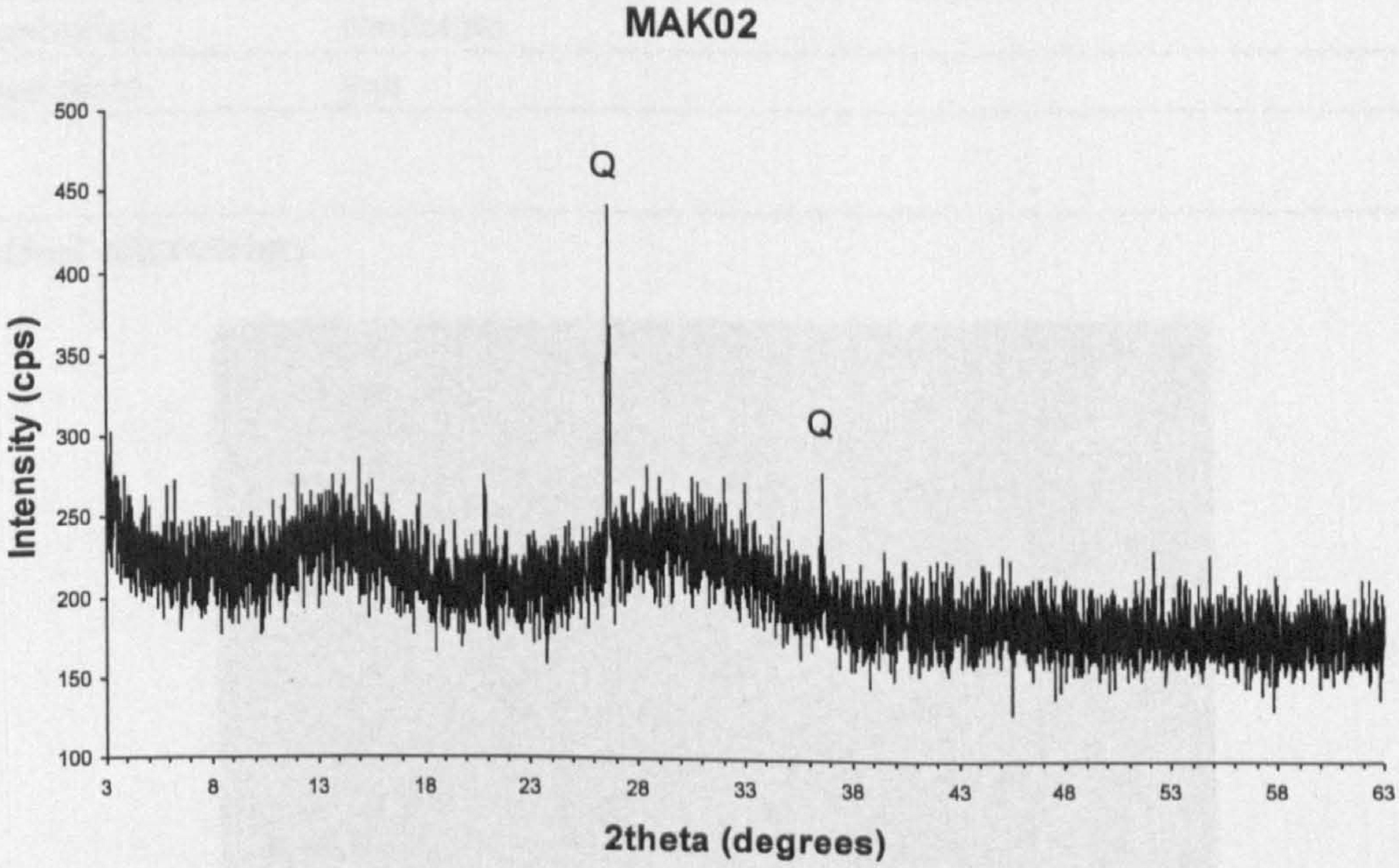
Glassy matrix/Traces of decomposed wüstite dendrites/Occasional clusters of metallic prills (x 400)

SEM image



The micrograph shows a dark glassy phase with no diagnostic minerals present. The spherical bright inclusion is an iron prill. Such microstructural characteristics are not typical for bloomery slag but rather point to late industrial metallurgical residues.

XRD



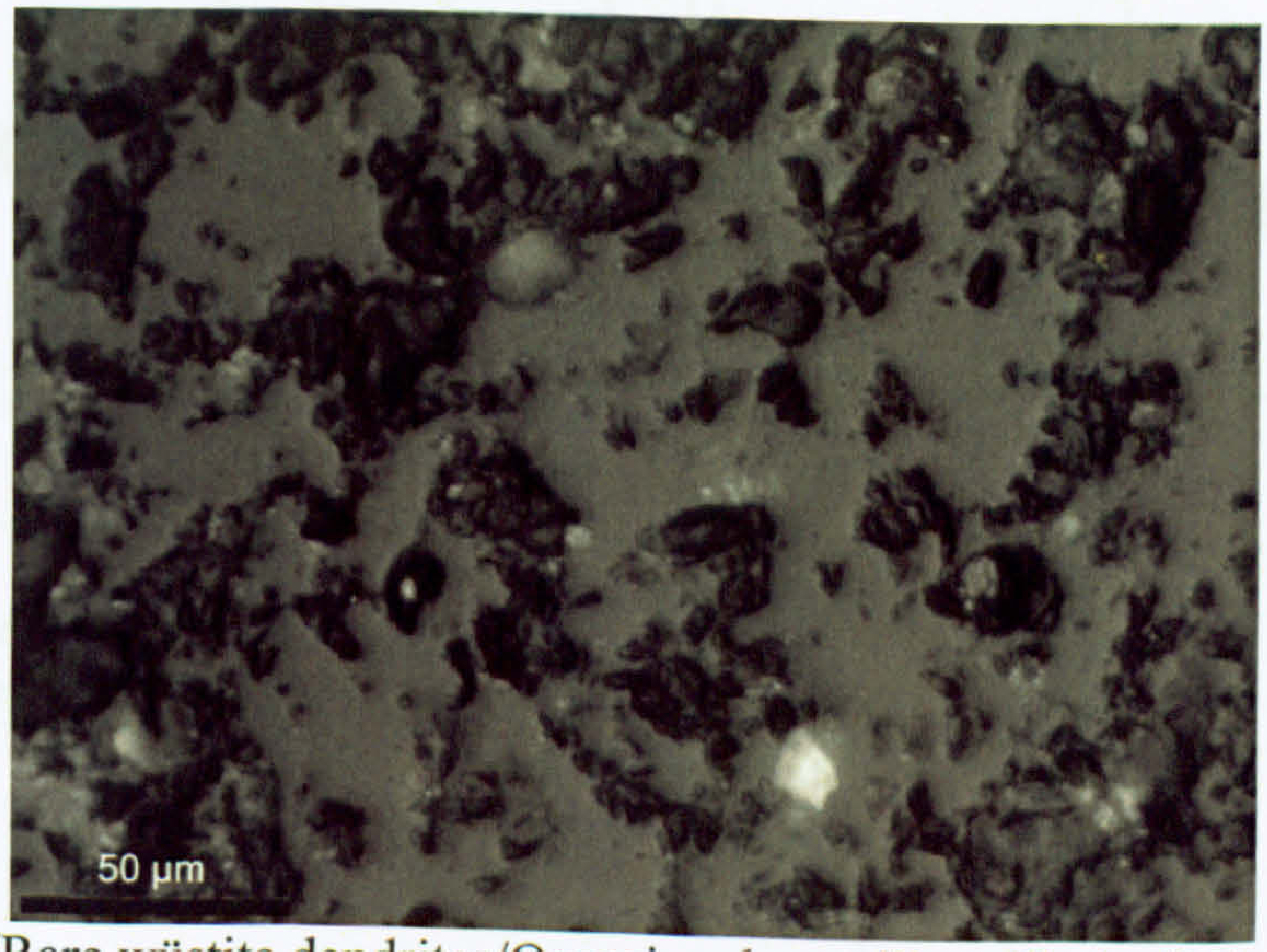
Intensity curve of sample:
Qz: Quartz-SiO_2

Sample No. MAK03

Macroscopic features

Size	2.50 cm
Weight	16.50 g
Colour	dark grey/black
Texture	ropey (conchoidal)
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy

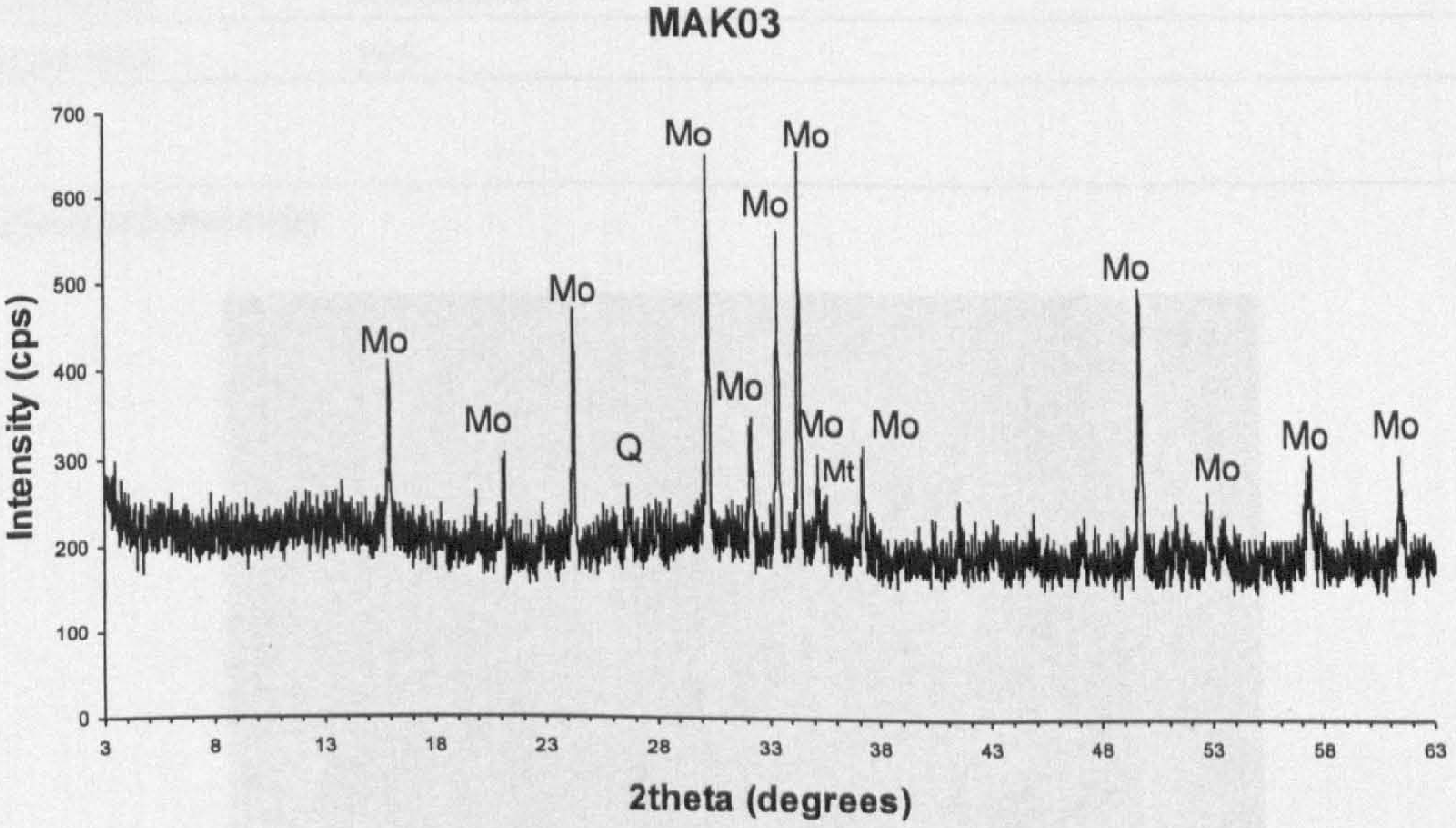


Glassy matrix/Rare wüstite dendrites/Occasional metallic prills (x 400)

SEM image

The dark matrix is glassy in texture and highly siliceous in composition. A dark spherical inclusion in the centre is surrounded by small bright spots which represent metallic inclusions.

XRD



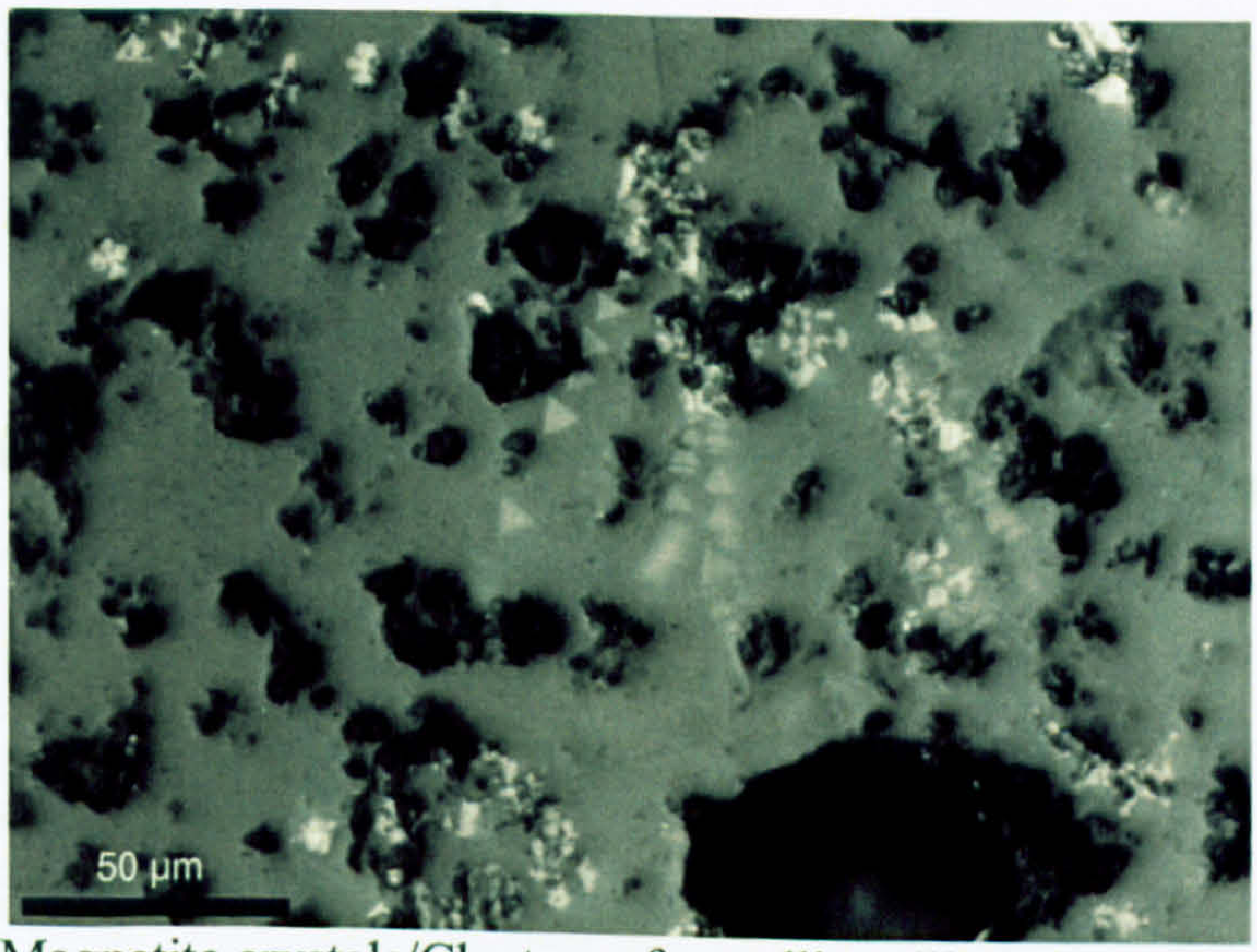
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Mo: Monticellite-$CaMgSiO_4$, Qz: Quartz-SiO_2

Sample No. MAK04

Macroscopic features

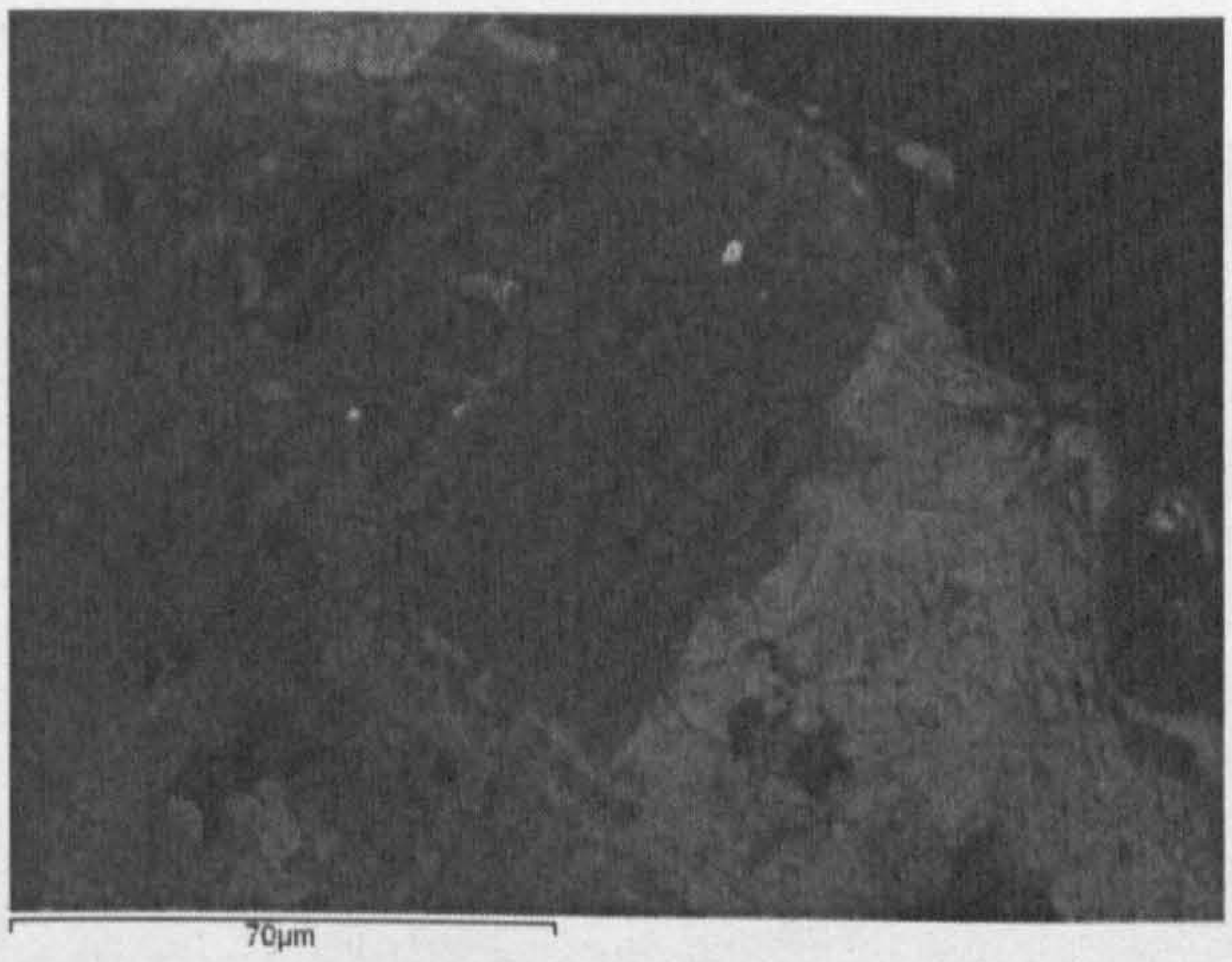
Size	2.50 cm
Weight	16.50 g
Colour	dark grey/black
Texture	ropey (conchoidal)
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



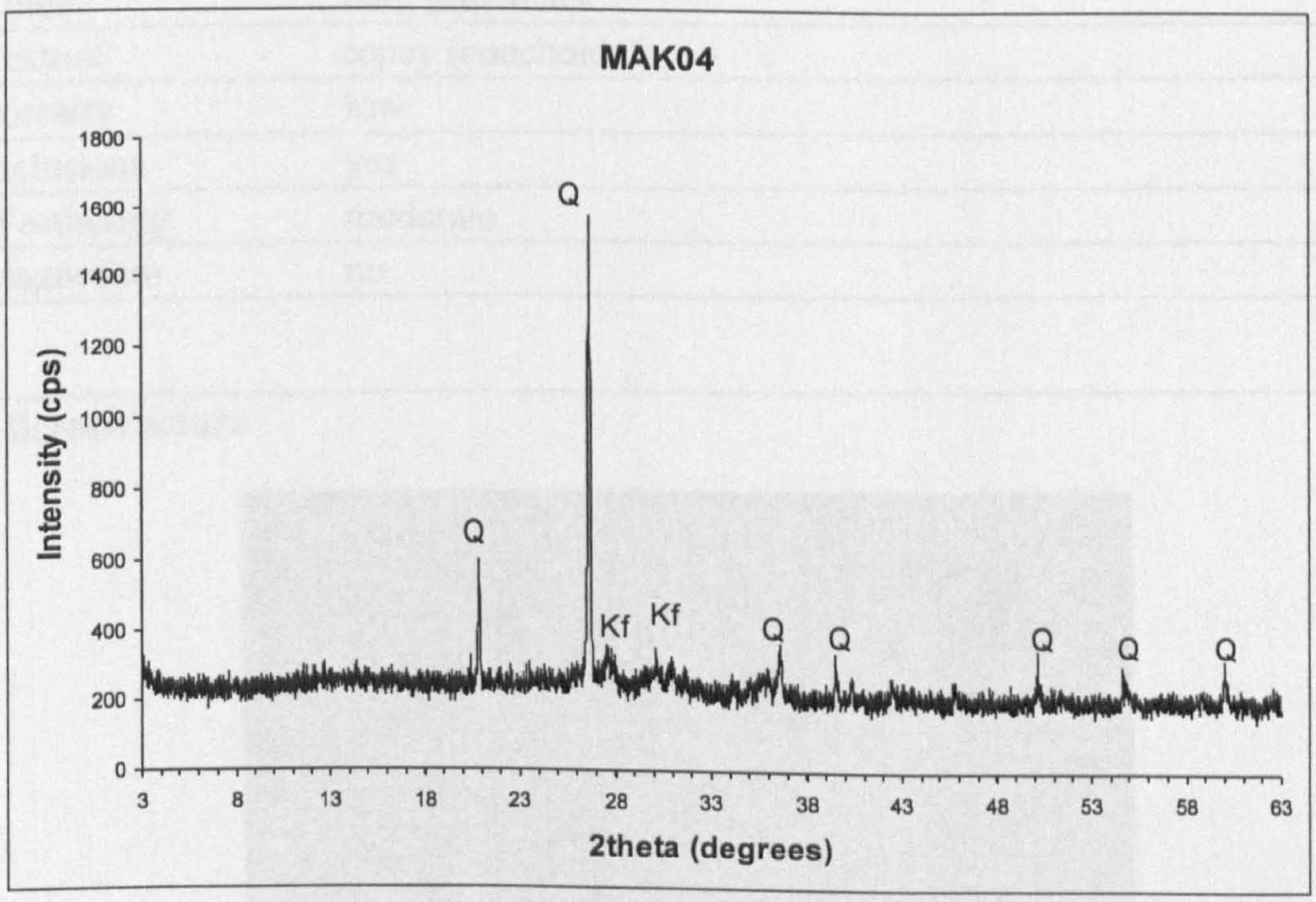
Glassy matrix/Magnetite crystals/Clusters of metallic prills (x 400)

SEM image



Crystalline material and siliceous matrix form distinct phases while small prills of iron could be found.

XRD



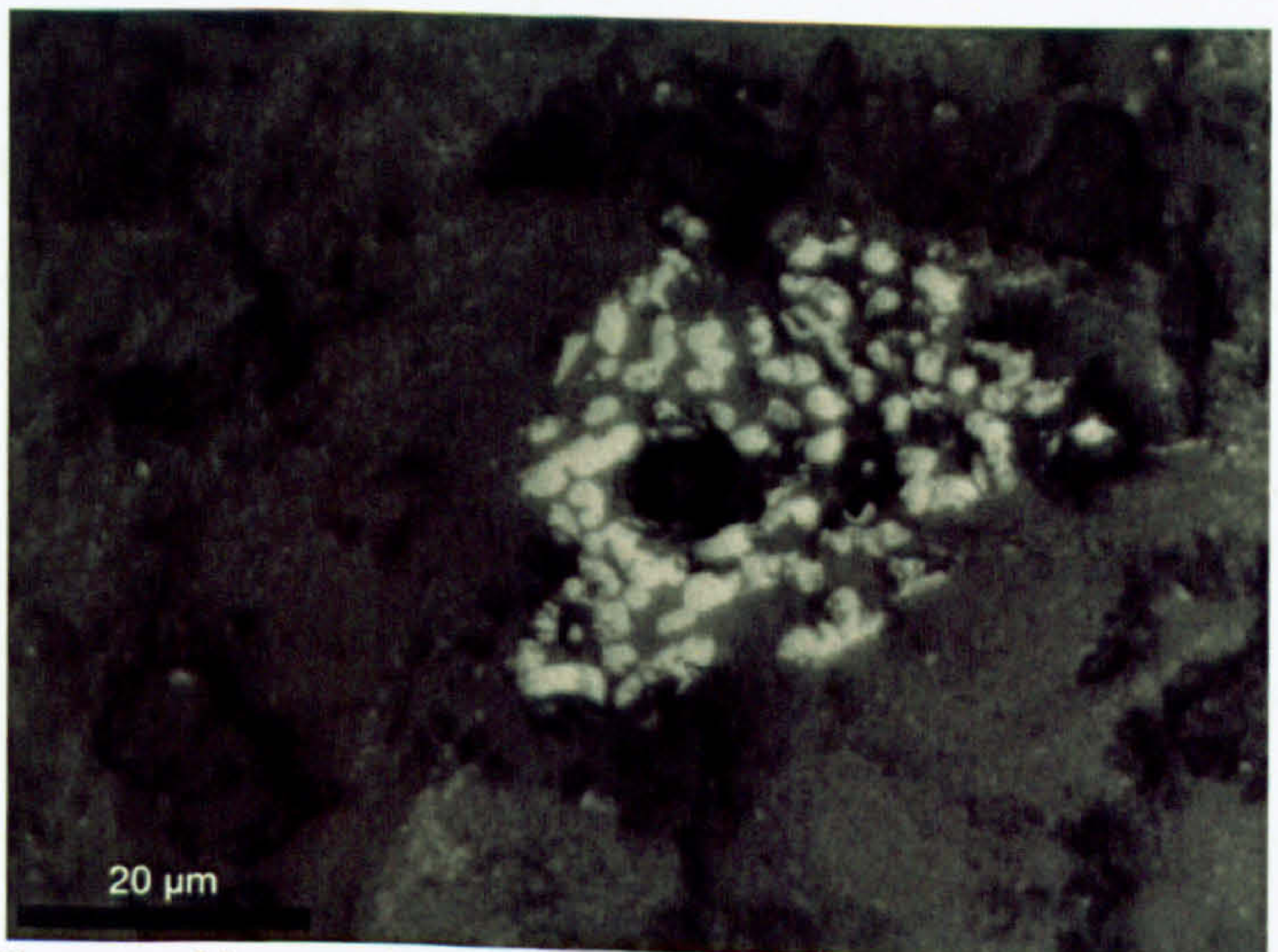
Intensity curve of sample:
Qz: Quartz-SiO_2, Kf: Alkali feldspar-$KAlSi_3O_8$

Sample No. MAK05

Macroscopic features

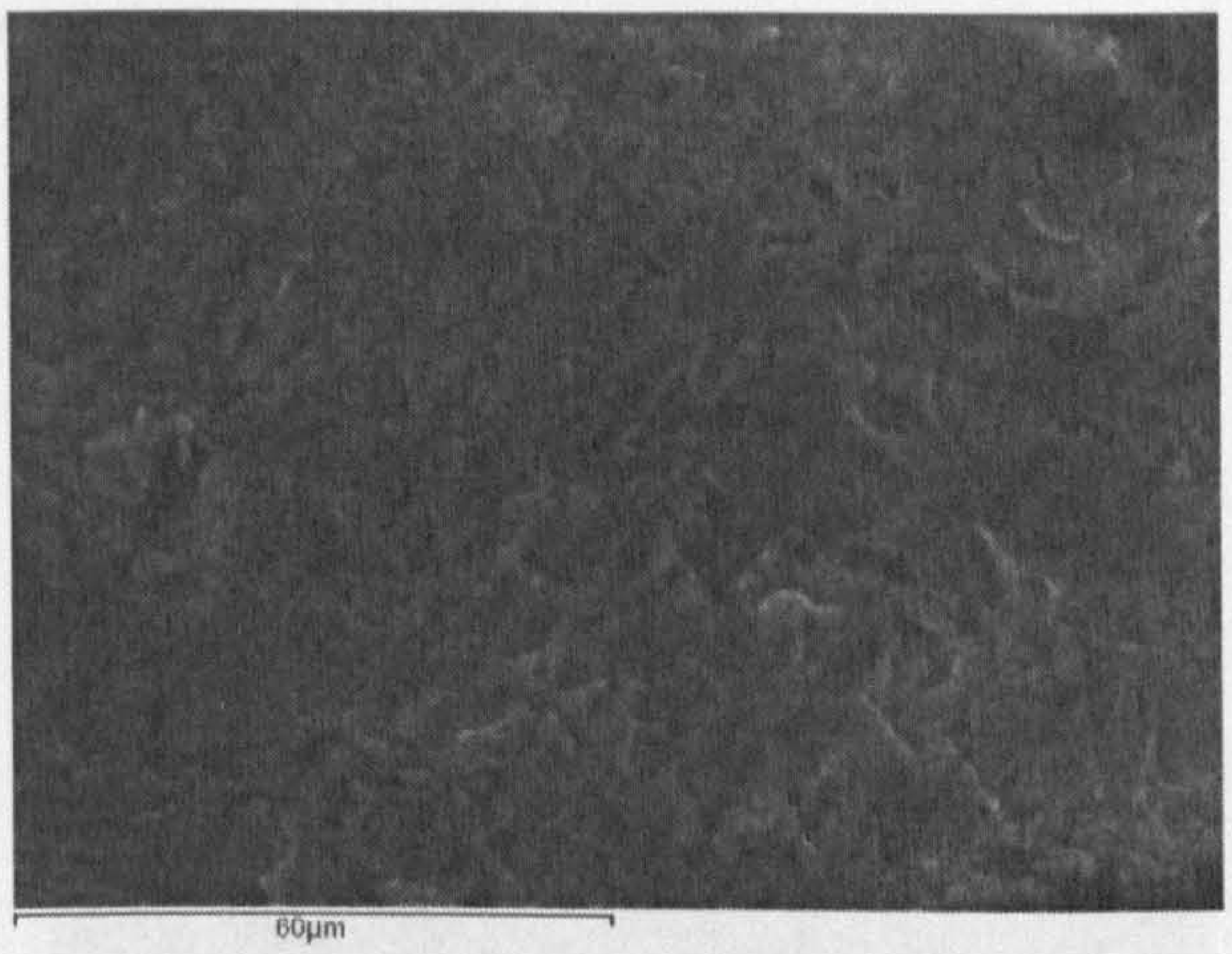
Size	2.50 cm
Weight	16.50 g
Colour	dark grey/black
Texture	ropey (conchoidal)
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	no

Microstructure



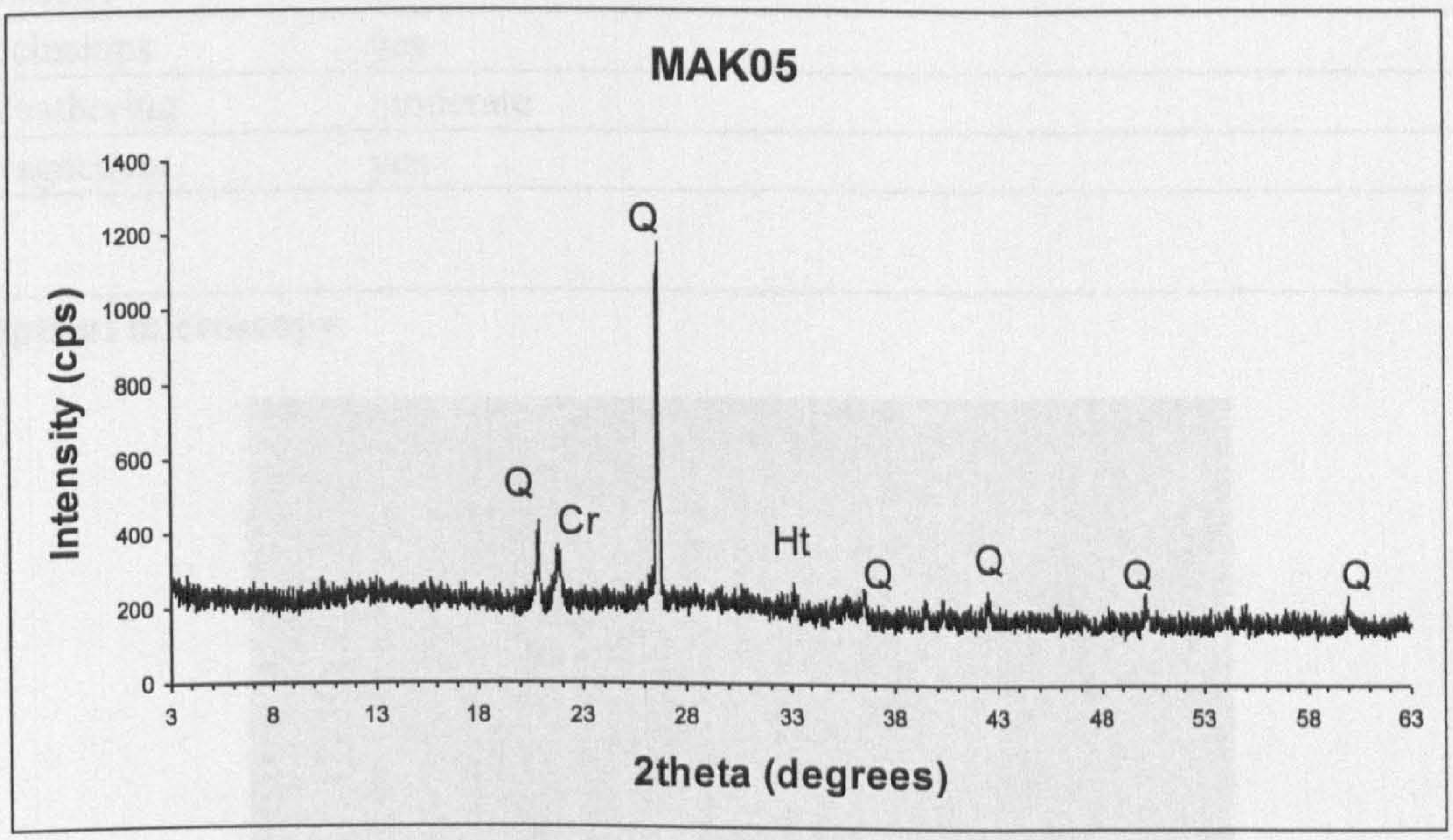
Glassy matrix/Cluster of iron oxide inclusions (x 1000)

SEM



A glassy matrix dominates the whole extent of the micrograph. No mineral phases or any metallic prills are present. Such a microstructure is not representative of a slag but rather a highly fired ceramic and could be part of furnace lining material.

XRD



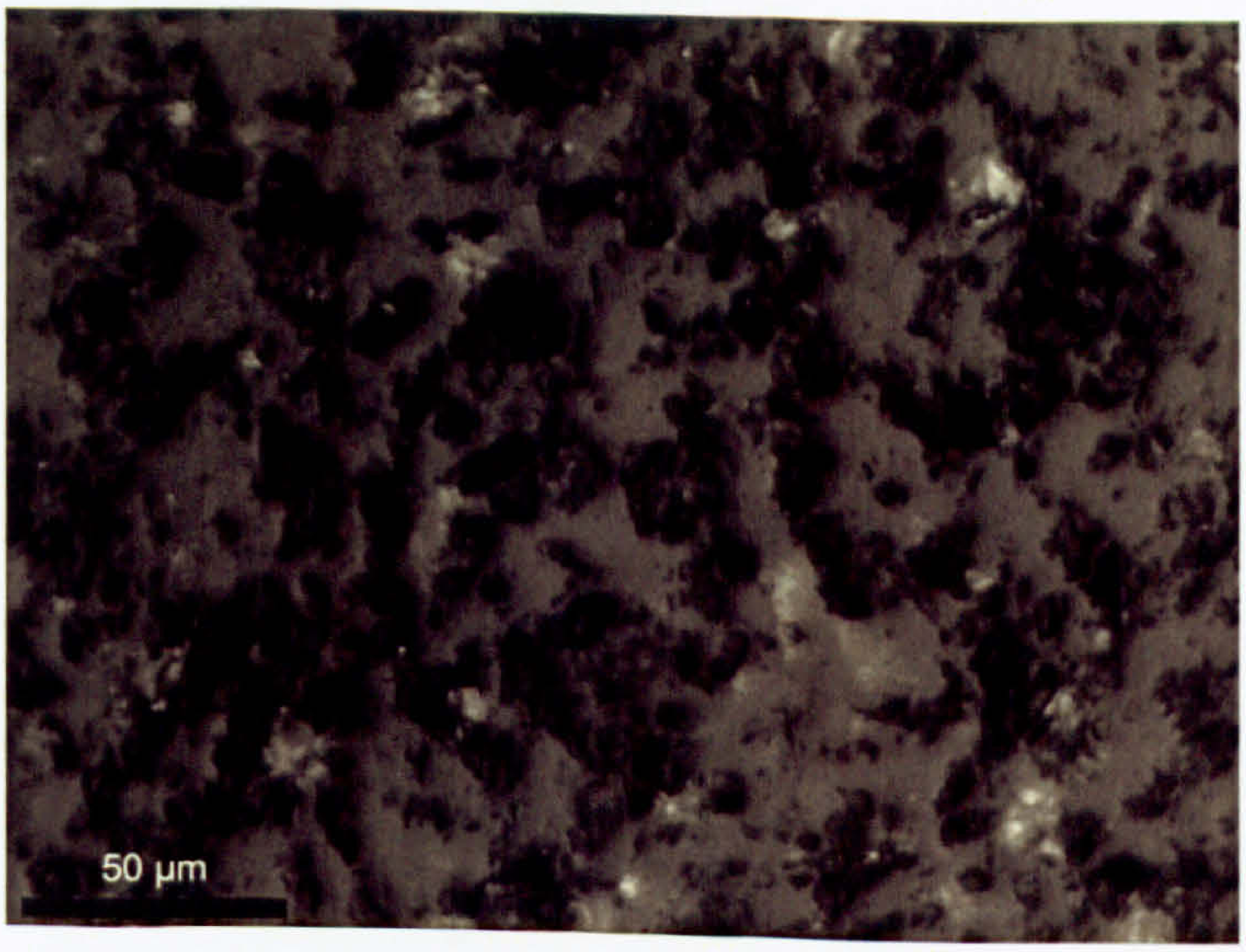
Intensity curve of sample:
Ht: Hematite-Fe_2O_3, Qz: Quartz-SiO_2, Cr: Cristobalite-SiO_2

Sample No. MAK06

Macroscopic features

Size	2.50 cm
Weight	16.50 g
Colour	dark grey/black
Texture	ropey (conchoidal)
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy

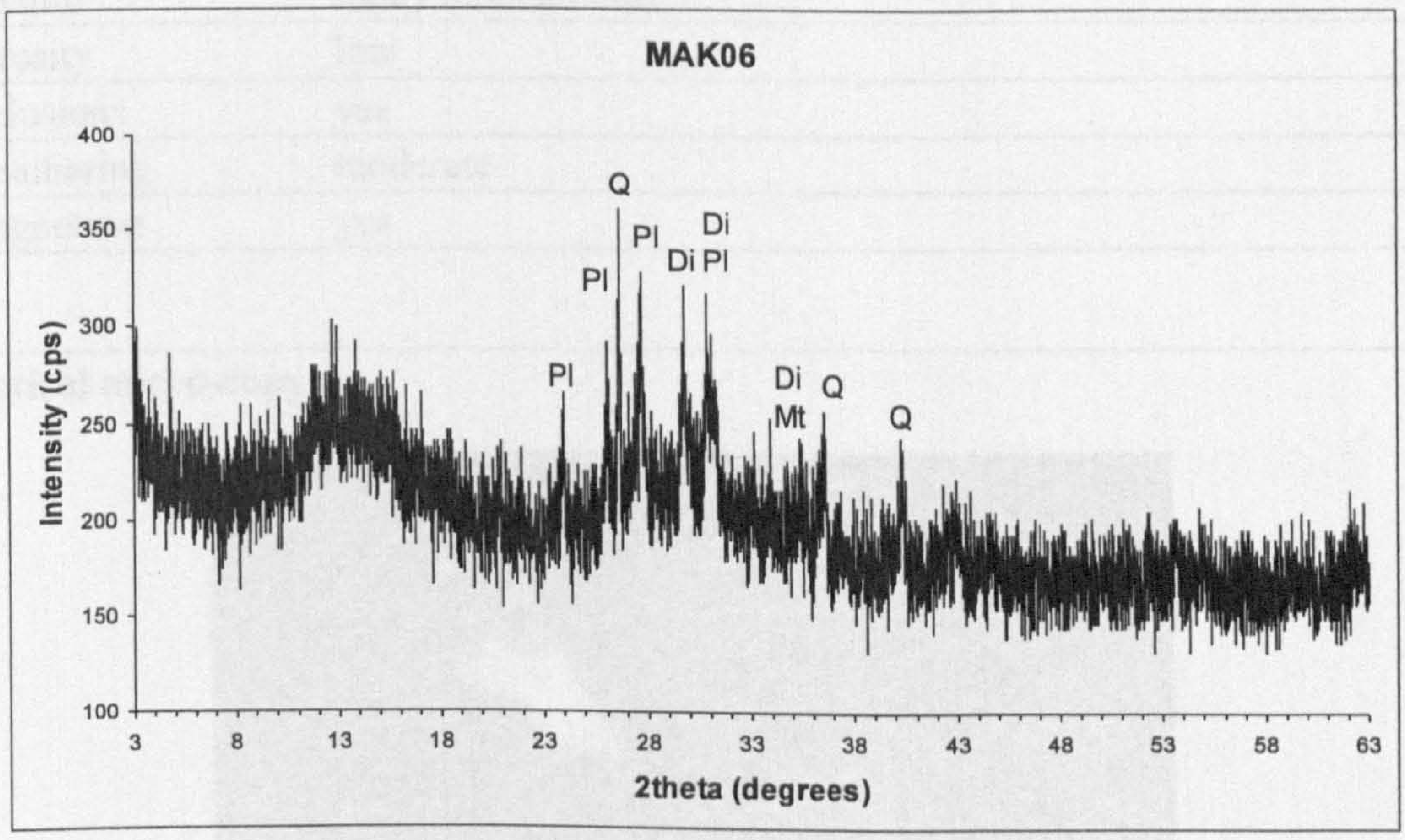


Glassy matrix/Frequent metallic prills (x 400)

SEM image

The matrix is highly siliceous and glassy in texture with only minor distinctive phases. At the centre an amorphous bright inclusion which appears as a metallic inclusion.

XRD



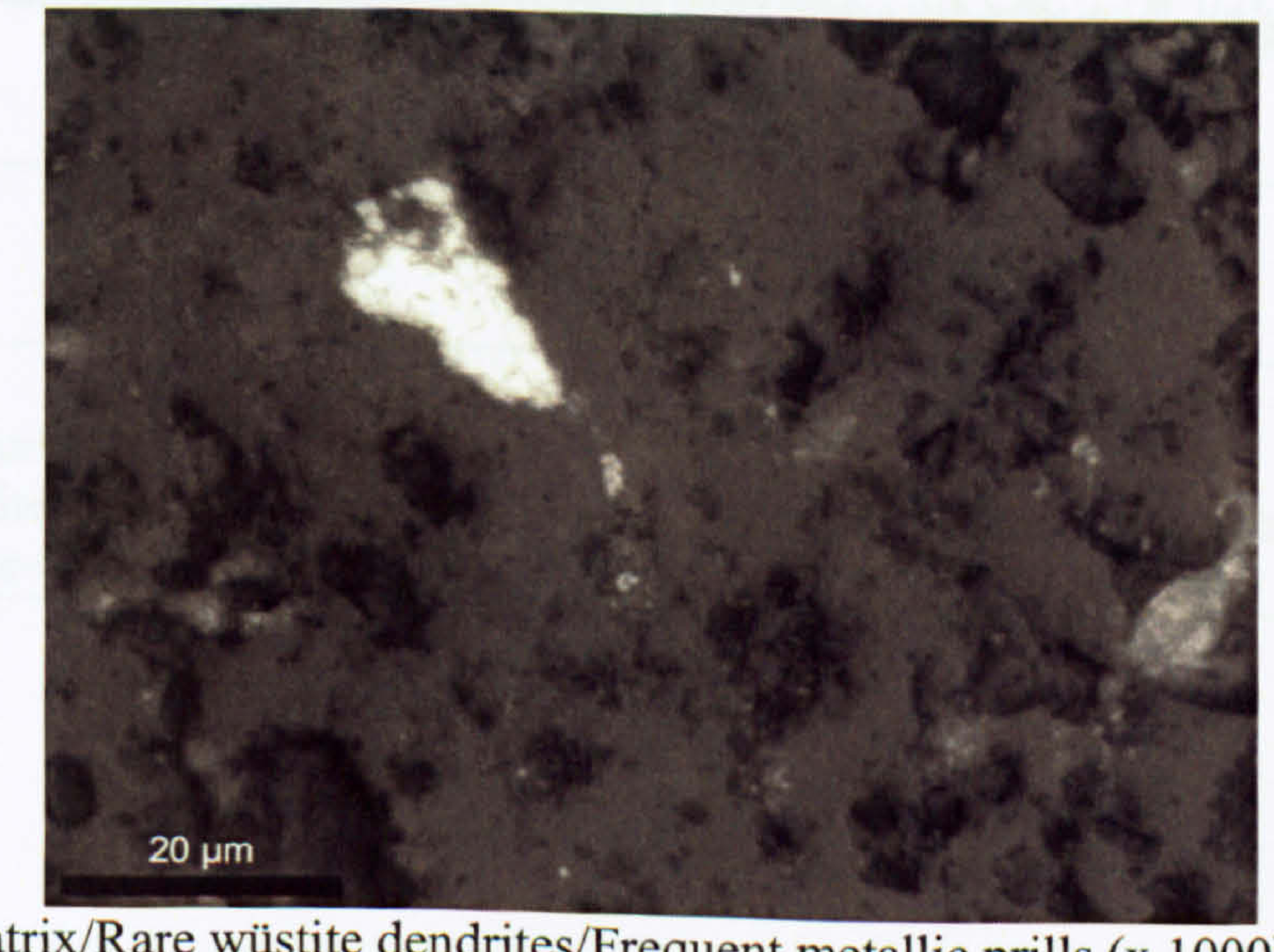
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Qz: Quartz-SiO_2, Pl: Plagioclase-$NaAlSi_3O_8$, Di: Diopside-$Mg_{0.6}Fe_{0.2}Al_{0.2})Ca(Si_{1.5}Al_{0.5})O_6$,

Sample No. MAK07

Macroscopic features

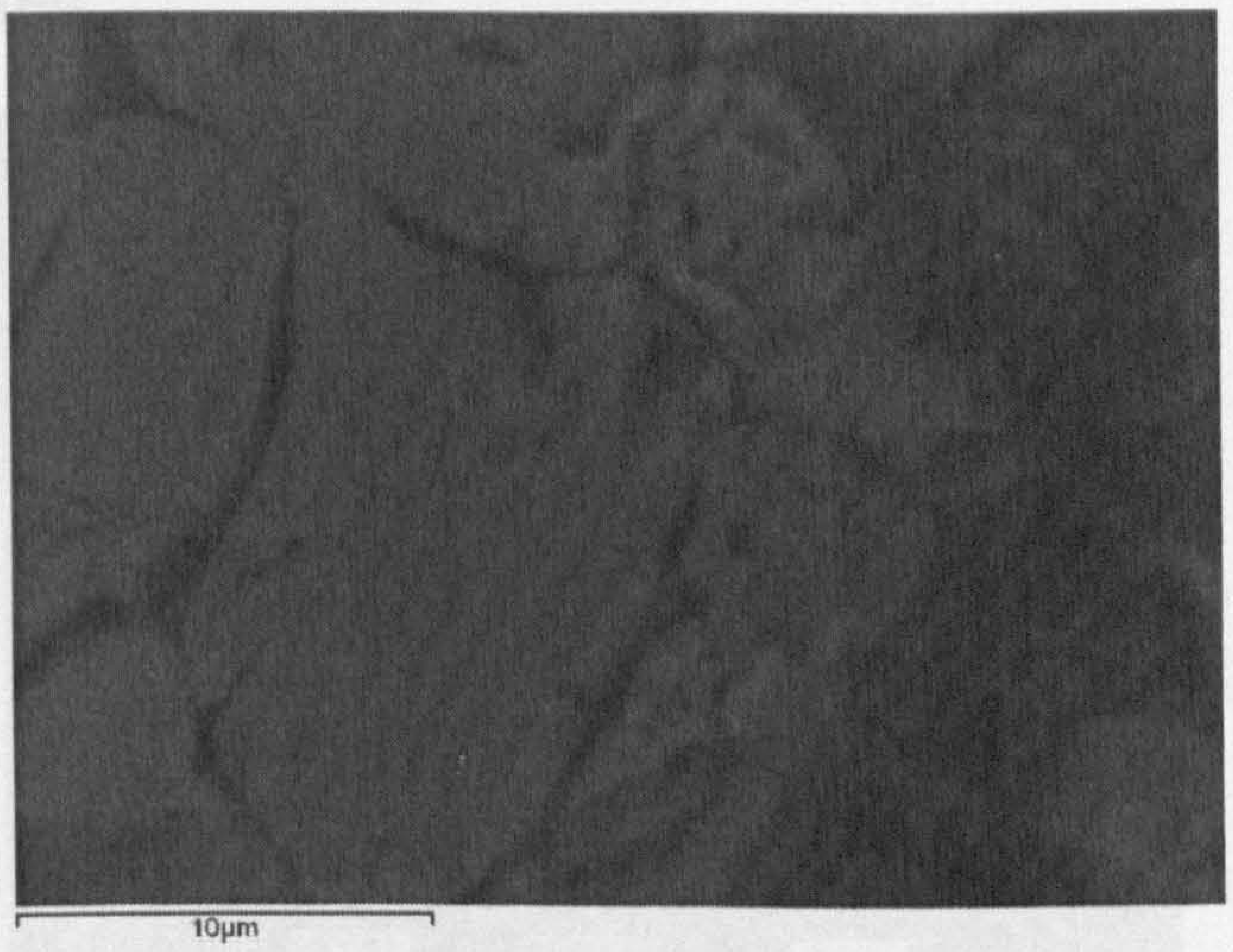
Size	2.50 cm
Weight	16.50 g
Colour	dark grey/black
Texture	ropey (conchoidal)
Porosity	low
Inclusions	yes
Weighting	moderate
Magnetism	yes

Optical microscopy



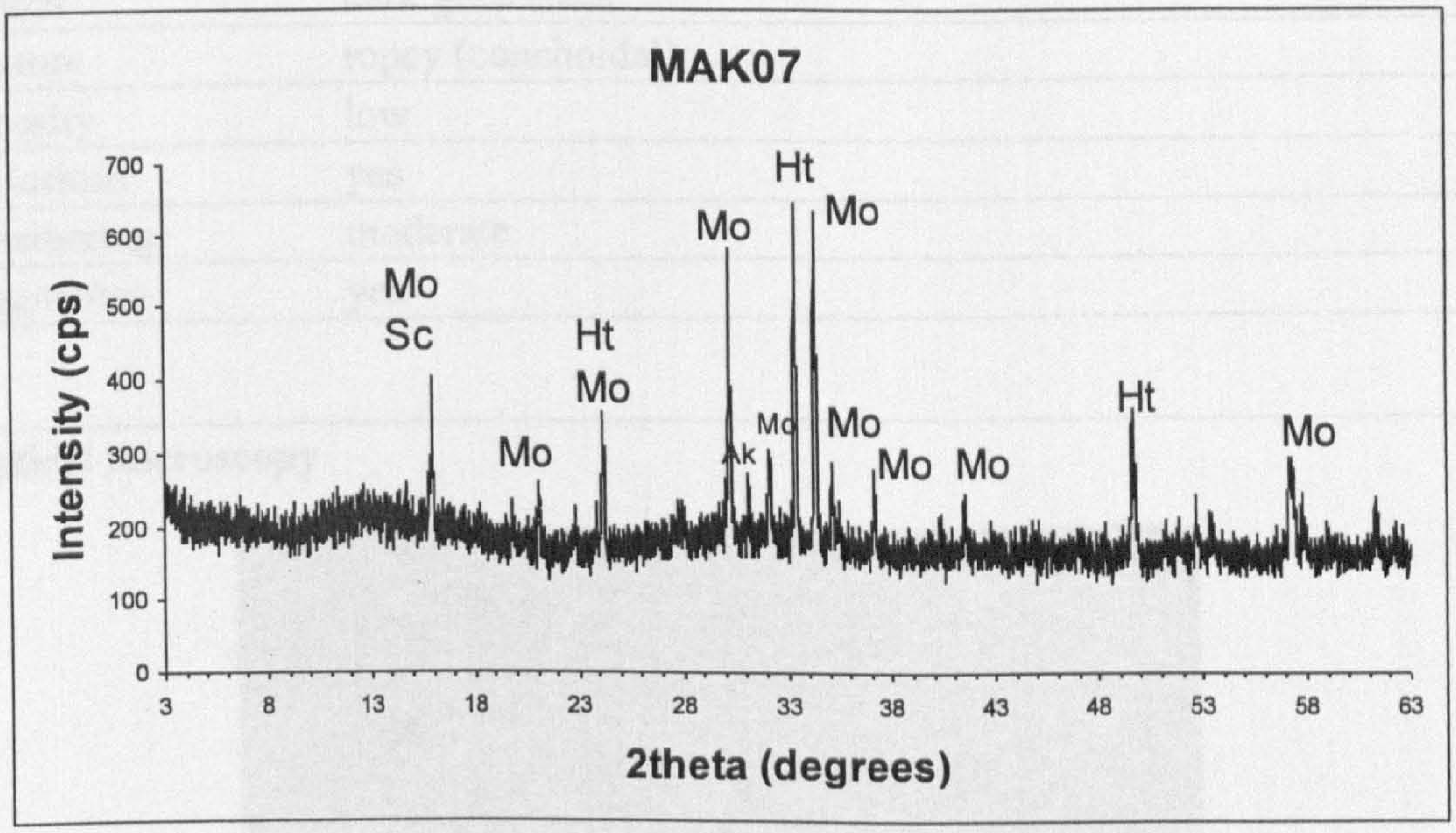
Vesicular matrix/Rare wüstite dendrites/Frequent metallic prills (x 1000)

SEM image



A glassy structure is evident with no crystalline material or any prills of metals.

XRD



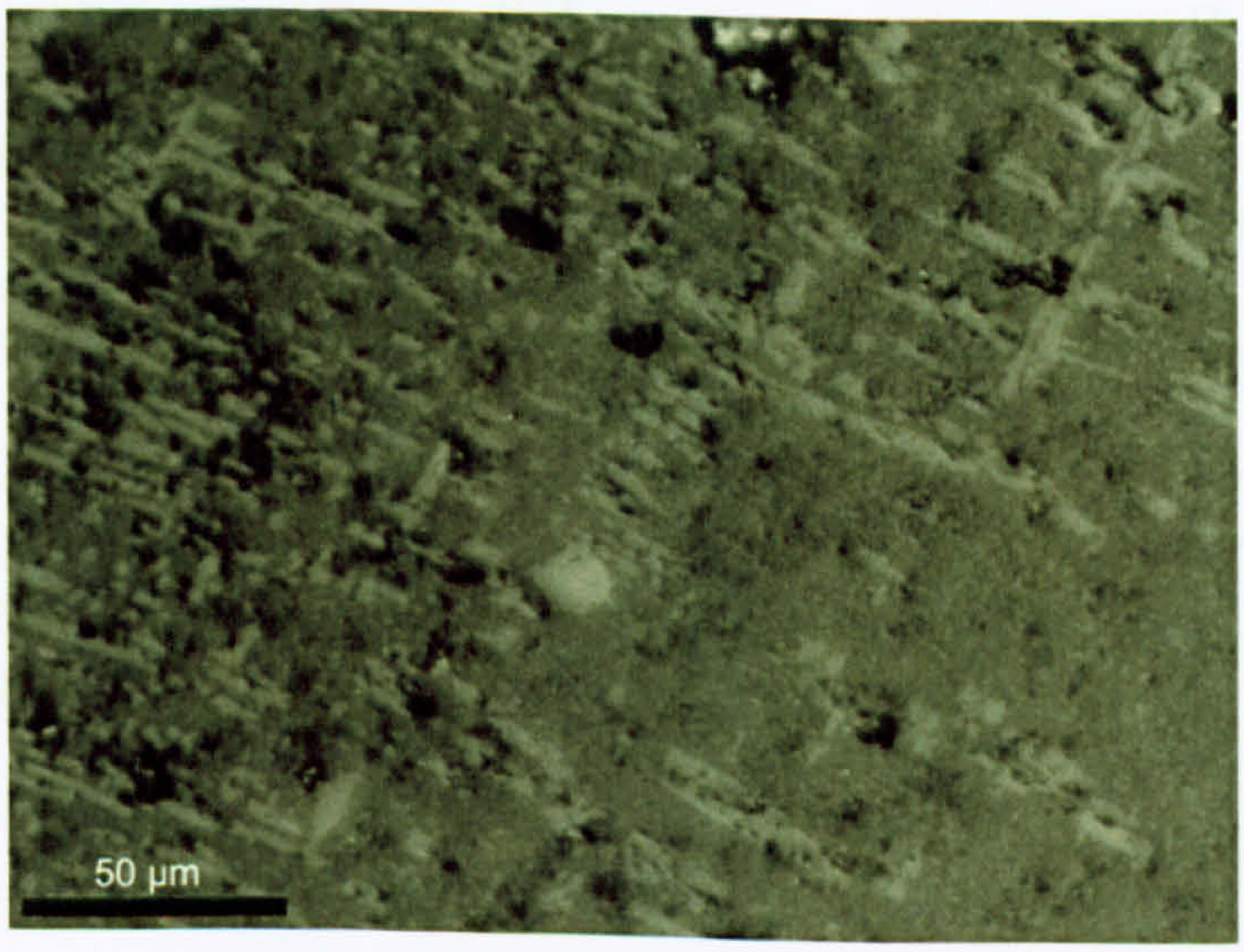
Intensity curve of sample:
Ht: Hematite-Fe_2O_3, Sc: Scorodite-$FeAsO_4(H_2O)_2$, Mo: Monticellite-$CaMgSiO_4$, Ak: Akermanite-$Ca_2Mg(Si_2O_7)$

Sample No. MAK08

Macroscopic features

Size	2.50 cm
Weight	16.50 g
Colour	dark grey/black
Texture	ropey (conchoidal)
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy

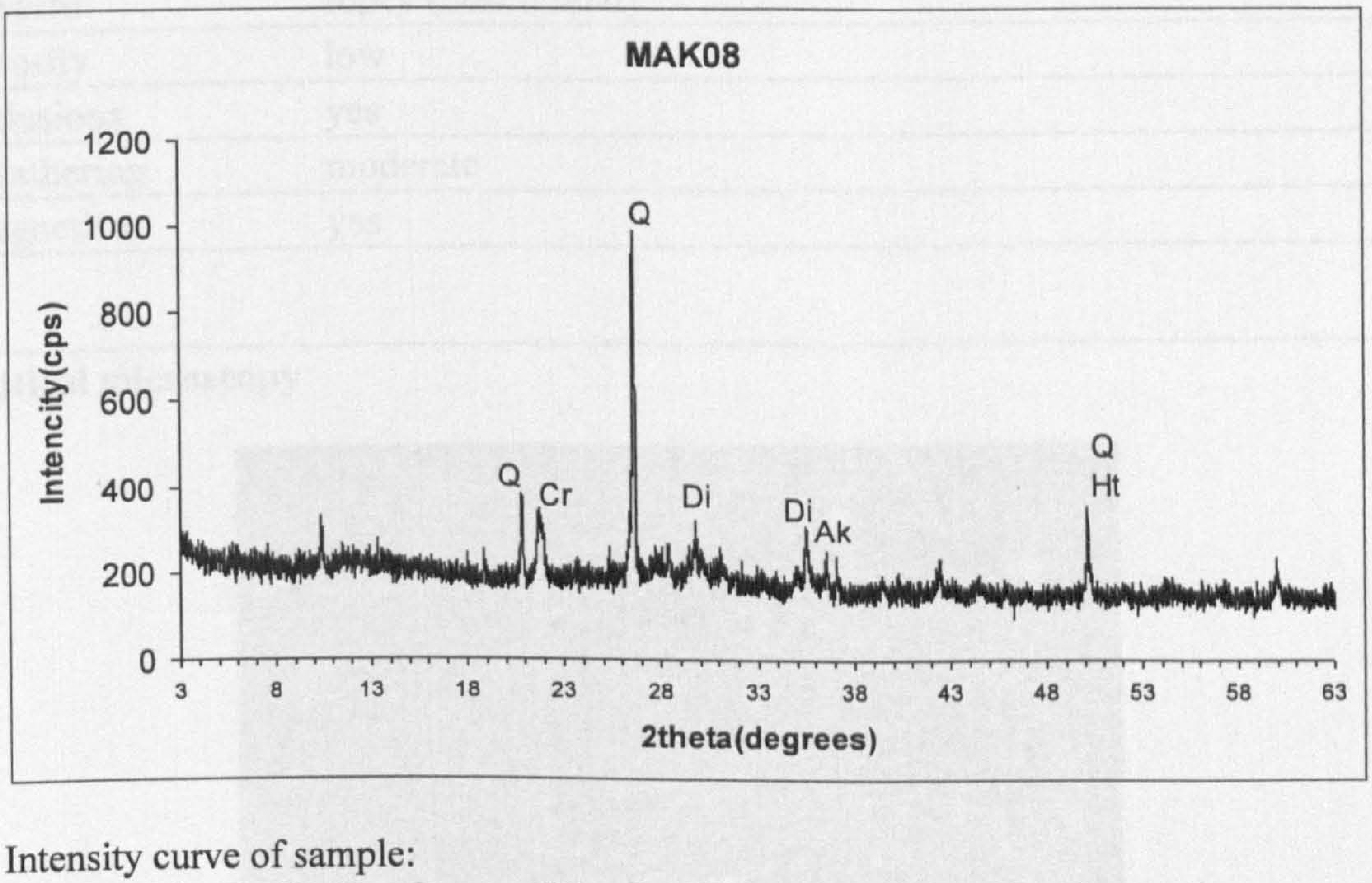


Vesicular matrix/Fayalite laths/Rare metallic prills (x 1000)

SEM image

Laths of fayalite with occasional wüstite are the major phases in addition to interstitial glass. The brighter white spots are metallic prills.

XRD



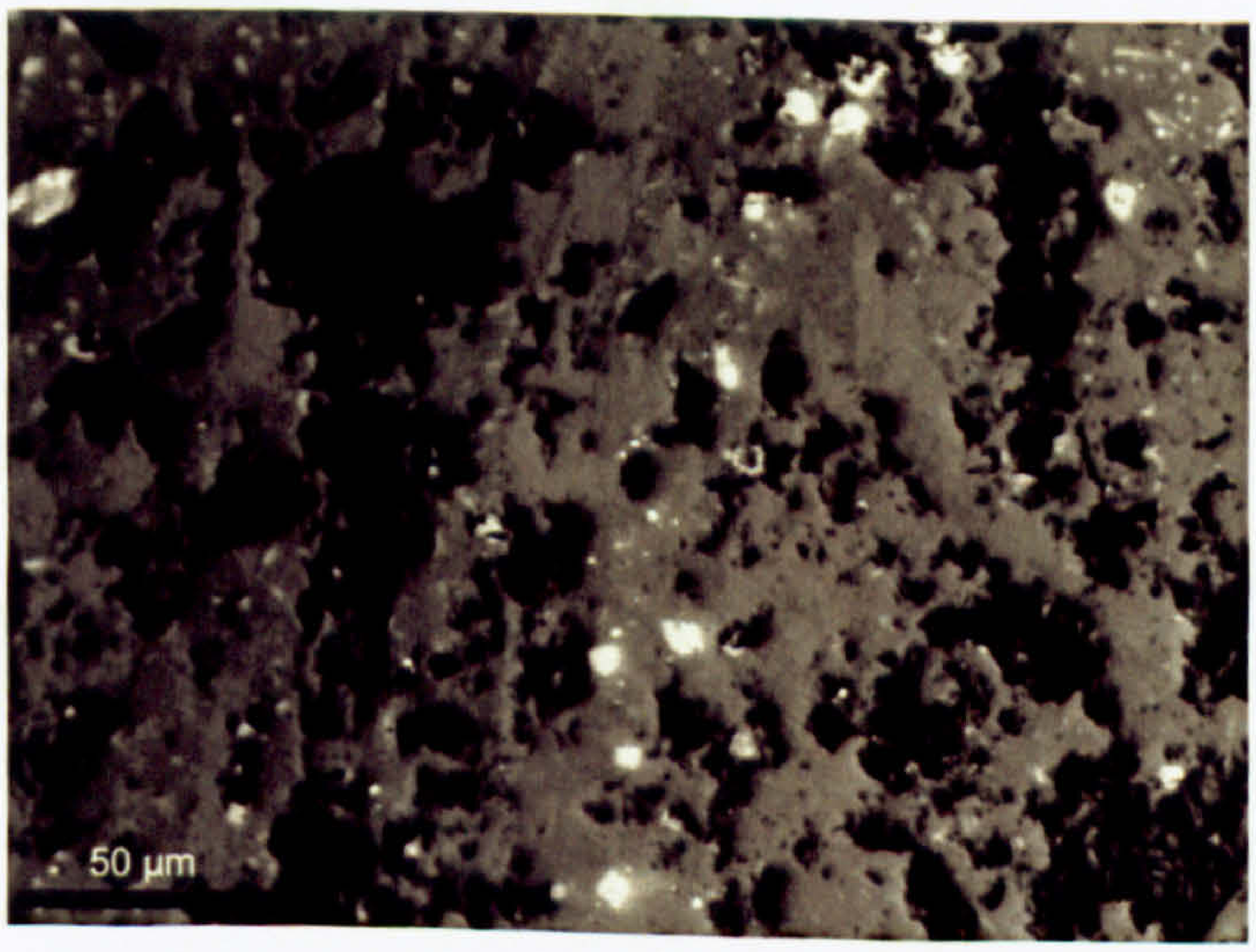
Intensity curve of sample:
Ht: Hematite-Fe_2O_3, Qz: Quartz-SiO_2, Cr: Cristobalite-SiO_2, Ak: Akermanite-$Ca_2Mg(Si_2O_7)$, Di: Diopside-$Mg_{0.6}Fe_{0.2}Al_{0.2})Ca(Si_{1.5}Al_{0.5})O_6$

Sample No. MAK09

Macroscopic features

Size	2.50 cm
Weight	16.50 g
Colour	dark grey/black
Texture	ropey (conchoidal)
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy

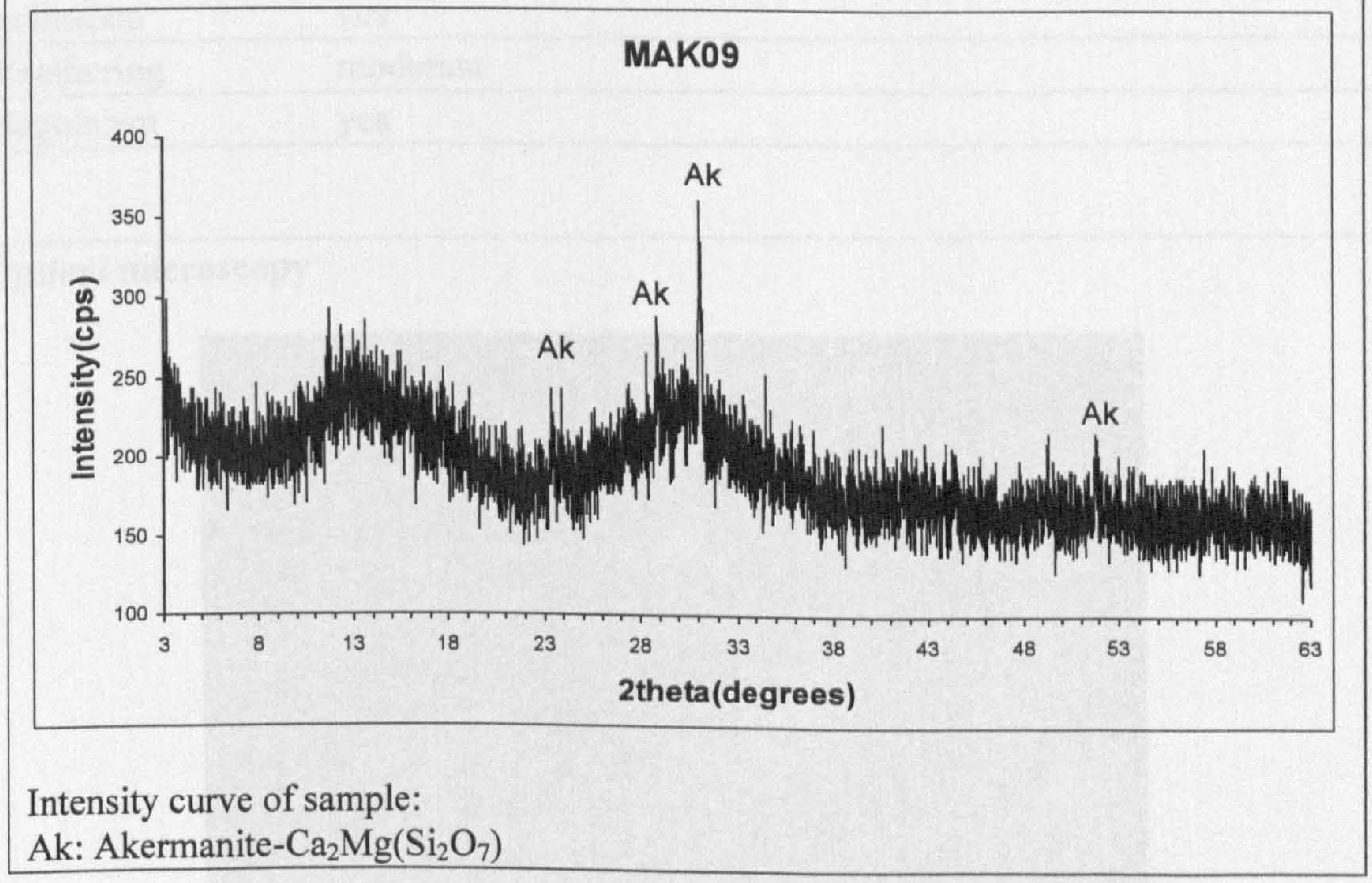


Glassy matrix/Frequent metallic prills/Occasional fayalite (x 400)

SEM image

The structure is predominantly glassy with some darker regions which of fayalitic composition.

XRD



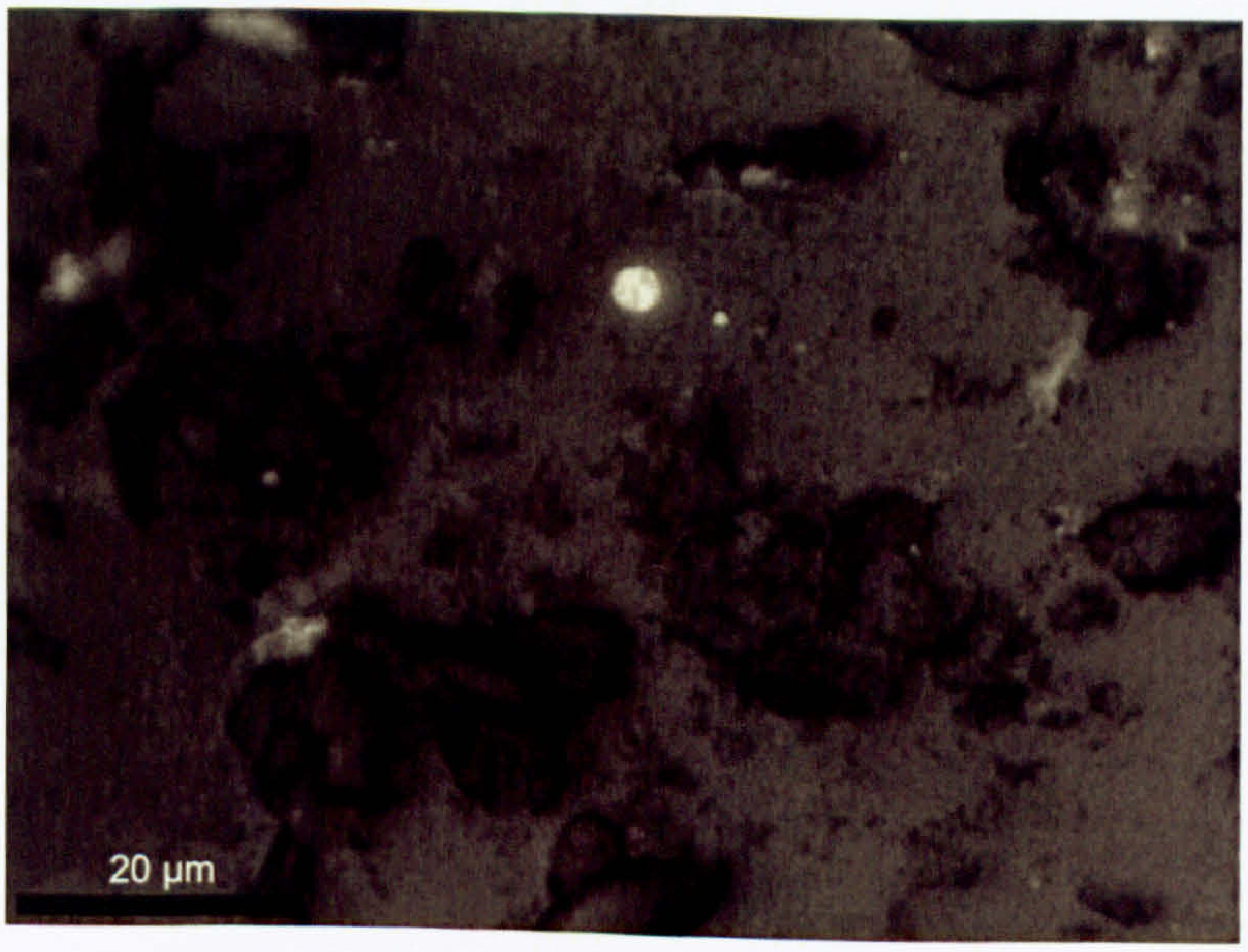
Intensity curve of sample:
Ak: Akermanite-$Ca_2Mg(Si_2O_7)$

Sample No. MAK10

Macroscopic features

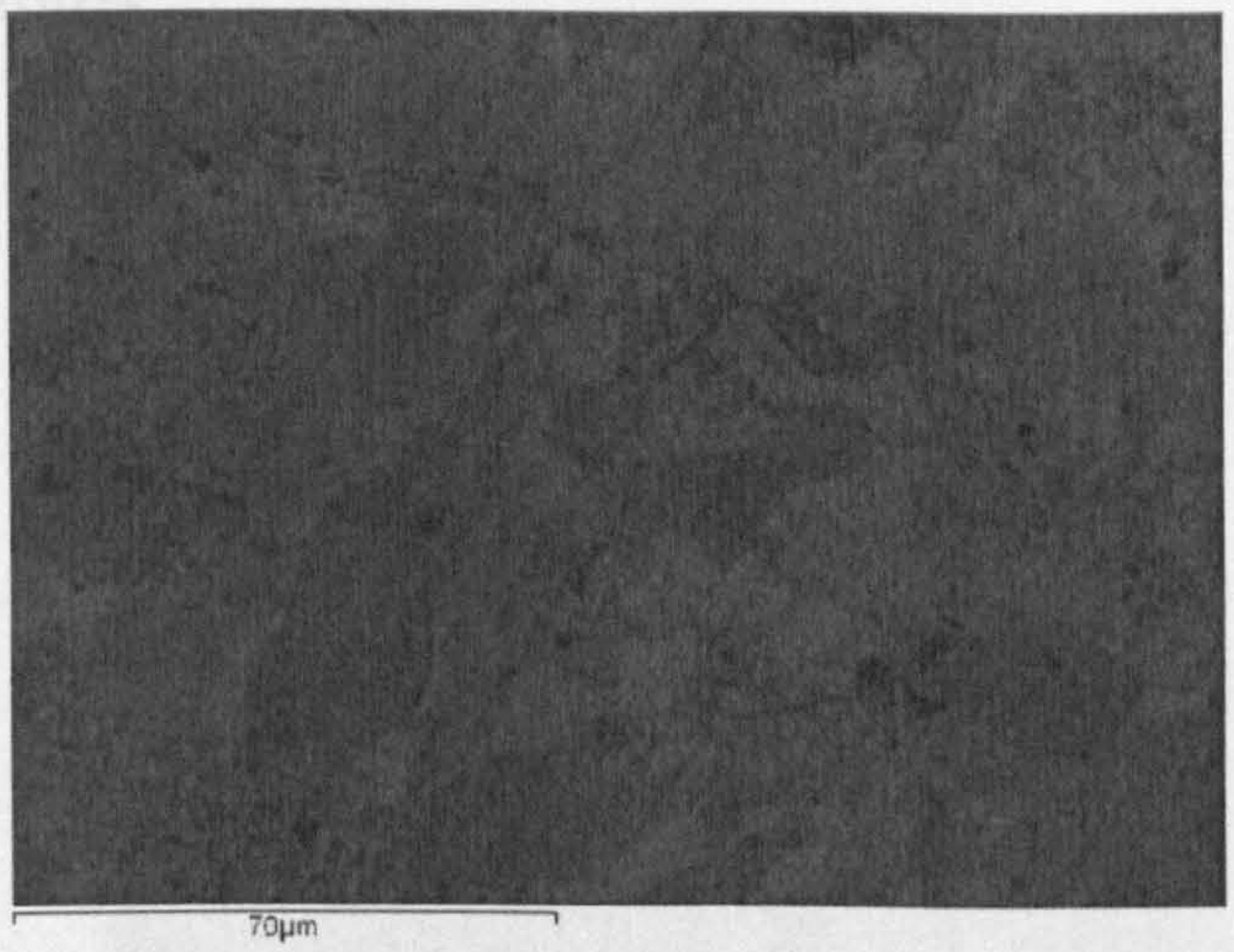
Size	2.50 cm
Weight	16.50 g
Colour	dark grey/black
Texture	ropey (conchoidal)
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



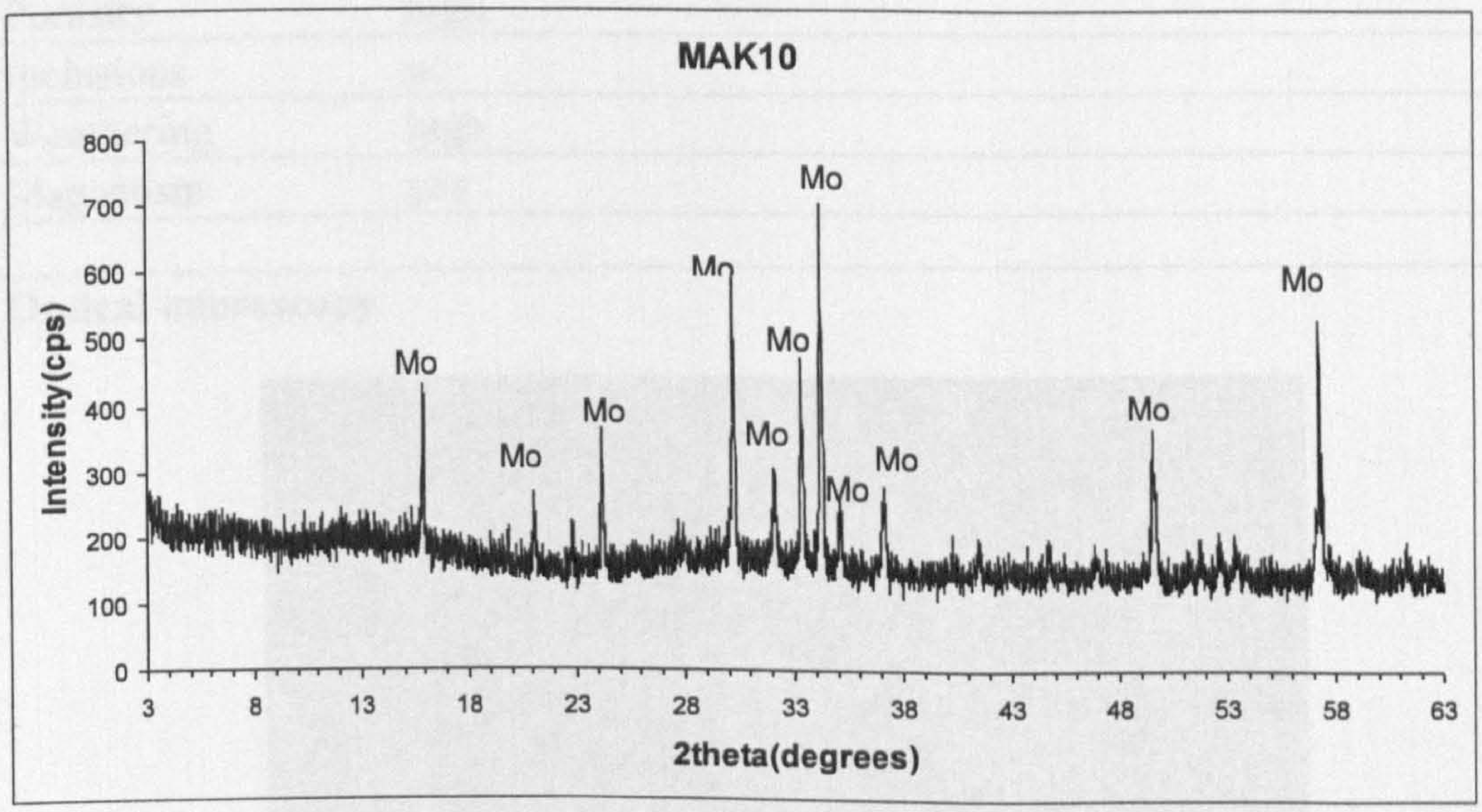
Glassy matrix/Traces of fayalite/Spheroid metallic prill (x 1000)

SEM image



Laths of fayalite show as darker regions with frequent wüstites and interstitial glass at the voids. No metallic inclusions are present.

XRD



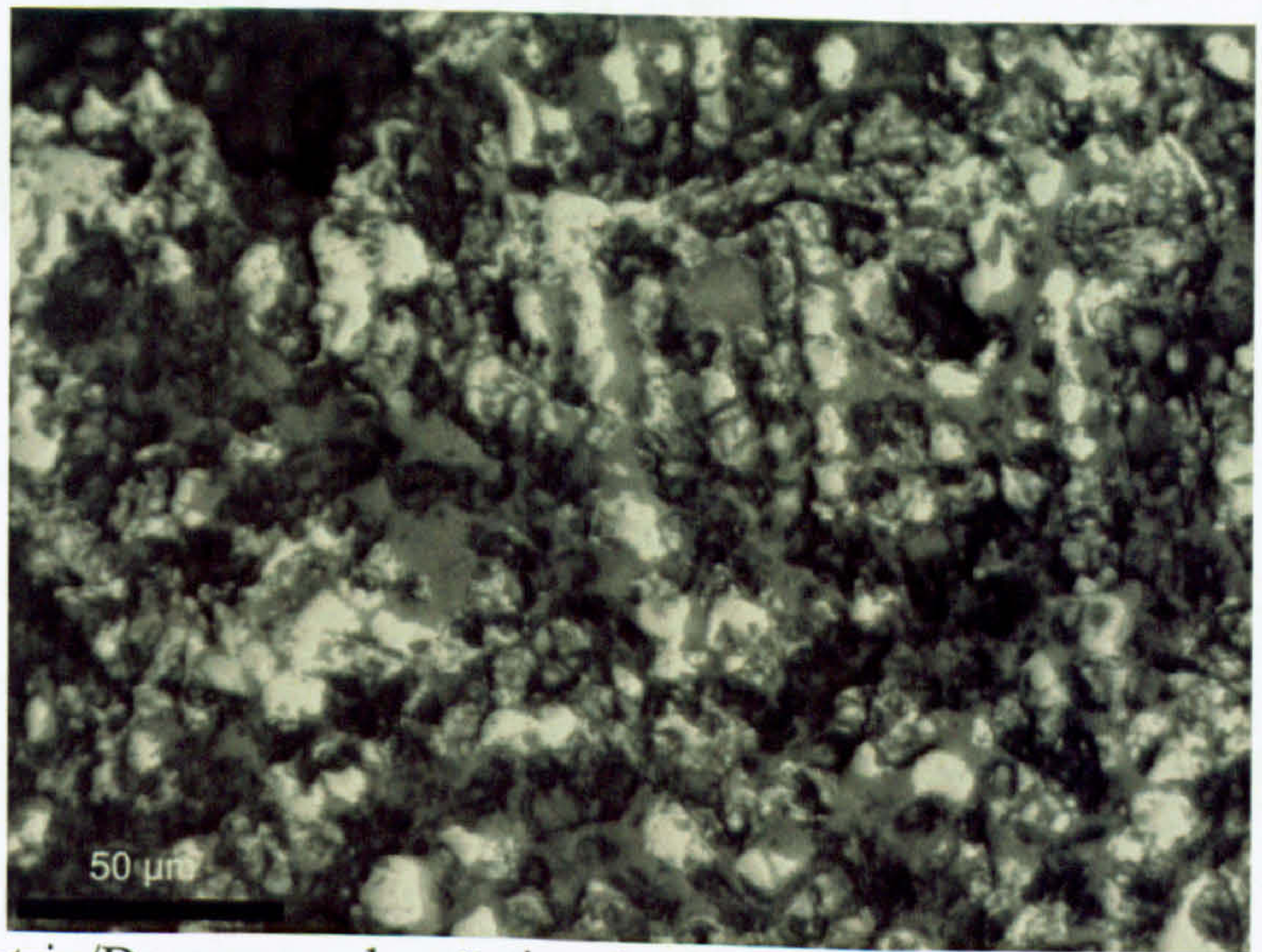
Intensity curve of sample:
Mo: Monticellite-$CaMgSiO_4$

Sample No. KAT01

Macroscopic features

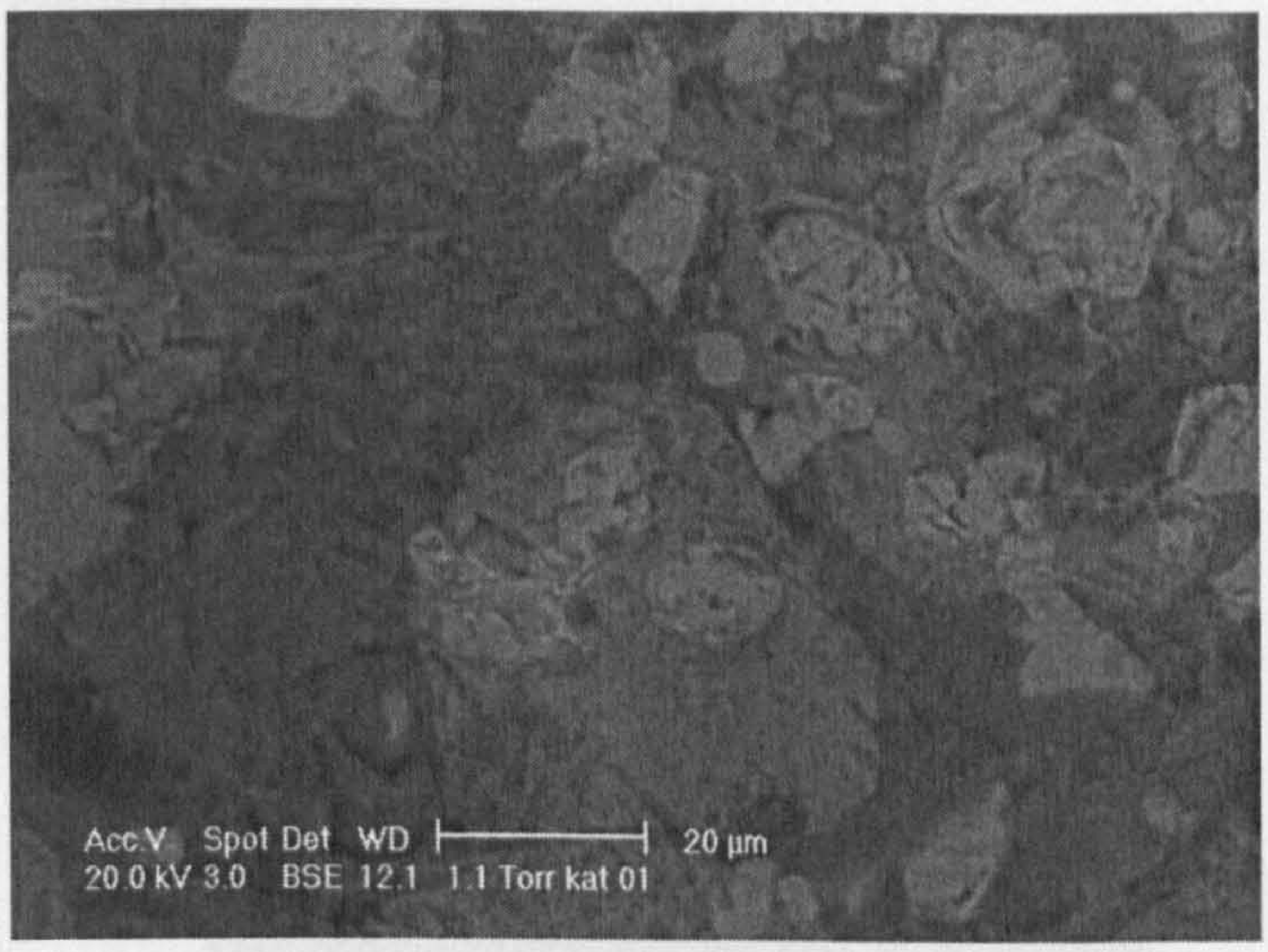
Size	8.50 cm
Weight	82.80 g
Colour	dark brown
Texture	droplike
Porosity	high
Inclusions	no
Weathering	high
Magnetism	yes

Optical microscopy



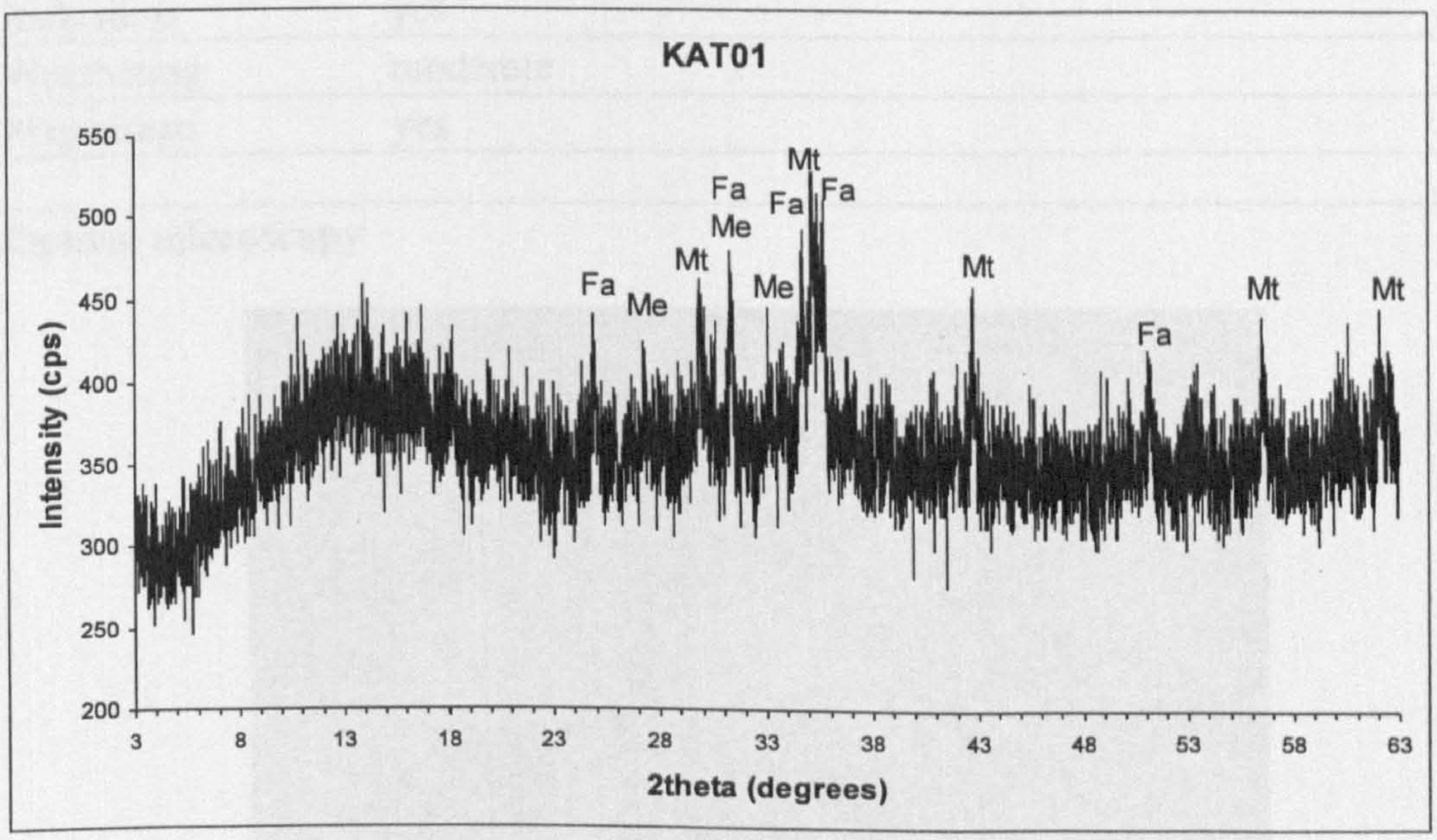
Vesicular matrix/Decomposed wüstite broken by numerous cavities/Triangular magnetite crystal (x 400)

SEM image



Three shades of grey represent three distinct phases of the microstructure. The matrix appearing darkest is siliceous. Large angular magnetite crystals show as lighter grey polygons while the rounded-profile spots are remnants of wüstite resulting from decomposition of their dendritic shape.

XRD



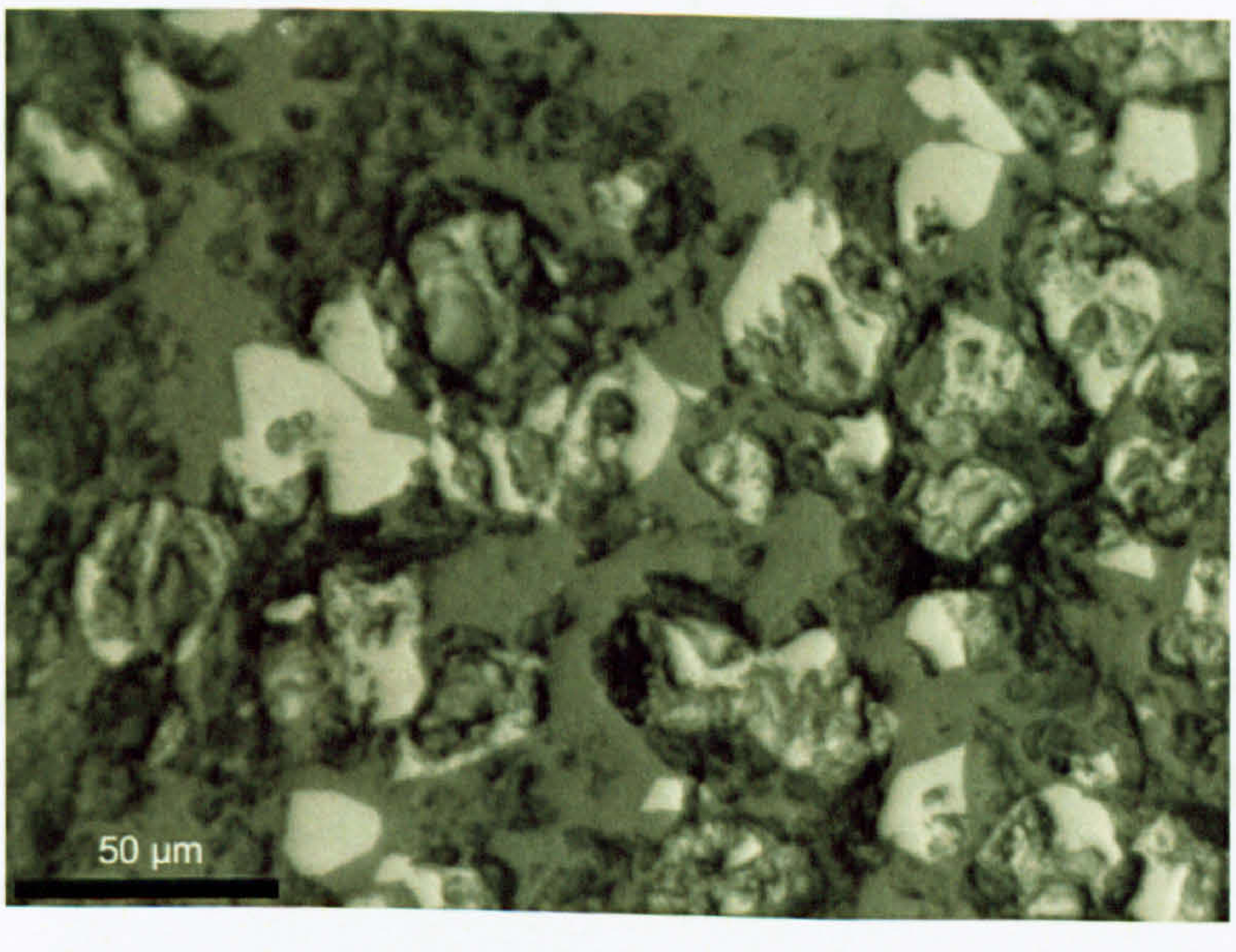
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$,

Sample No. KAT02	

Macroscopic features

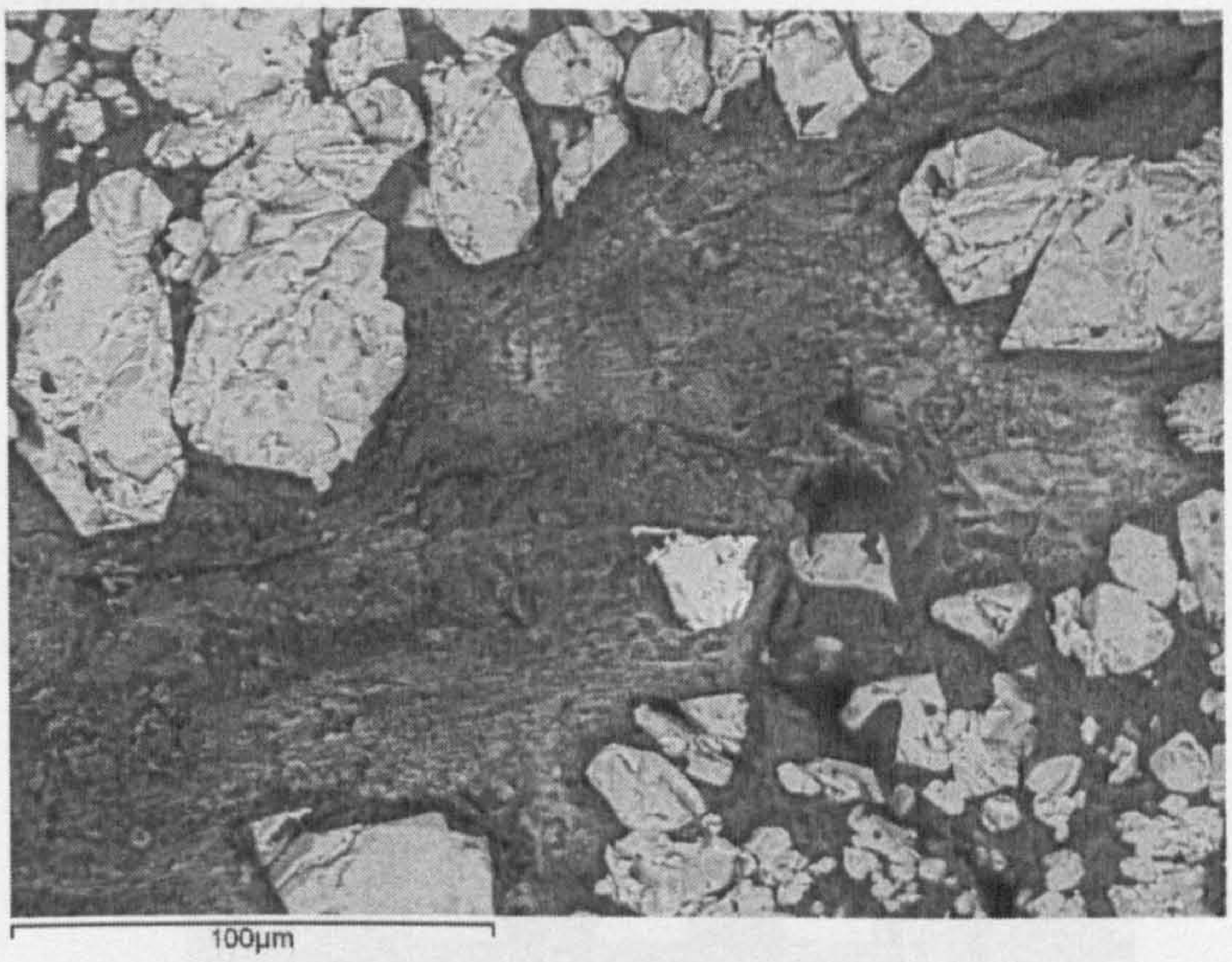
Size	7.00 cm
Weight	110.00 g
Colour	dark grey
Texture	spongy
Porosity	high
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



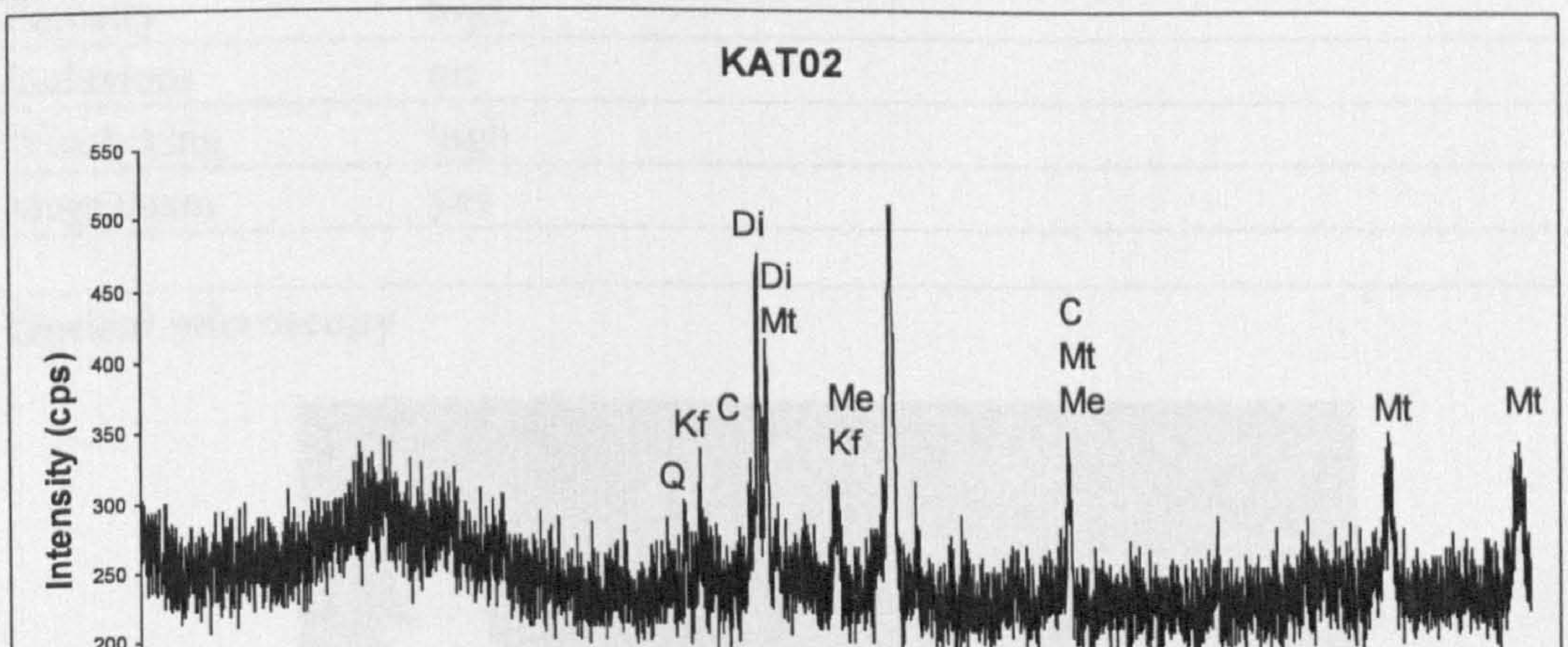
Vesicular matrix/Decomposed wüstite /Magnetite/Occasional metallic prills (x 400

SEM image



Large angular magnetite crystals appear in clusters over a dark grey siliceous matrix. The occasional rounded crystals are wüstite while the brighter spot in the centre of the micrograph appears as gangue mineral deriving from un-reacted ore constituents.

XRD



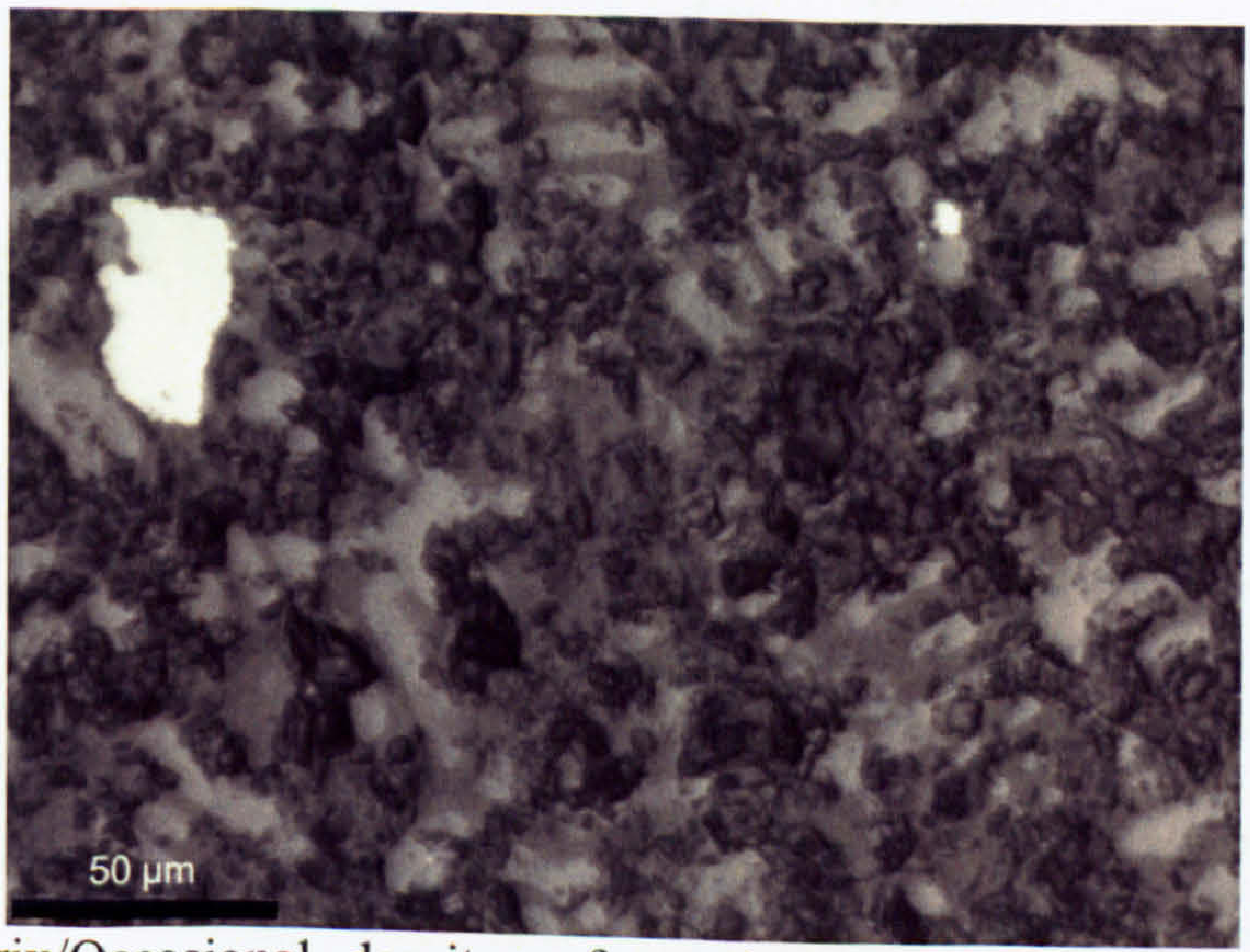
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Qz: Quartz-$SiO_2$, Cr: Cristobalite-$SiO_2$, Kf: Alkali feldspar-$KAlSi_3O_8$, Di: Diopside-$Mg_{0.6}Fe_{0.2}Al_{0.2})Ca(Si_{1.5}Al_{0.5})O_6$, Cc: Calcite-$CaCO_3$,

Sample No. KAT03

Macroscopic features

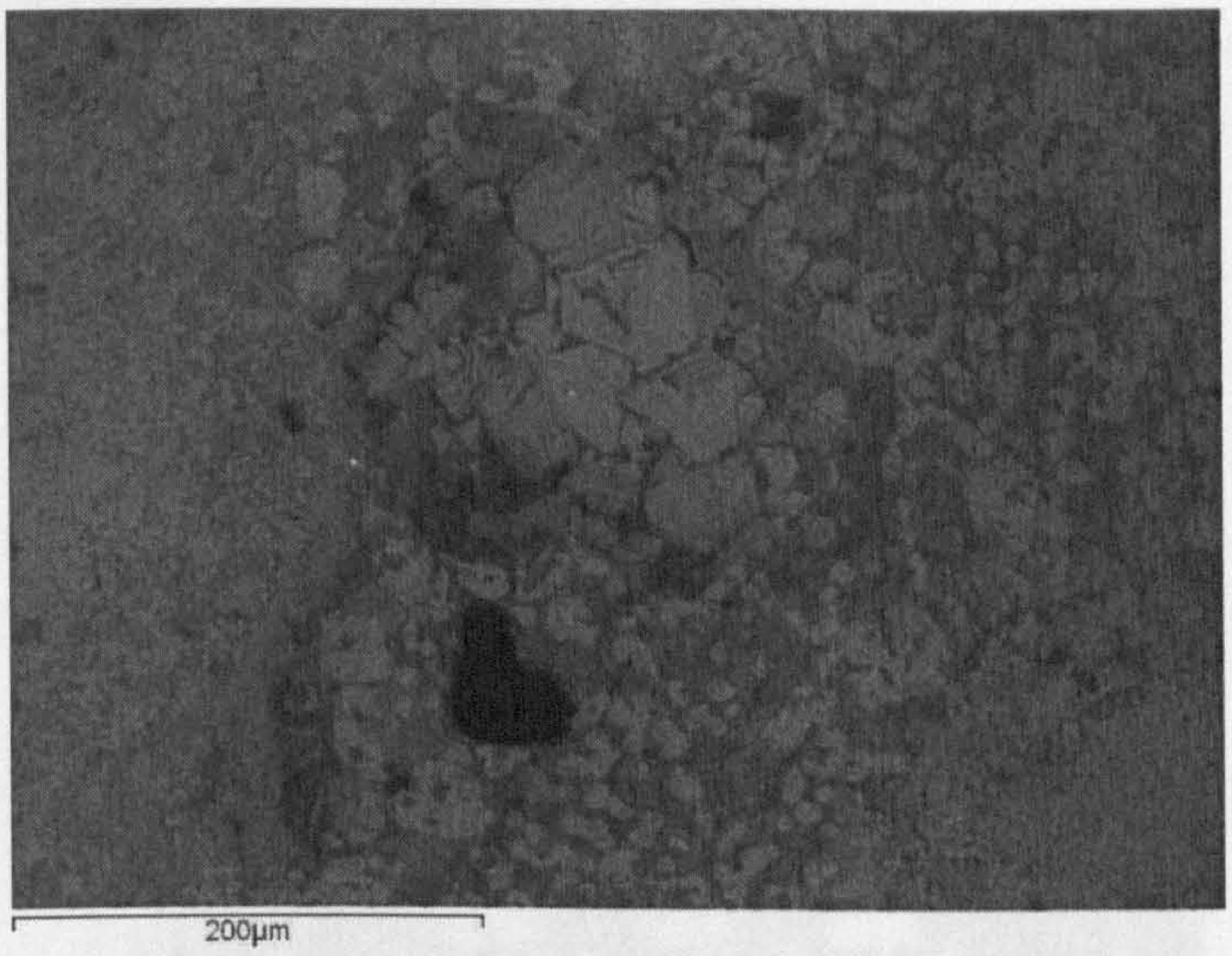
Size	6.50 cm
Weight	116.00 g
Colour	brown
Texture	spongy
Porosity	high
Inclusions	no
Weathering	high
Magnetism	yes

Optical microscopy



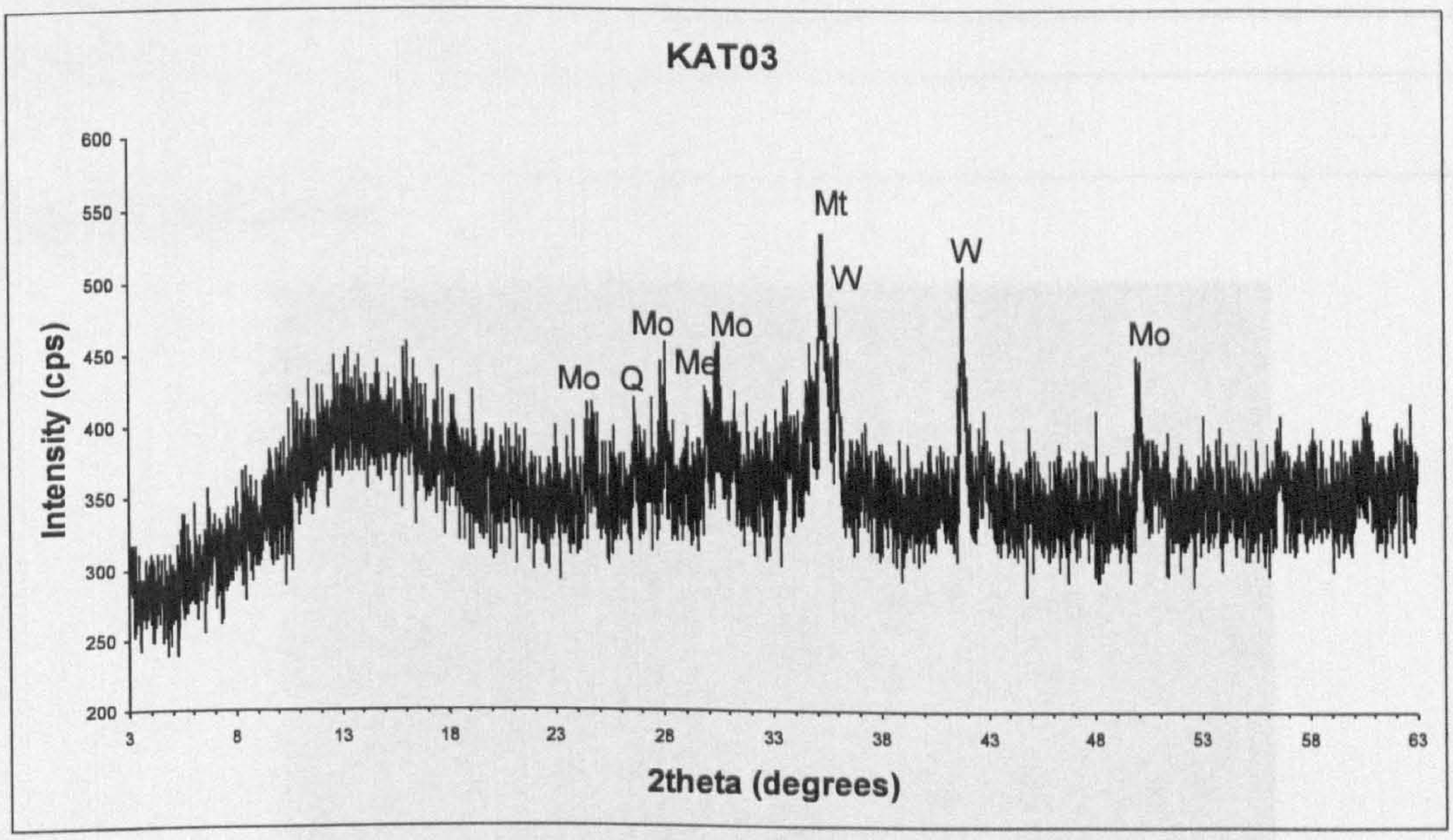
Vesicular matrix/Occasional denrites of wüstite/ large iron oxide inclusion and metallic prill (x 400)

SEM image



Three major phases could be distinguished. A dark matrix mainly siliceous, decomposed wüstite dendrites and large magnetite crystals clustering at the centre of the micrograph.

XRD



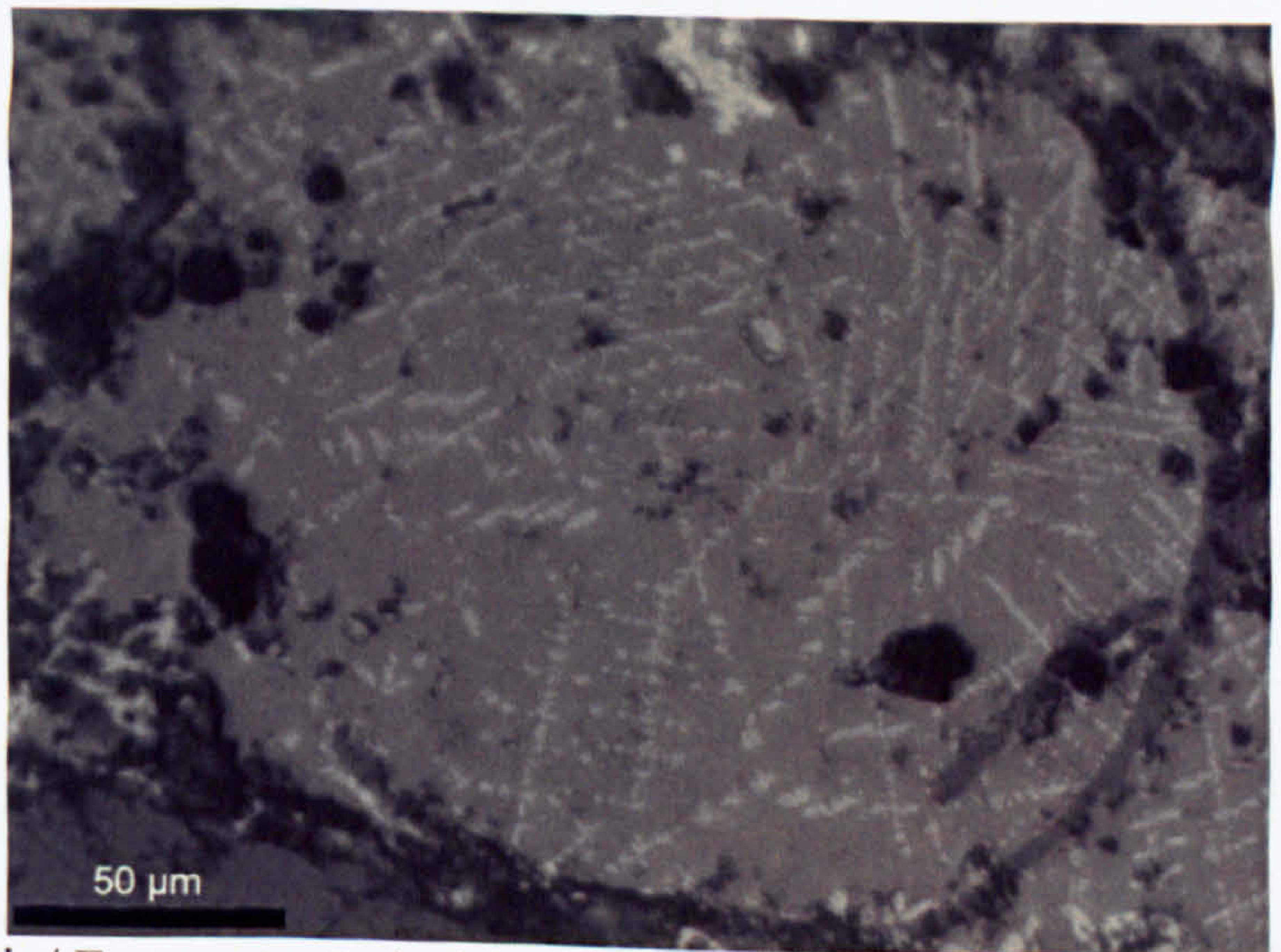
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wüstite-FeO, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$, Qz: Quartz-$SiO_2$

Sample No. KAT04

Macroscopic features

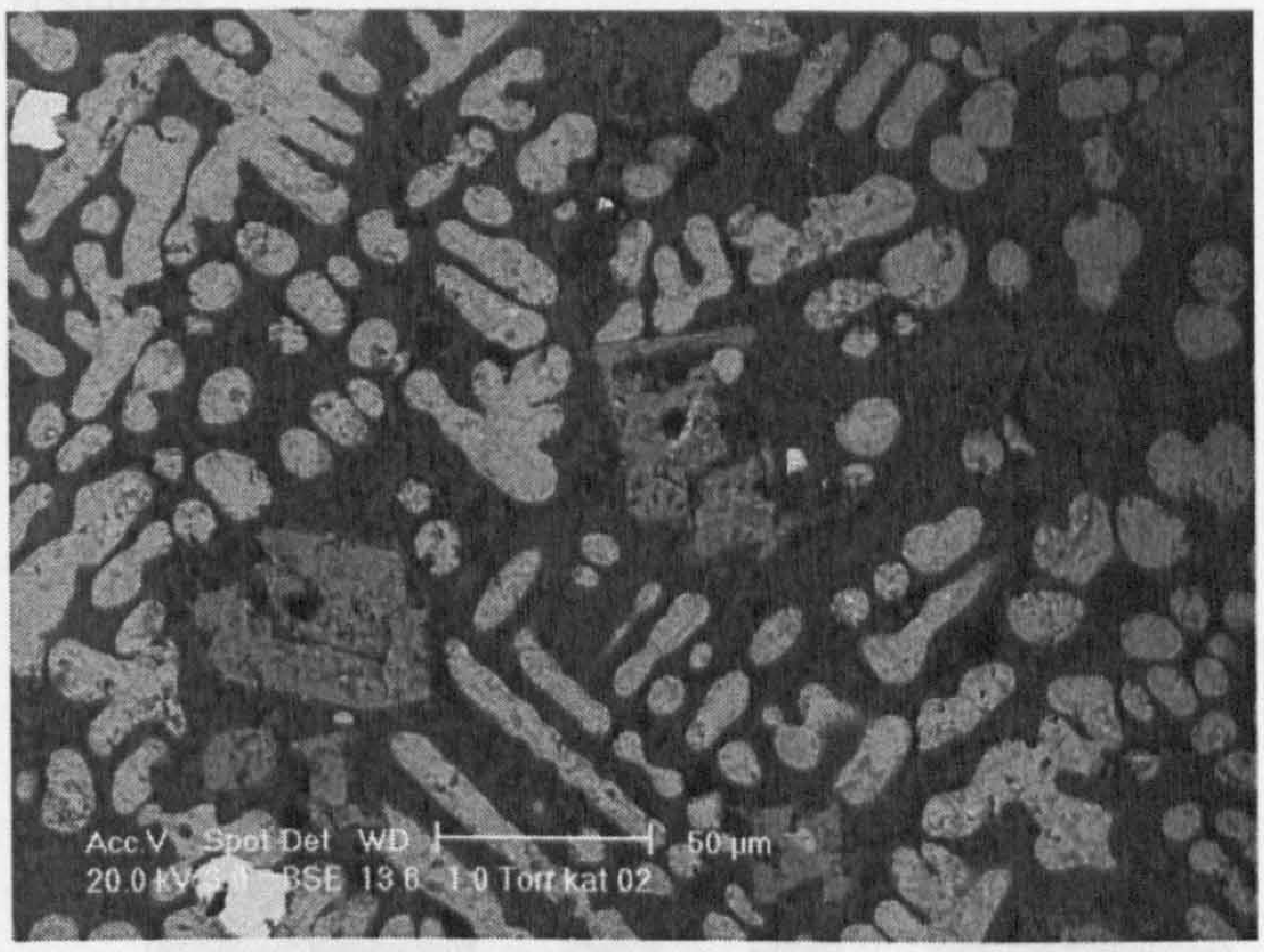
Size	7.00 cm
Weight	127.60 g
Colour	dark brown
Texture	spongy
Porosity	high
Inclusions	no
Weathering	high
Magnetism	yes

Optical microscopy



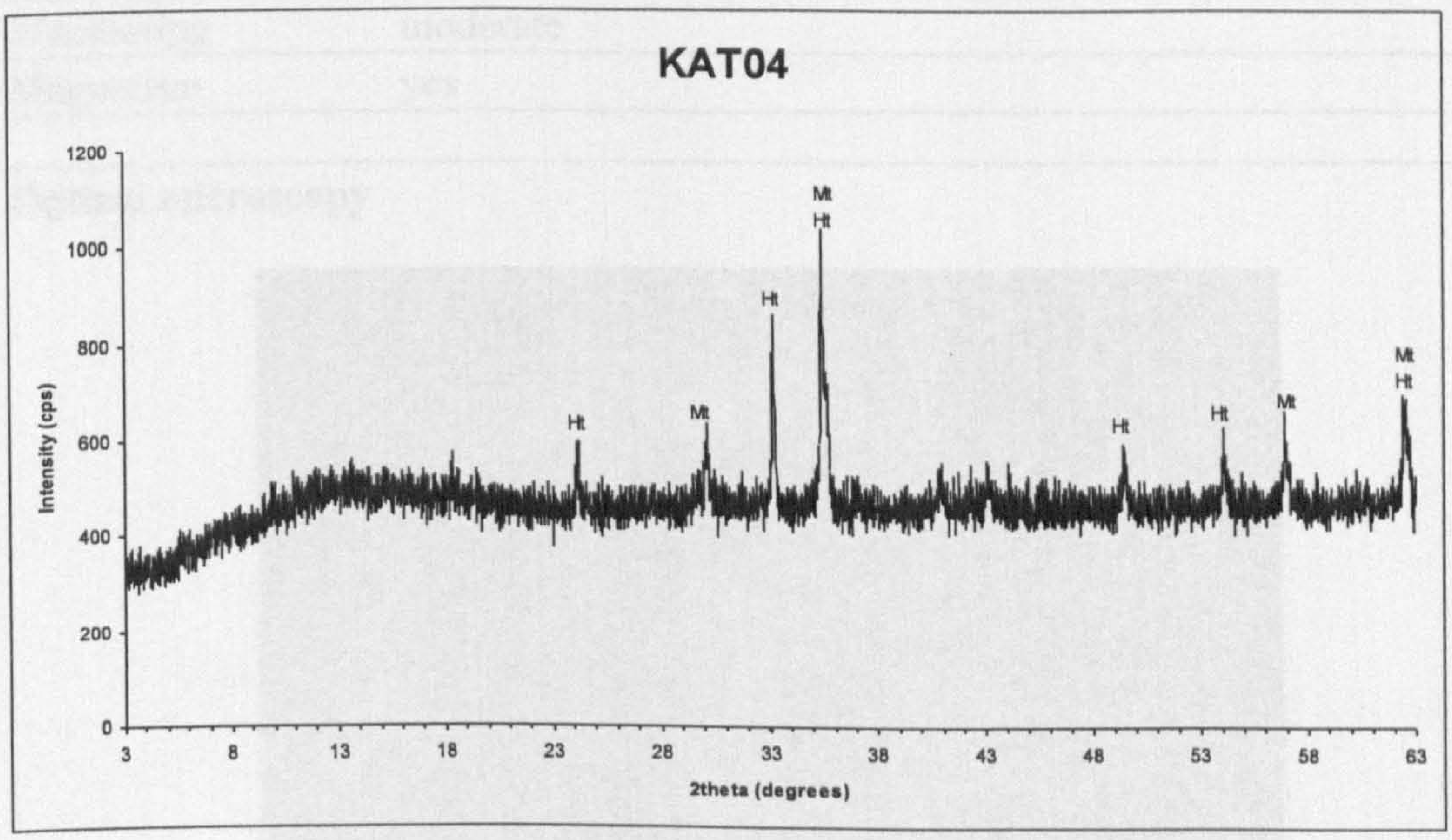
Vesicular matrix/ Frequent wüstite/ Occasional metallic prills/ (x 400)

SEM image



Dark matrix mainly siliceous in composition and the dendritic pattern of wüstites are the major phases. Triangular crystals appearing slightly darker than wüstite are spinels and two brighter spots (low and top right corner) are metallic, iron-rich inclusions.

XRD



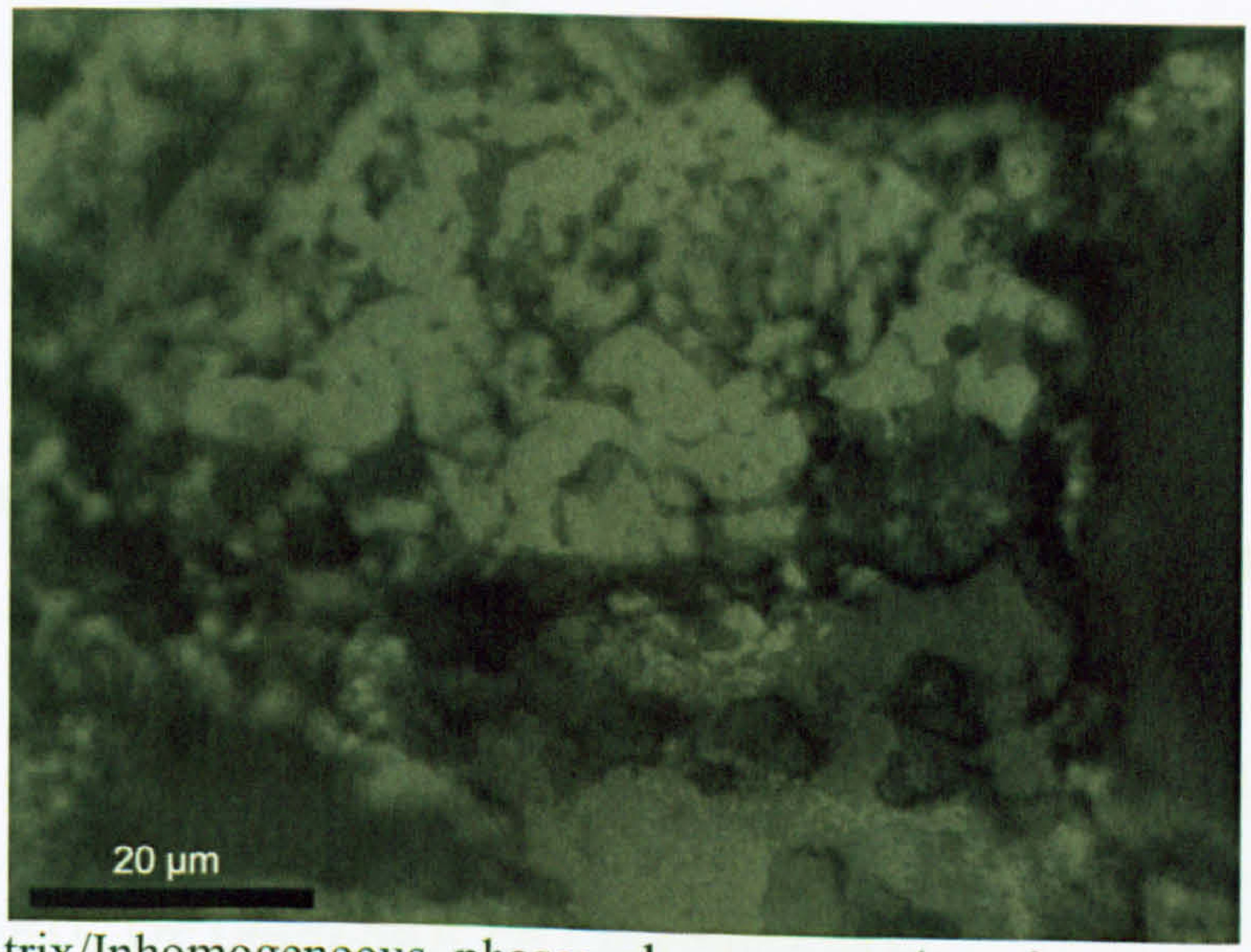
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Ht: Hematite-Fe_2O_3,

Sample No. KAT05

Macroscopic features

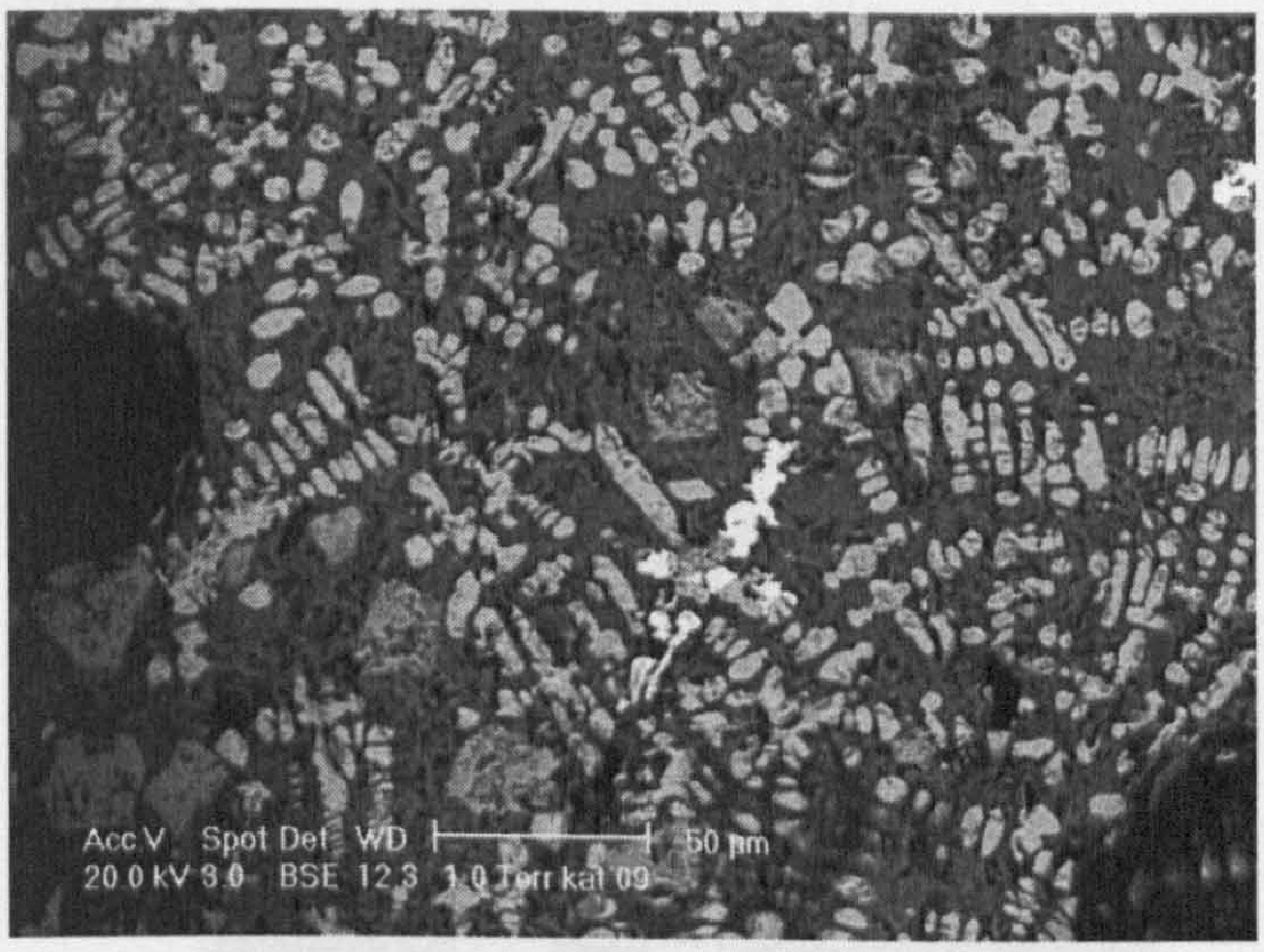
Size	6.00 cm
Weight	59.00 g
Colour	reddish brown
Texture	spongy
Porosity	high
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



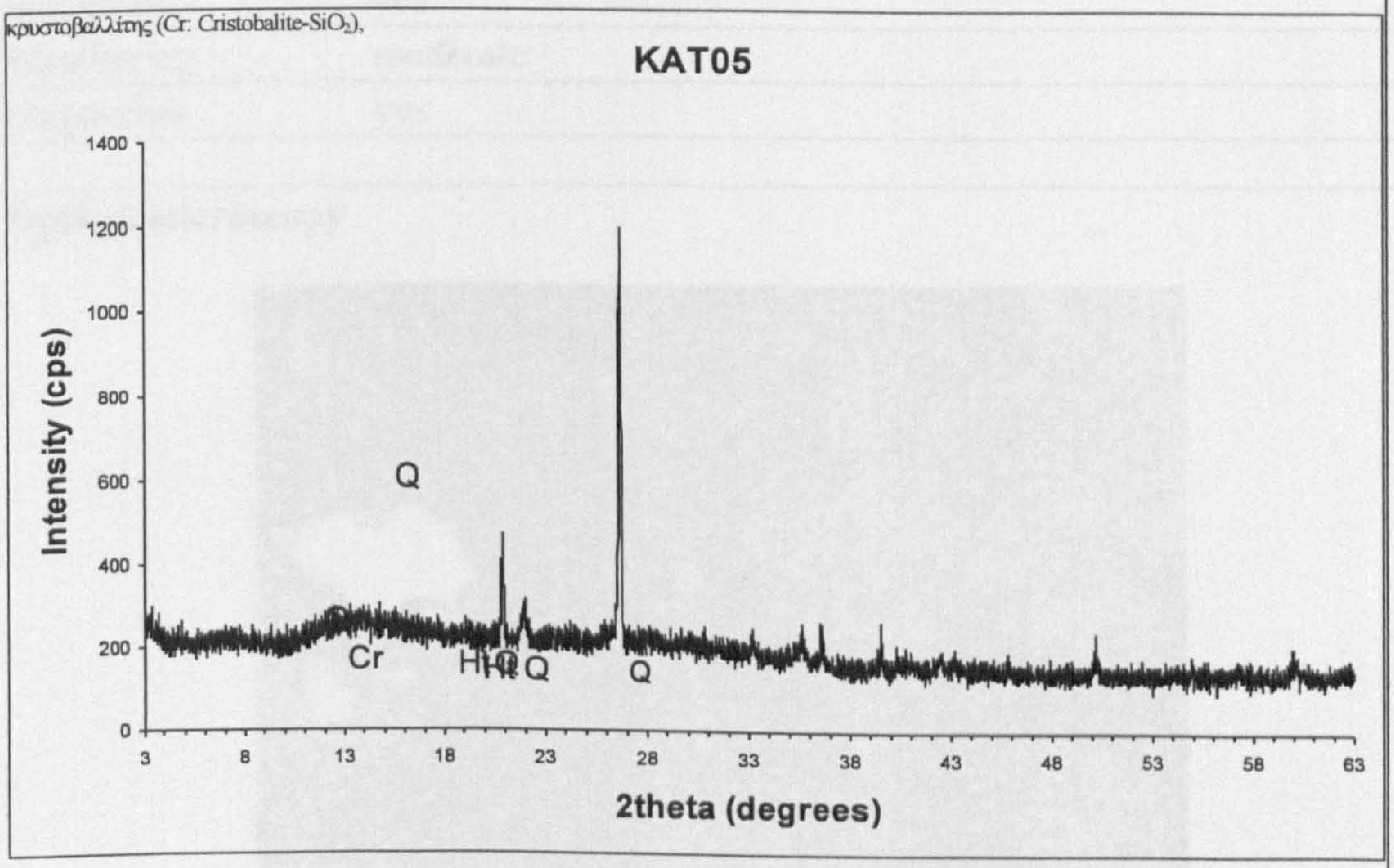
Vesicular matrix/Inhomogeneous phase: clay, quartz (ore fragments)/Decomposed wüstite (x 1000)

SEM image



A network of wüstite dendrites over a siliceous matrix are the dominant features of the microstructure. A cross-shaped formation of brighter crystals at the centre consists of metallic inclusions. Occasional spinels with their characteristic rhomboid shape also occur.

XRD



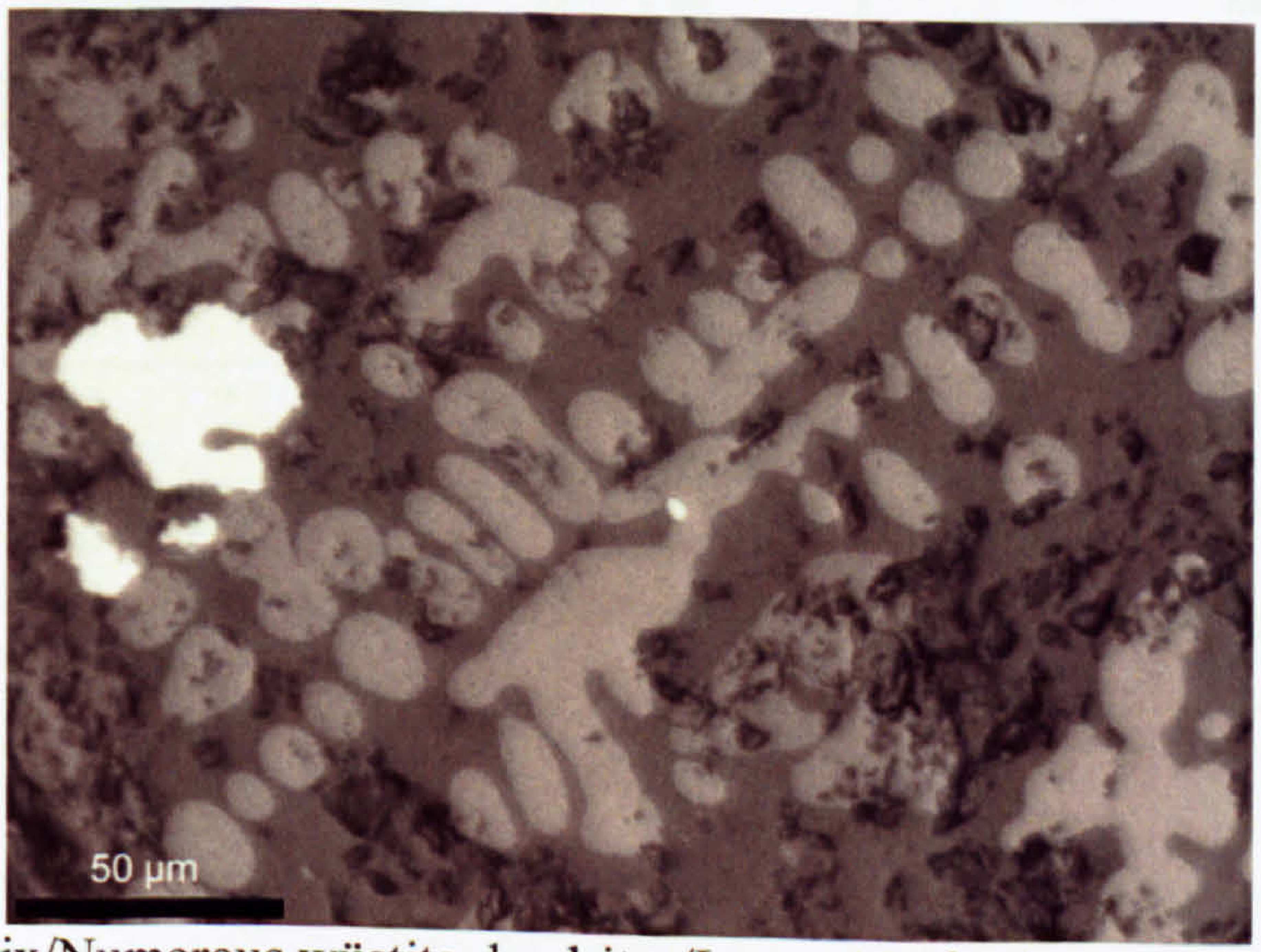
Intensity curve of sample:
Ht: Hematite-Fe_2O_3, Qz: Quartz-SiO_2, Cr: Cristobalite-SiO_2,

Sample No. KAT06

Macroscopic features

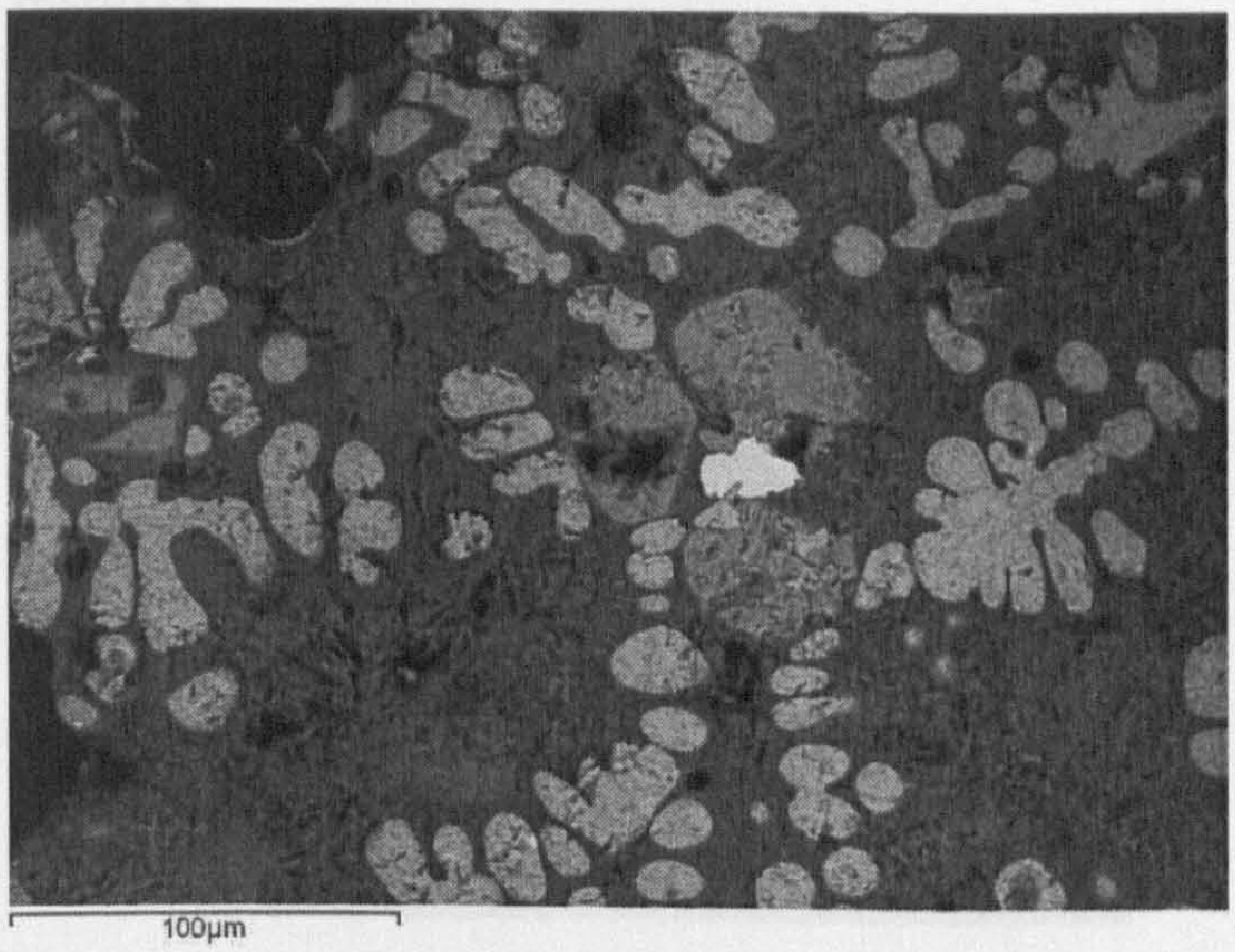
Size	5.00 cm
Weight	55.80 g
Colour	reddish brown
Texture	spongy
Porosity	high
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



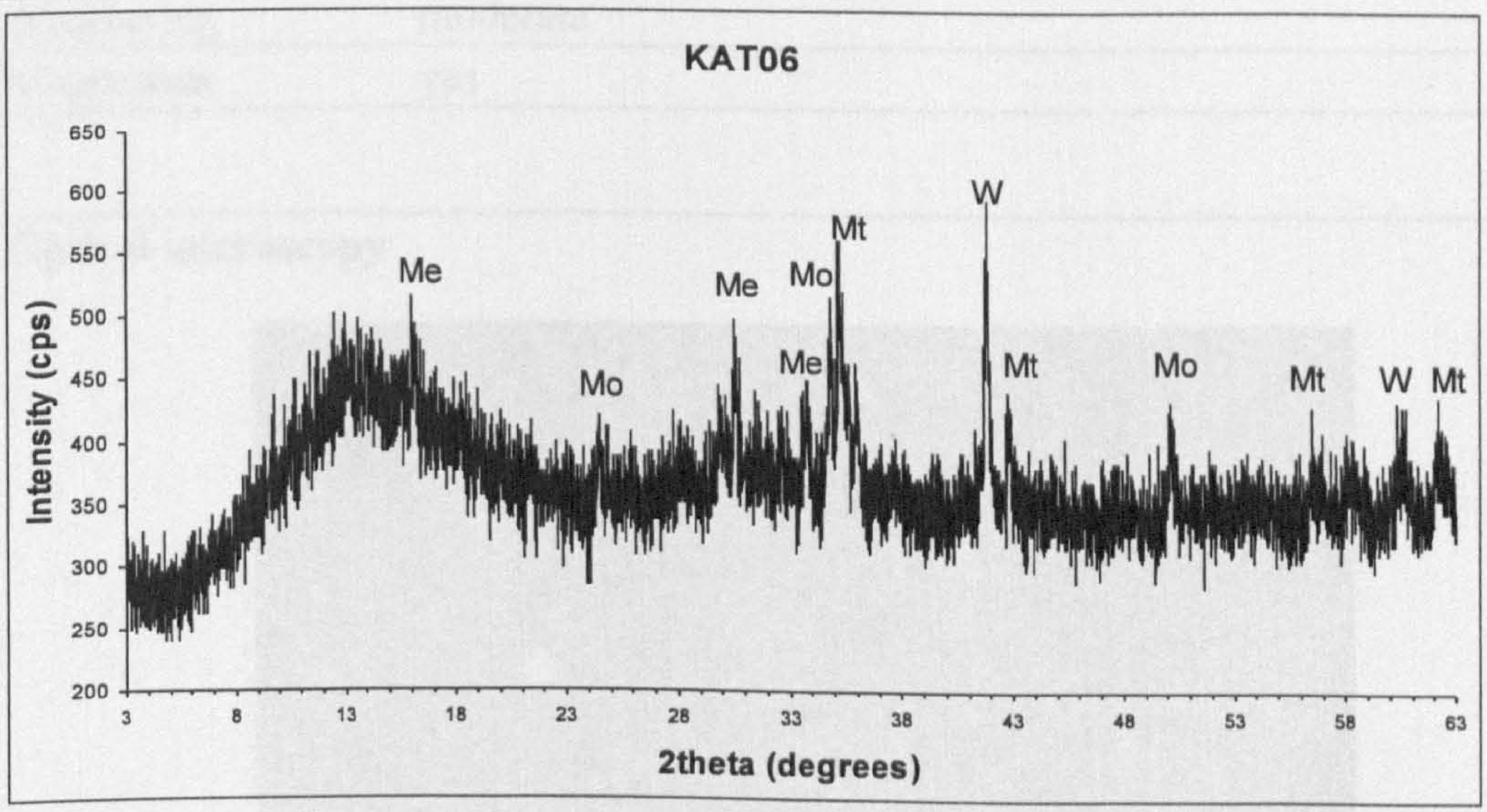
Vesicular matrix/Numerous wüstite dendrites/Large angular iron oxide prills (x 400)

SEM image



Four major phases are represented: the dark fayalitic matrix, grey dendrites of wüstite, rhomboid spinels and a bright metallic inclusion. Occasional magnetite also exists examples of which are among the wüstite at the left of the micrograph.

XRD



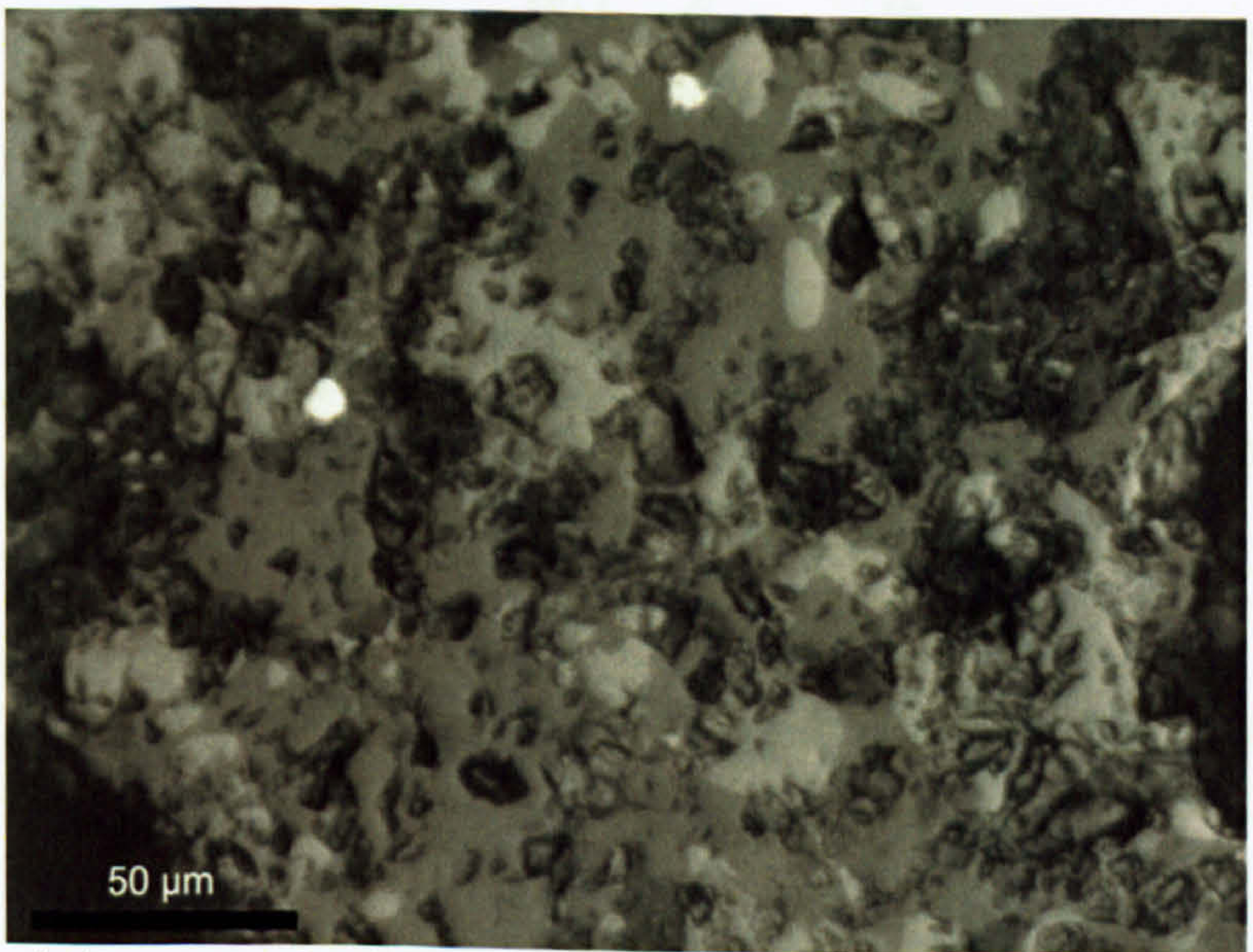
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wüstite-FeO, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$,

Sample No. KAT07

Macroscopic features

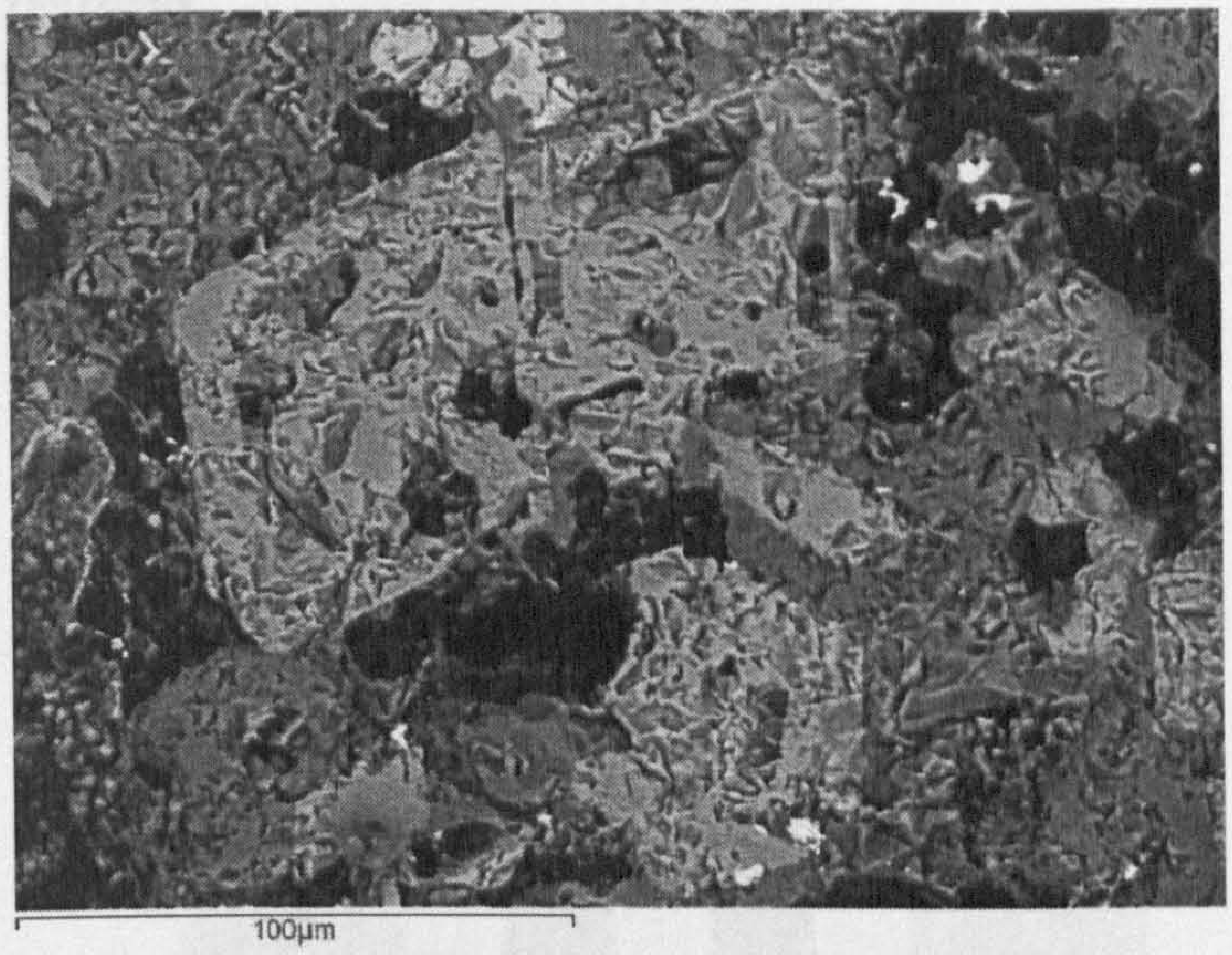
Size	4.00 cm
Weight	19.20 g
Colour	brown
Texture	spongy
Porosity	high
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy



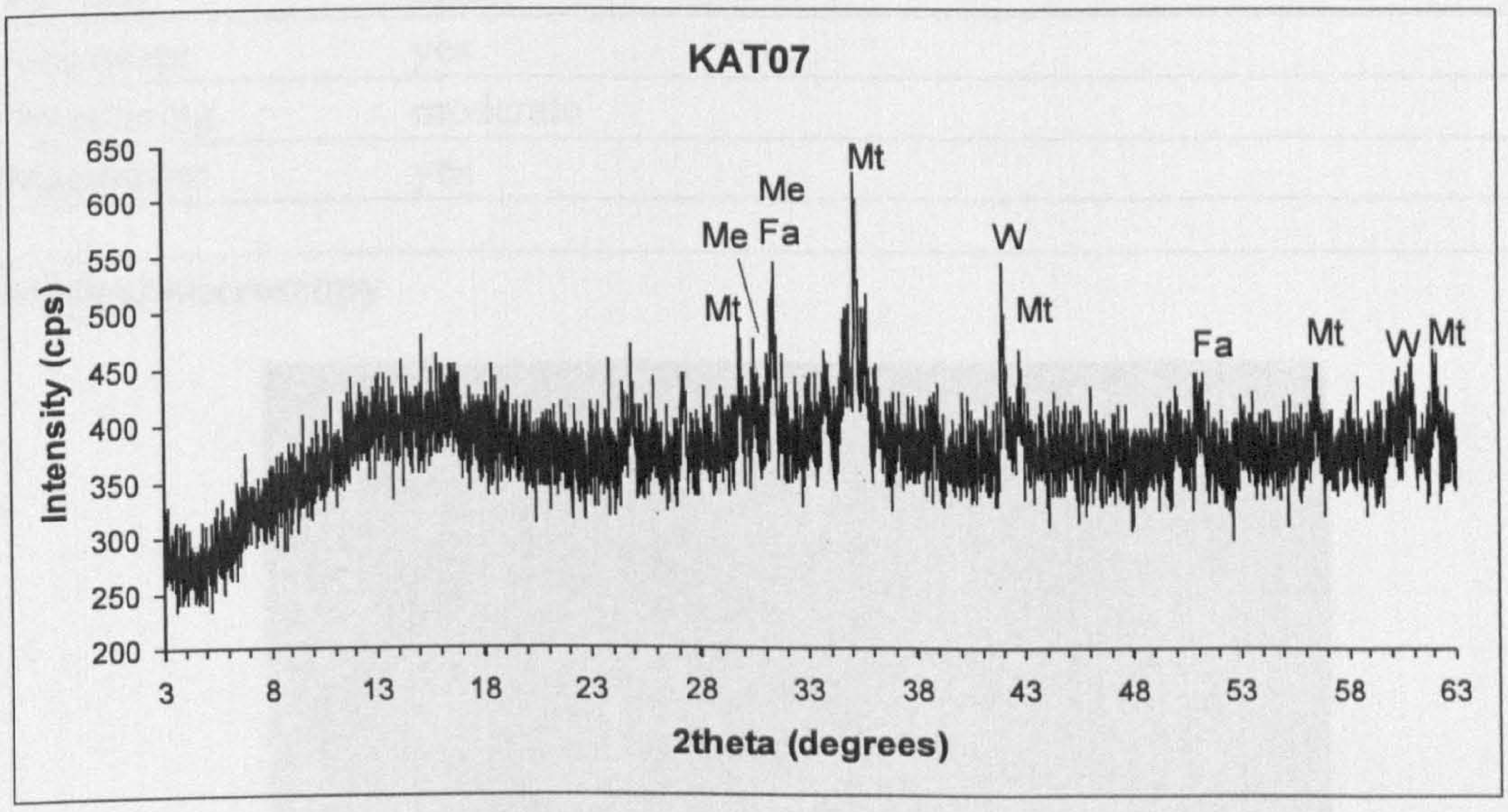
Vesicular matrix/Rare wüstite / Occasional magnetite/ Rare metallic prills (x 400)

SEM image



The fayalitic composition of the matrix is clearly apparent in the micrograph while two large spinel crystals dominate the centre. Small bright spots represent metallic prills and reminiscent wustites at the top appear as the lighter grey phase.

XRD



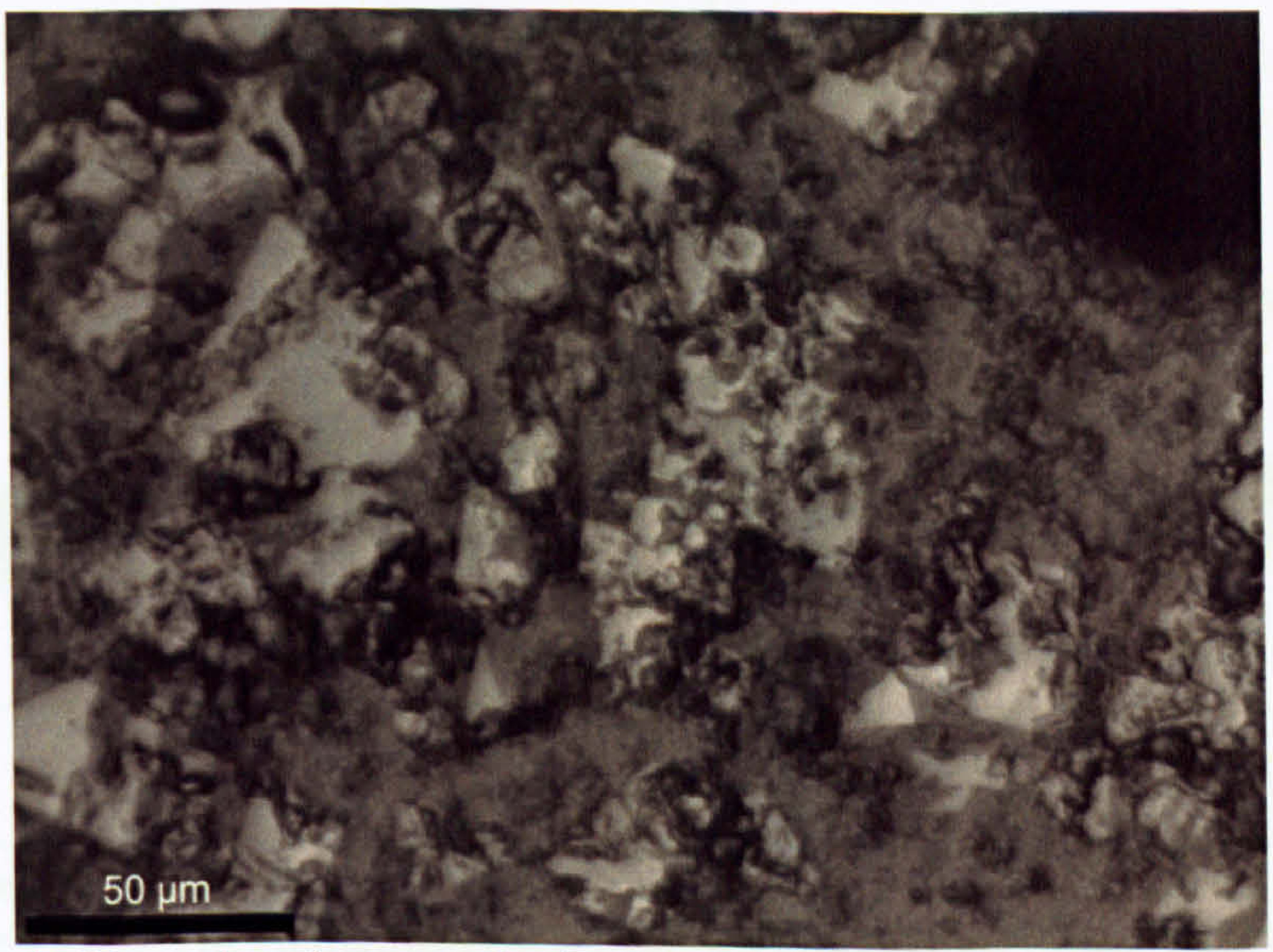
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, 4,

Sample No. KAT08

Macroscopic features

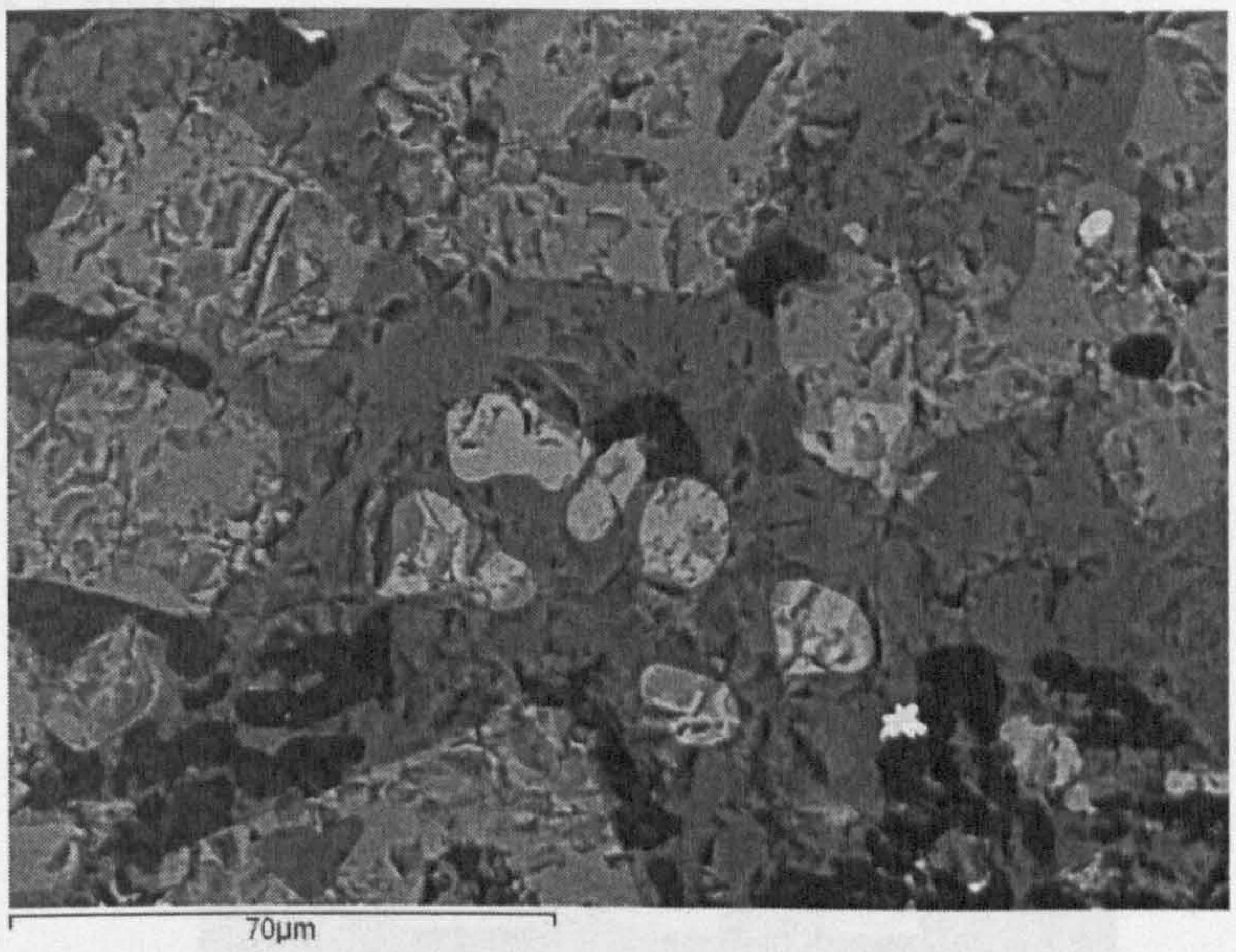
Size	4.50 cm
Weight	34.80 g
Colour	dark grey
Texture	droplike
Porosity	high
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



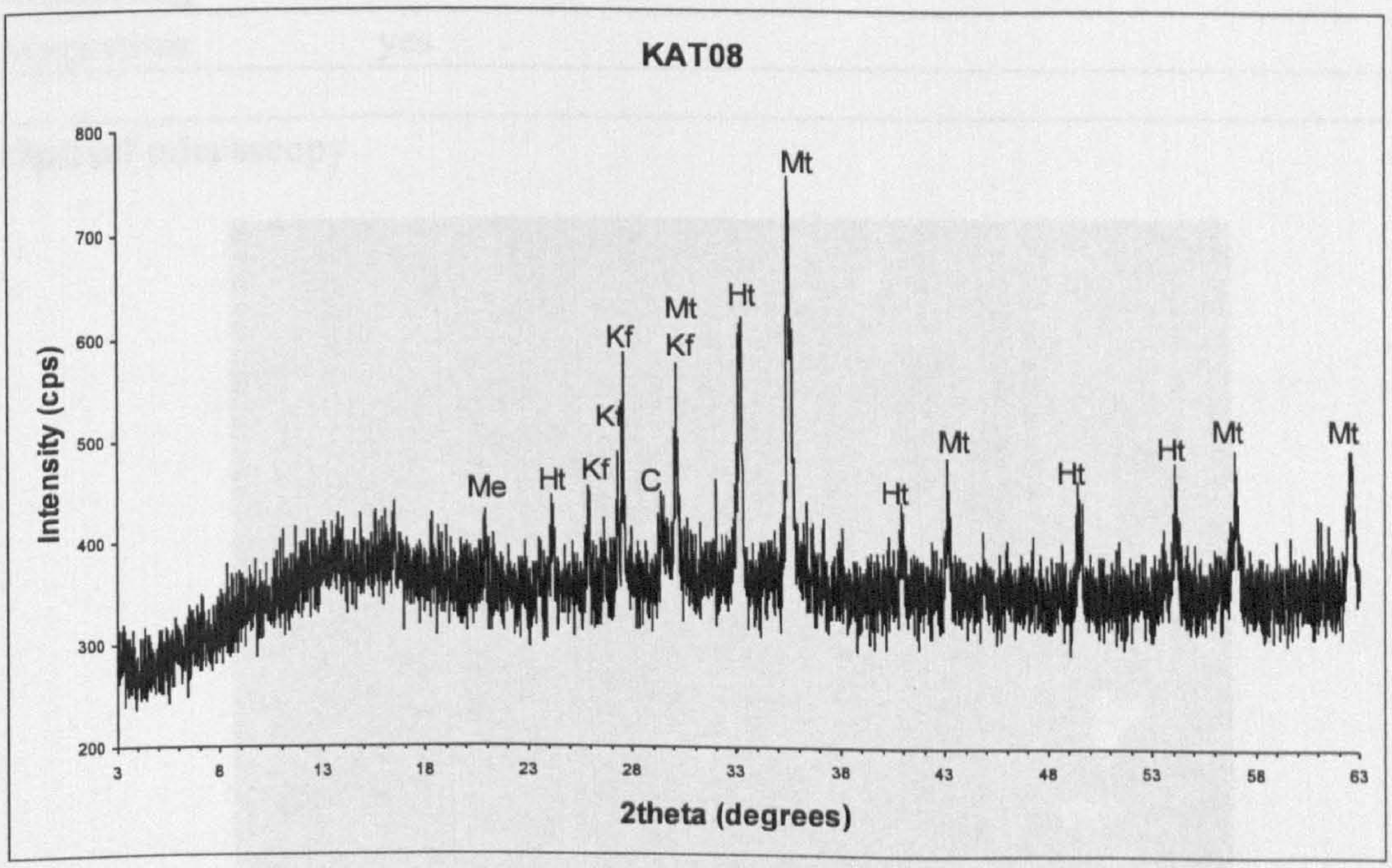
Vesicular matrix/Occasional magnetite/Rare wüstite (x 400)

SEM image



Fayalite laths appear as dark regions in the matrix which is also rich in magnetite crystals of a lighter grey shade. Remnants of wustite of rounded profiles cluster in the centre. The larger angular crystals are spinels and there is also a small, bright white prill of iron.

XRD



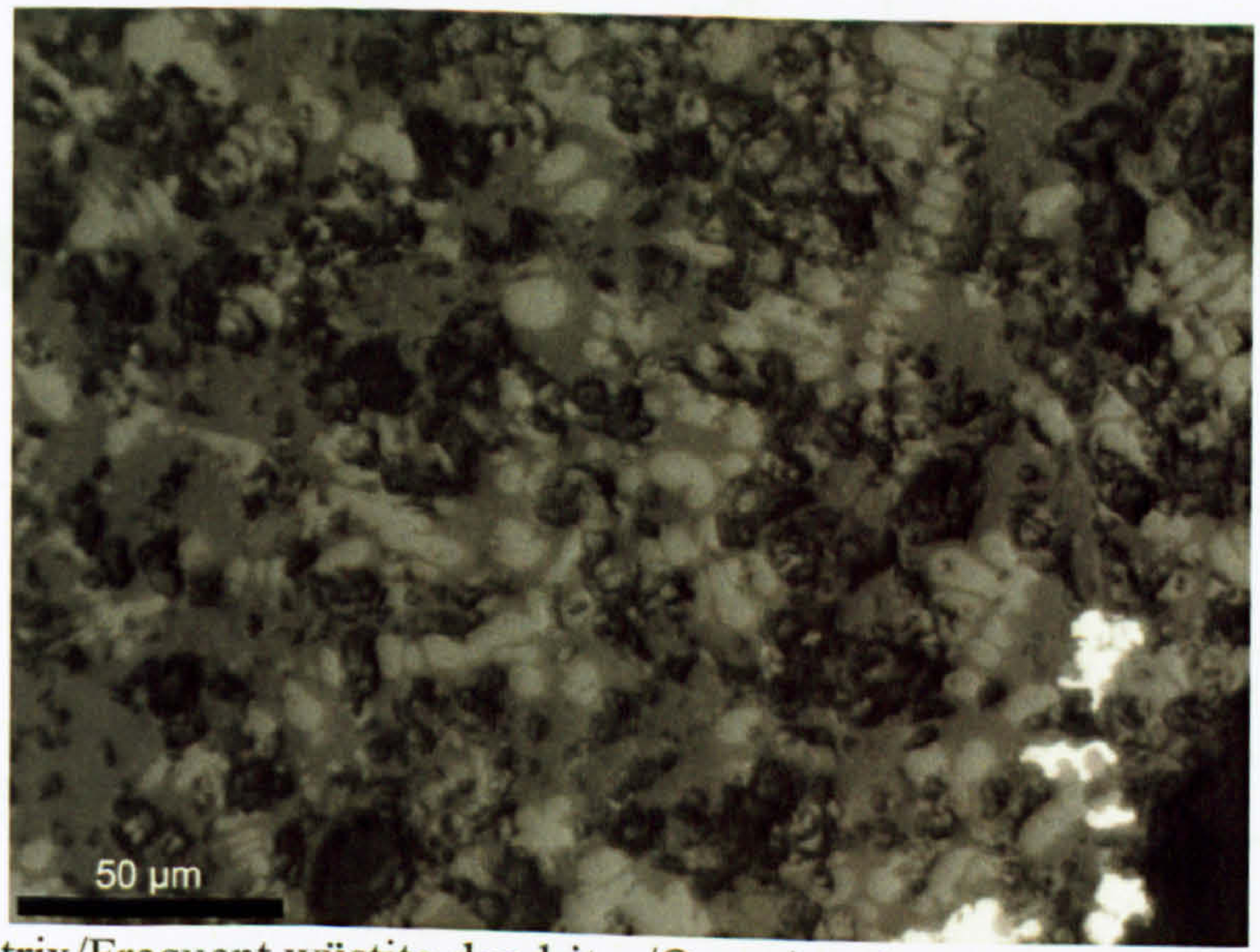
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Ht: Hematite-Fe_2O_3, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Kf: Alkali feldspar-$KAlSi_3O_8$, Cc: Calcite-$CaCO_3$

Sample No. KAT09

Macroscopic features

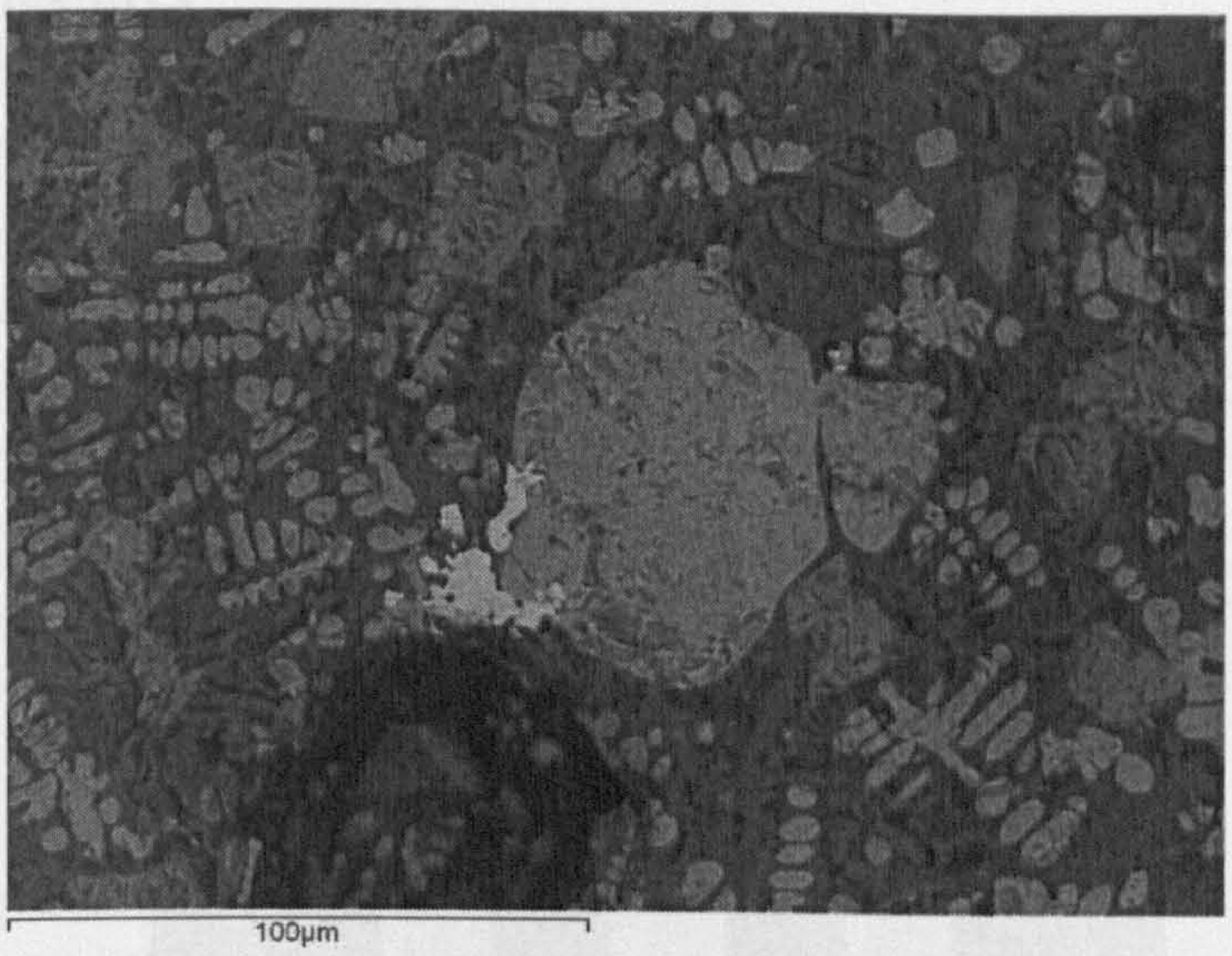
Size	3.00 cm
Weight	16.50 g
Colour	dark grey
Texture	droplike
Porosity	low
Inclusions	no
Weathering	low
Magnetism	yes

Optical microscopy



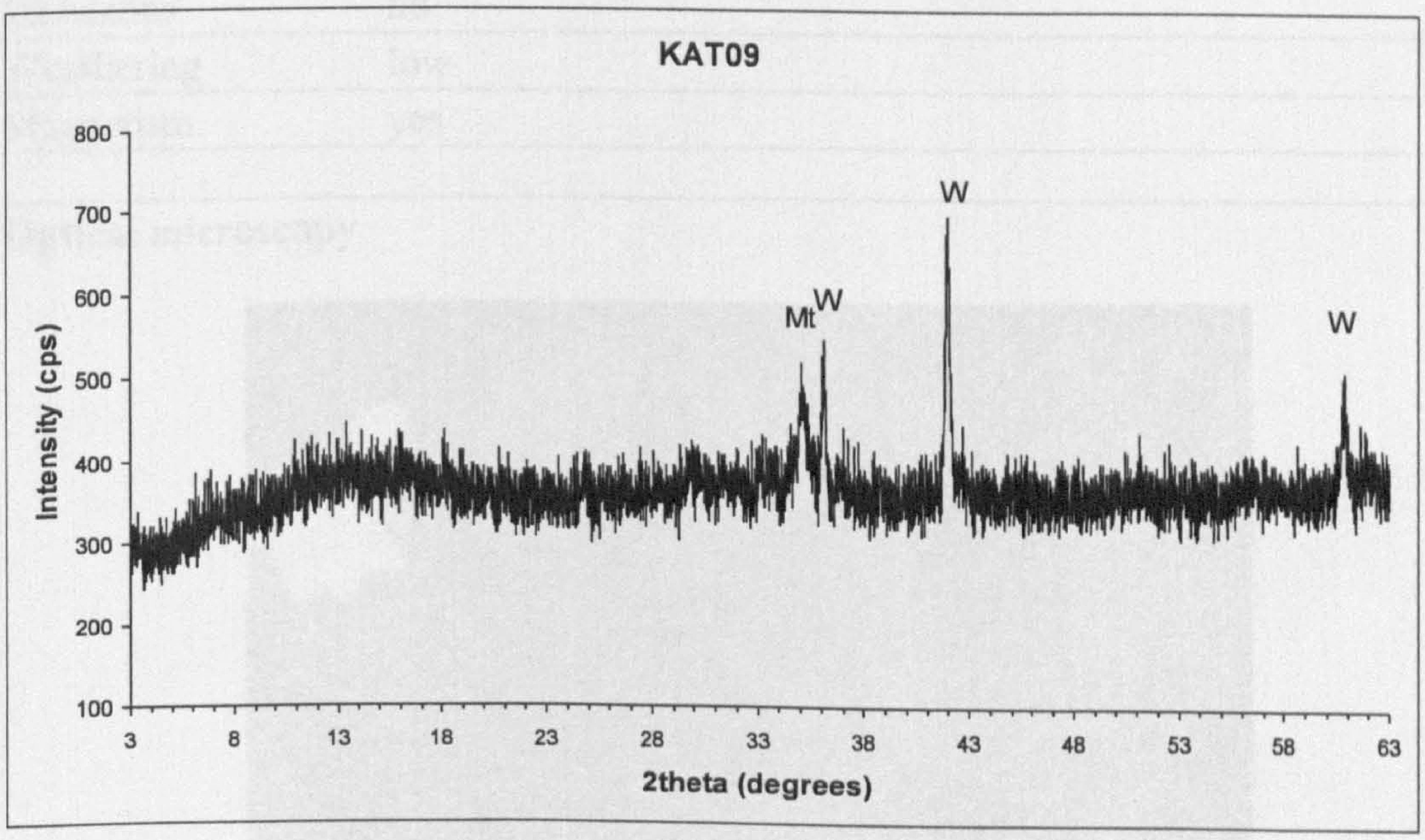
Vesicular matrix/Frequent wüstite dendrites/Occasional metallic prills (x 400)

SEM image



The micrograph is composed of a dendritic network of wustite surrounded by falyalites in the dark matrix. Frequent rhomboid ulvospinels and occasional metallic inclusions are also present while the centre is dominated by a large crystal of fayalite.

XRD



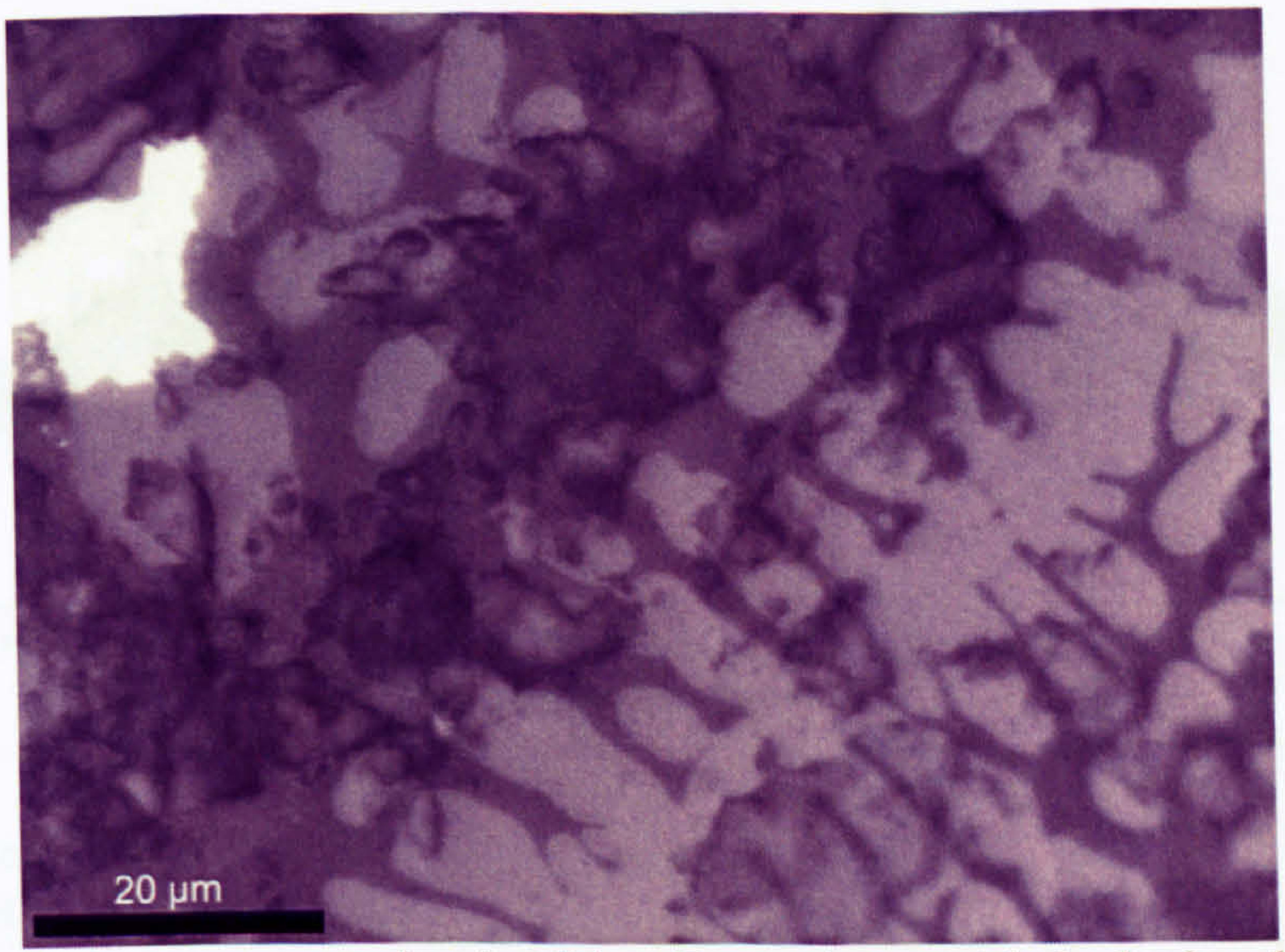
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO

Sample No. KAT10

Macroscopic features

Size	3.00 cm
Weight	16.00 g
Colour	black
Texture	ropey
Porosity	low
Inclusions	no
Weathering	low
Magnetism	yes

Optical microscopy

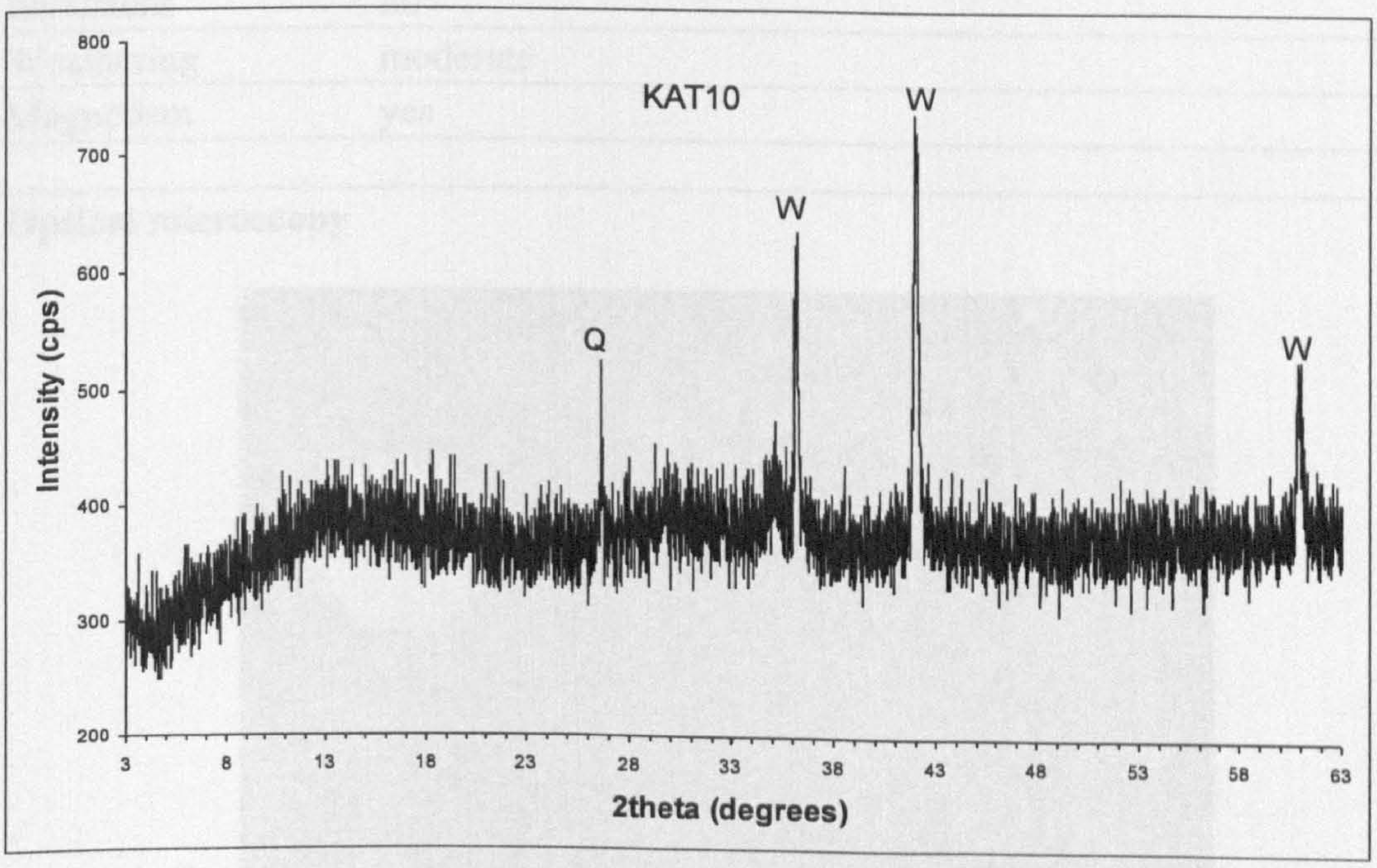


Vesicular matrix/Frequent wüstite dendrites/Large iron oxide inclusion (x 1000)

SEM image

Faylite crystals in a glassy dark matrix with wustite dendrites are the major phases. Magnetite is also present in form of dark grey crystals and small droplets of metallic iron appear as white spots.

XRD



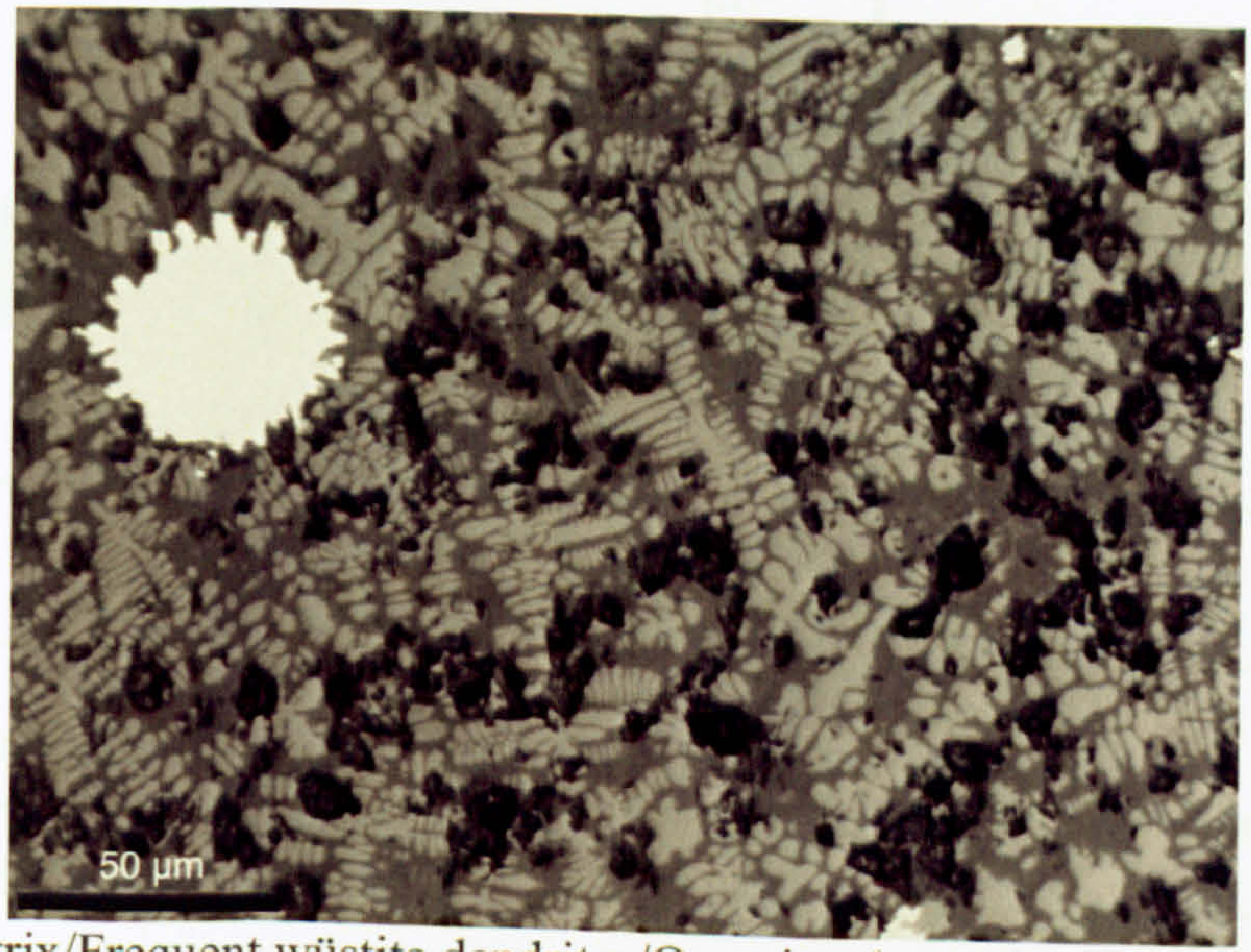
Intensity curve of sample:
Qz: Quartz-SiO_2, Wu: Wustite-FeO

Sample No. VTH01

Macroscopic features

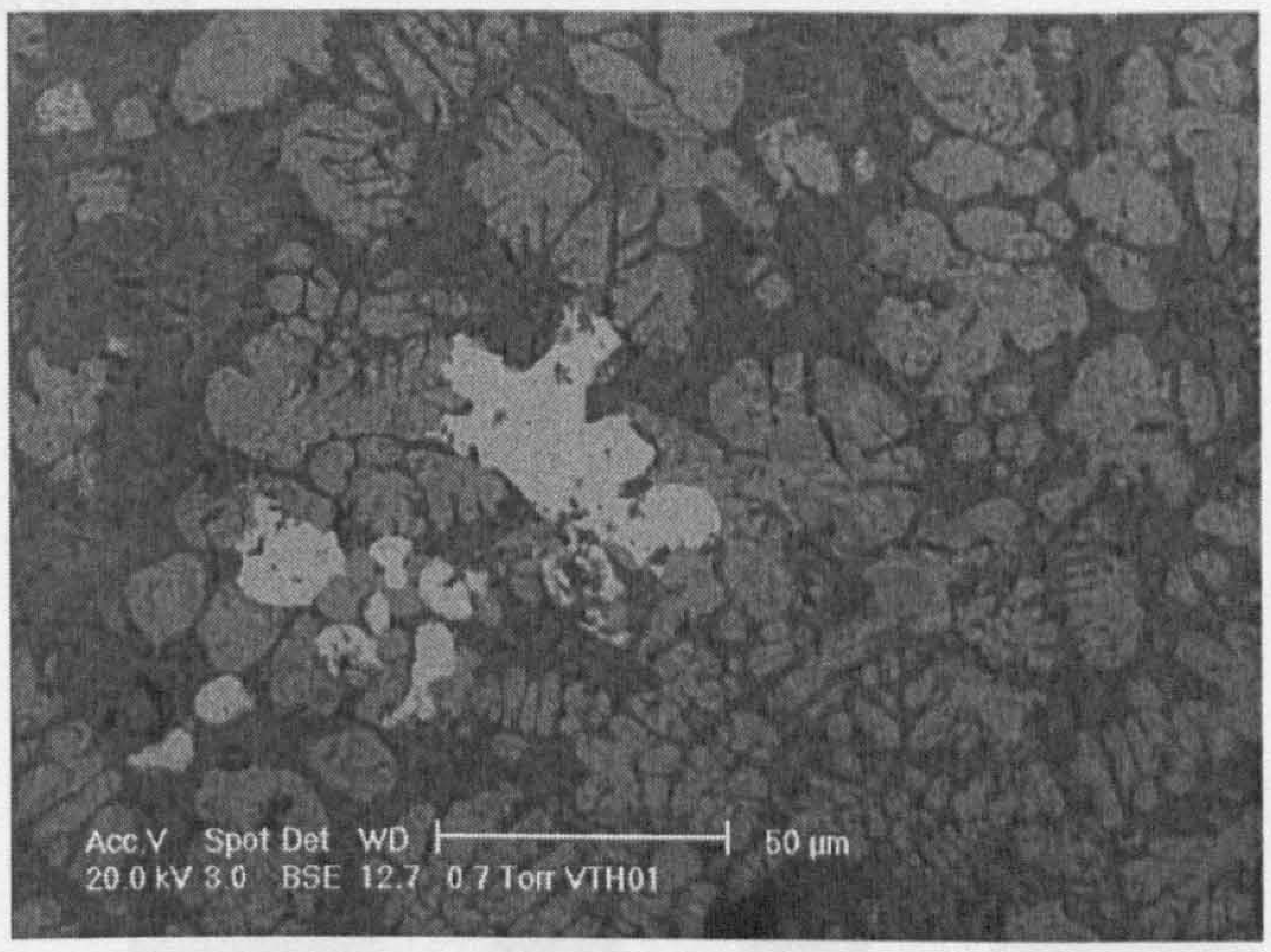
Size	5.00 cm
Weight	90.00 g
Colour	black
Texture	spongy
Porosity	high
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy



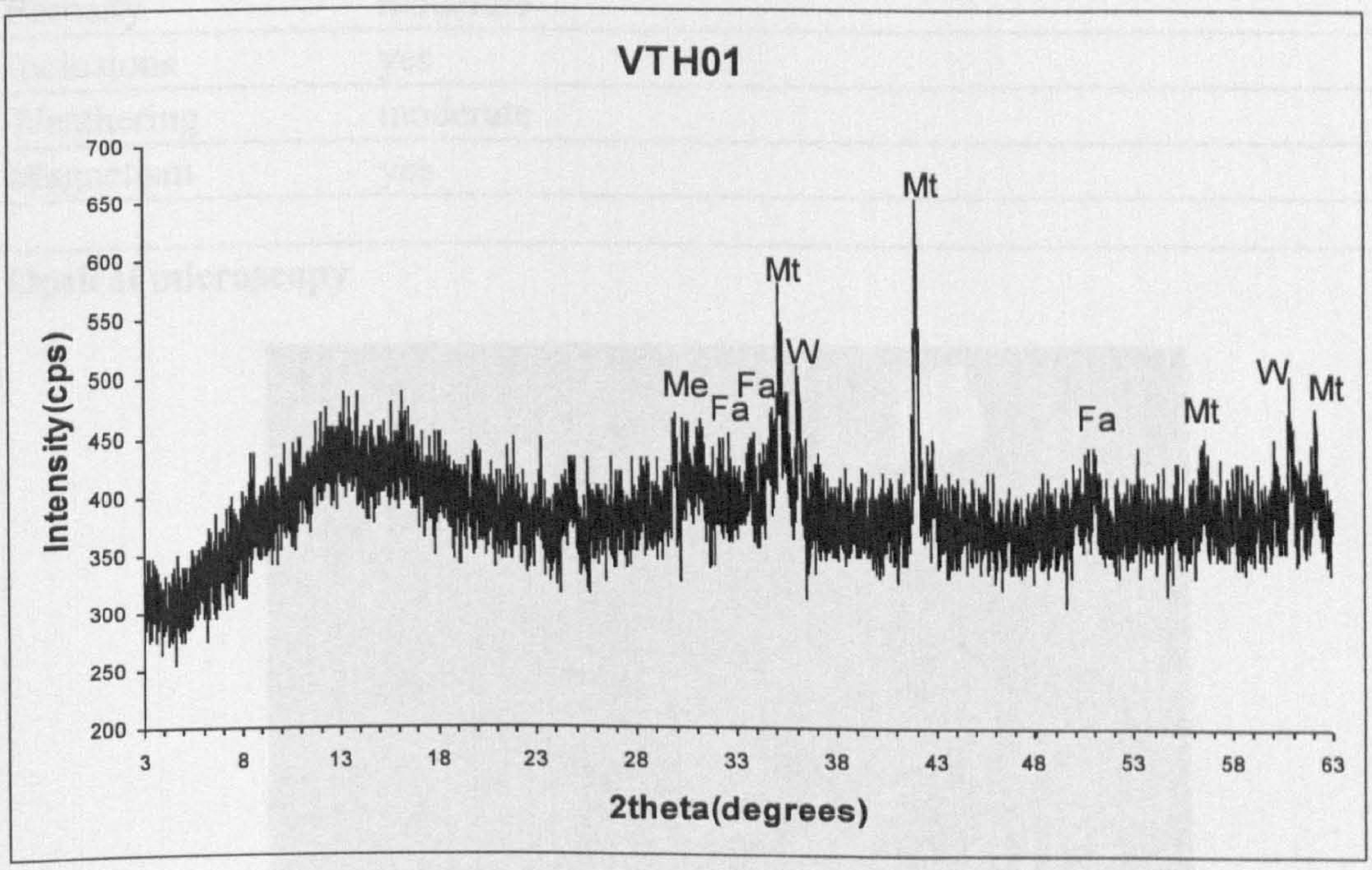
Vesicular matrix/Frequent wüstite dendrites/Occasional rounded metallic prills (200x)

SEM image



The fayalitic matrix shows as a dark grey background over which magnetite and wüstite phases spread across the area. Occasional brighter crystals are condensate iron prills.

XRD



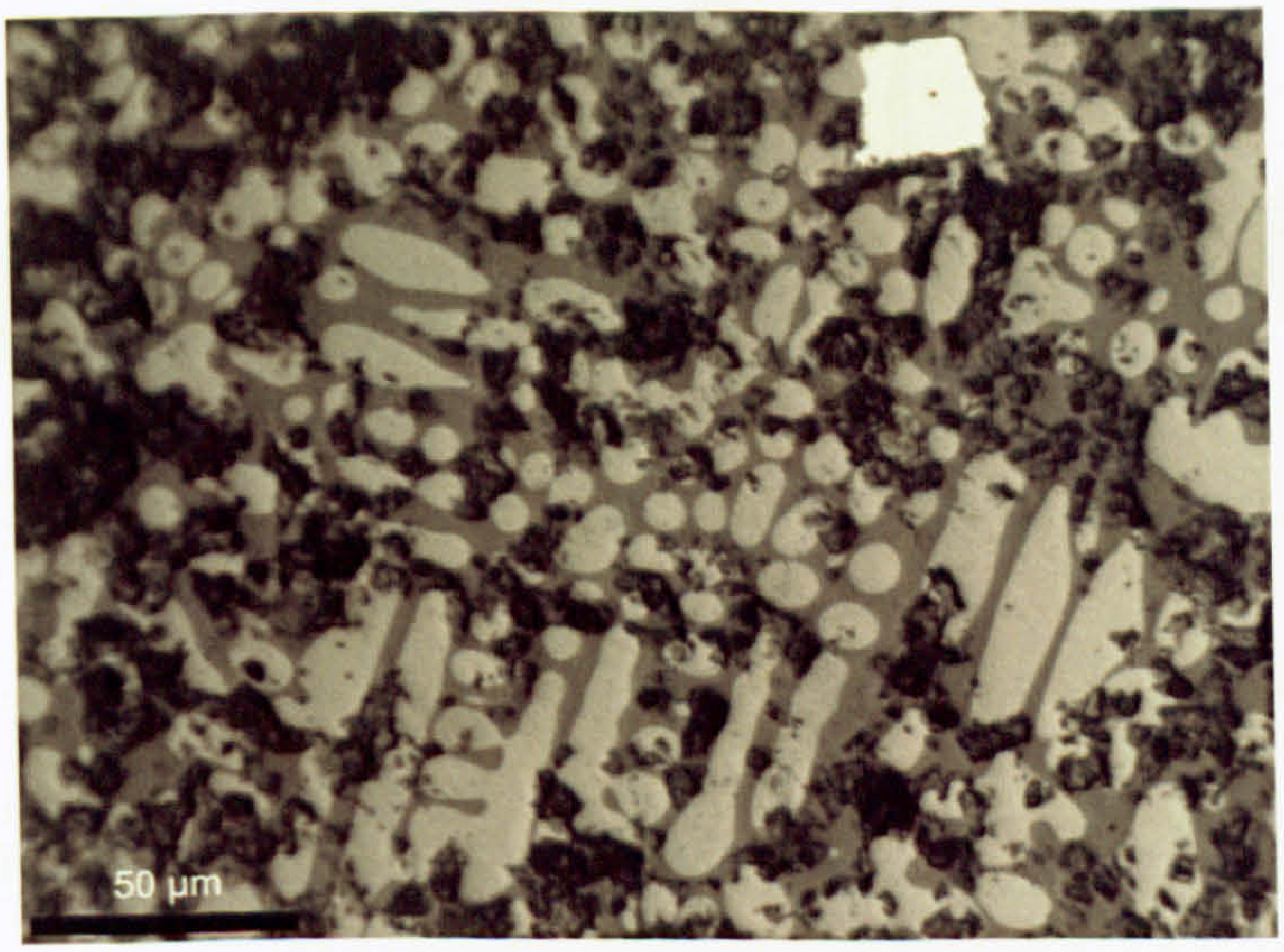
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$

Sample No. VTH02

Macroscopic features

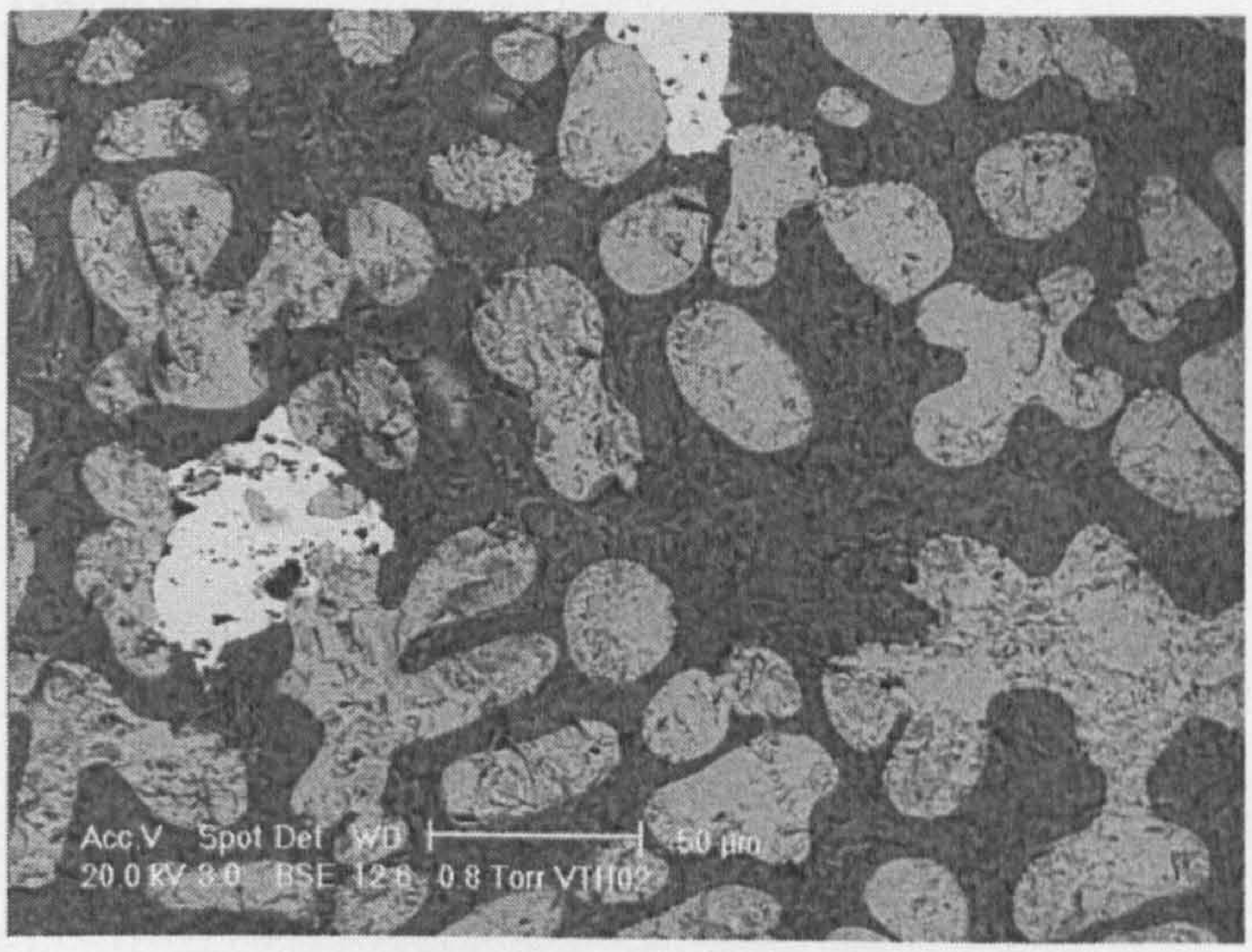
Size	5.50 cm
Weight	73.00 g
Colour	dark brown
Texture	flow
Porosity	moderate
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



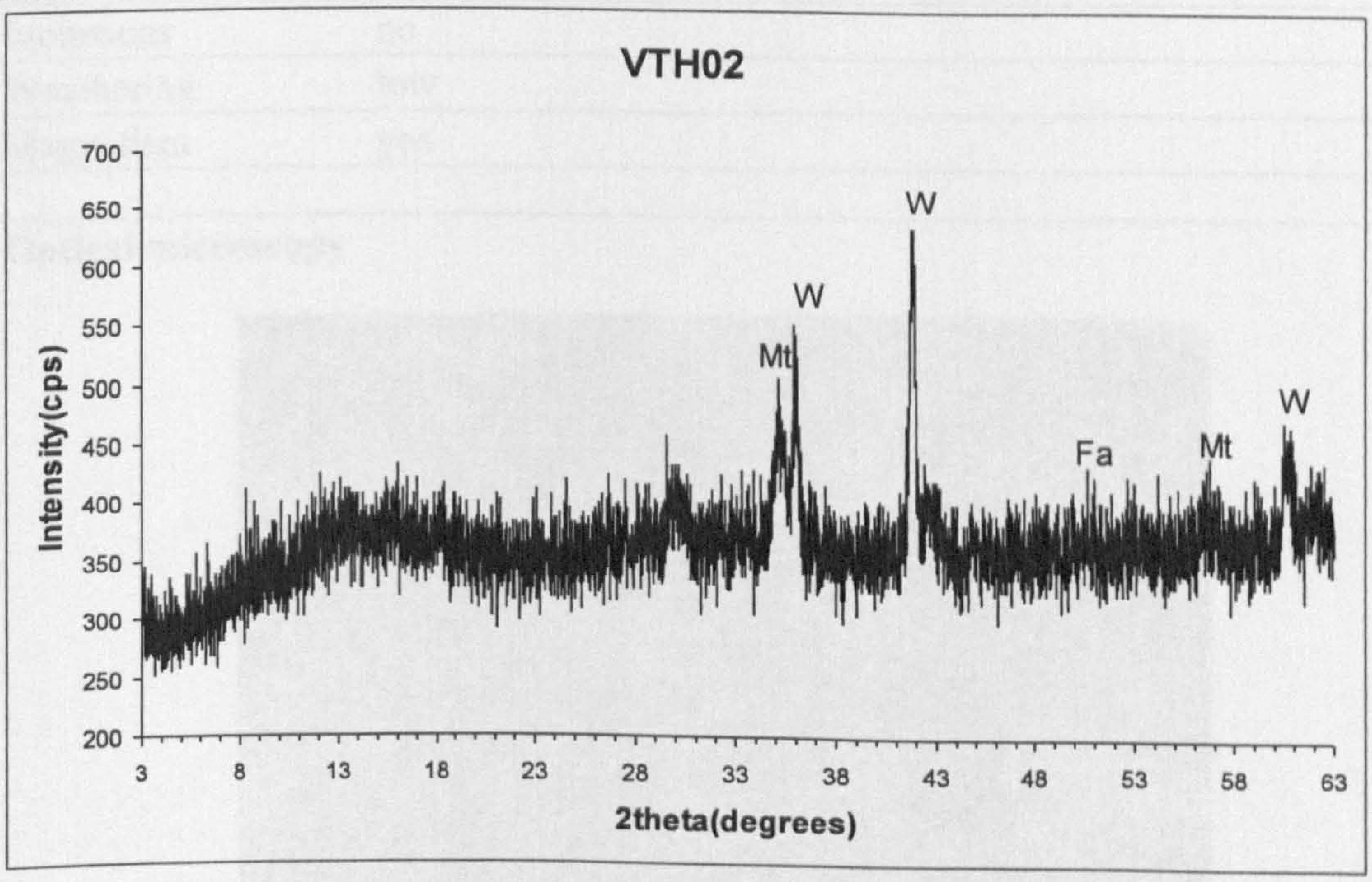
Vesicular matrix/Frequent wüstite dendrites/Occasional metallic prills (200x)

SEM image



Three major phases exist, a darker in colour fayalitic matrix, wustite dendrites of lighter grey and white iron prills.

XRD



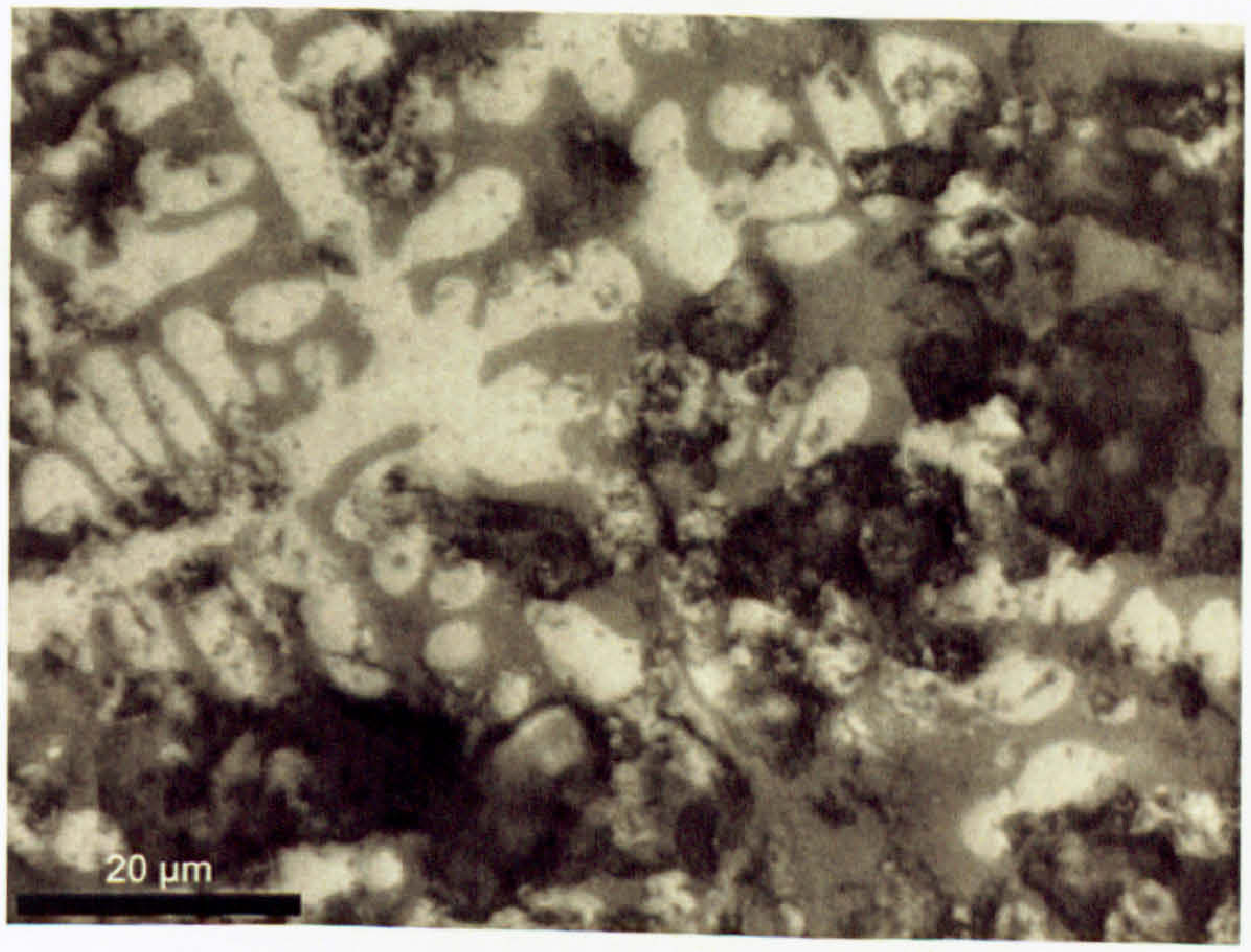
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Fa: Fayalite, Wu: Wustite-FeO

Sample No. VTH03

Macroscopic features

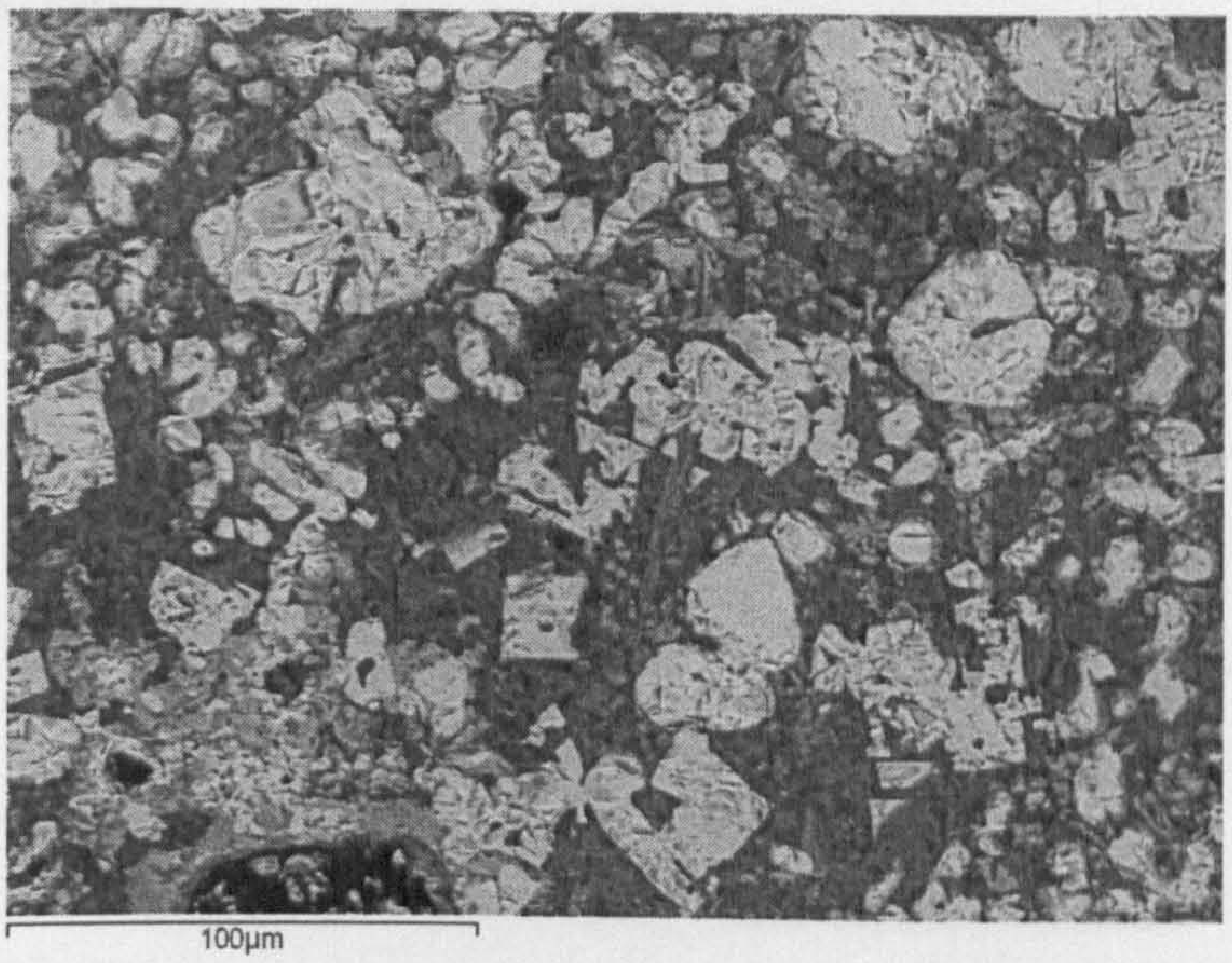
Size	6.50 cm
Weight	125.50 g
Colour	black
Texture	flow
Porosity	high
Inclusions	no
Weathering	low
Magnetism	yes

Optical microscopy



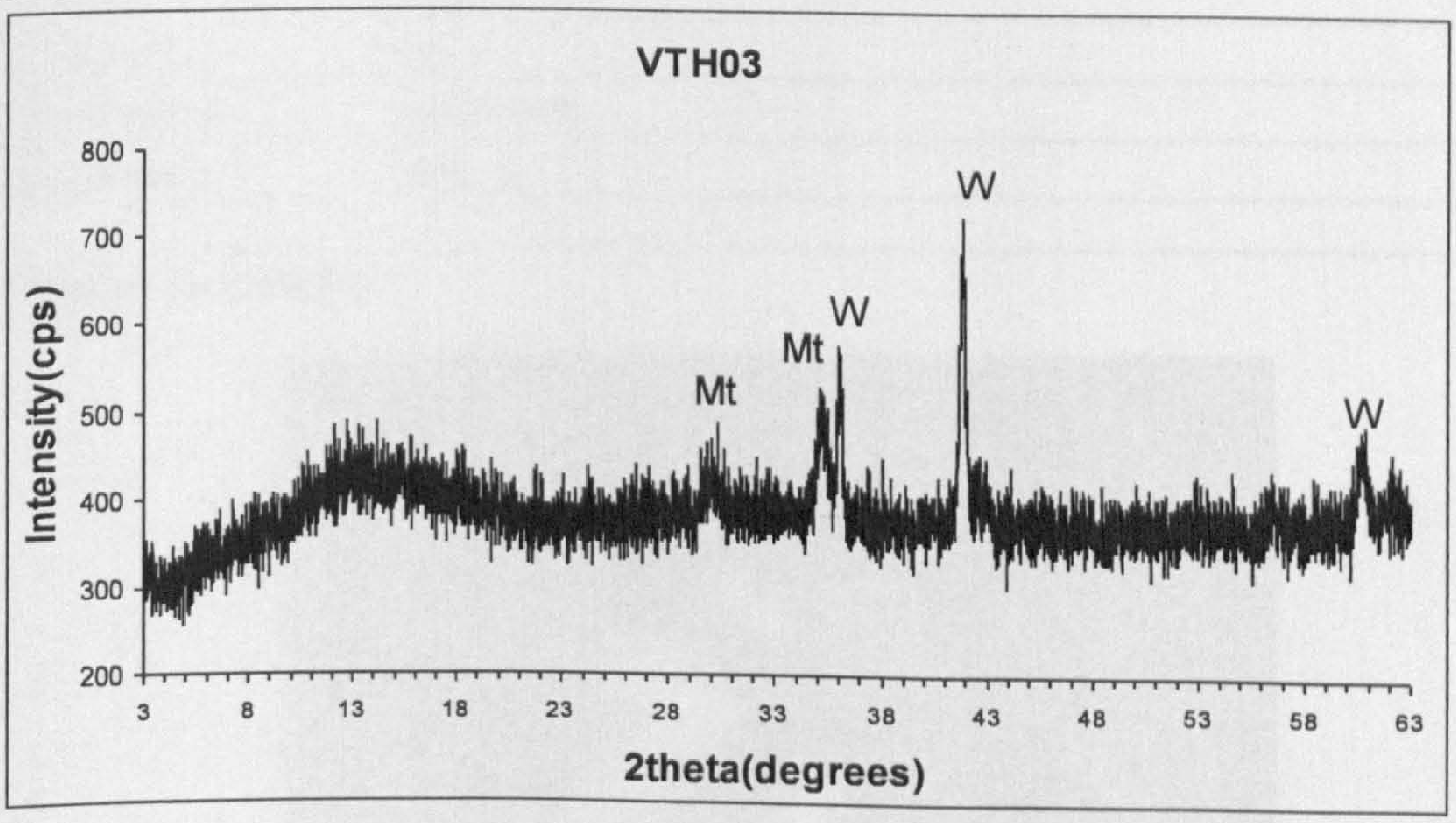
Vesicular matrix/Occasional wüstite dendrites/Some metallic prills (200x)

SEM image



The microstructure is characterized by a fayalitic matrix with frequent wüstite dendrites and occasional magnetite crystals.

XRD



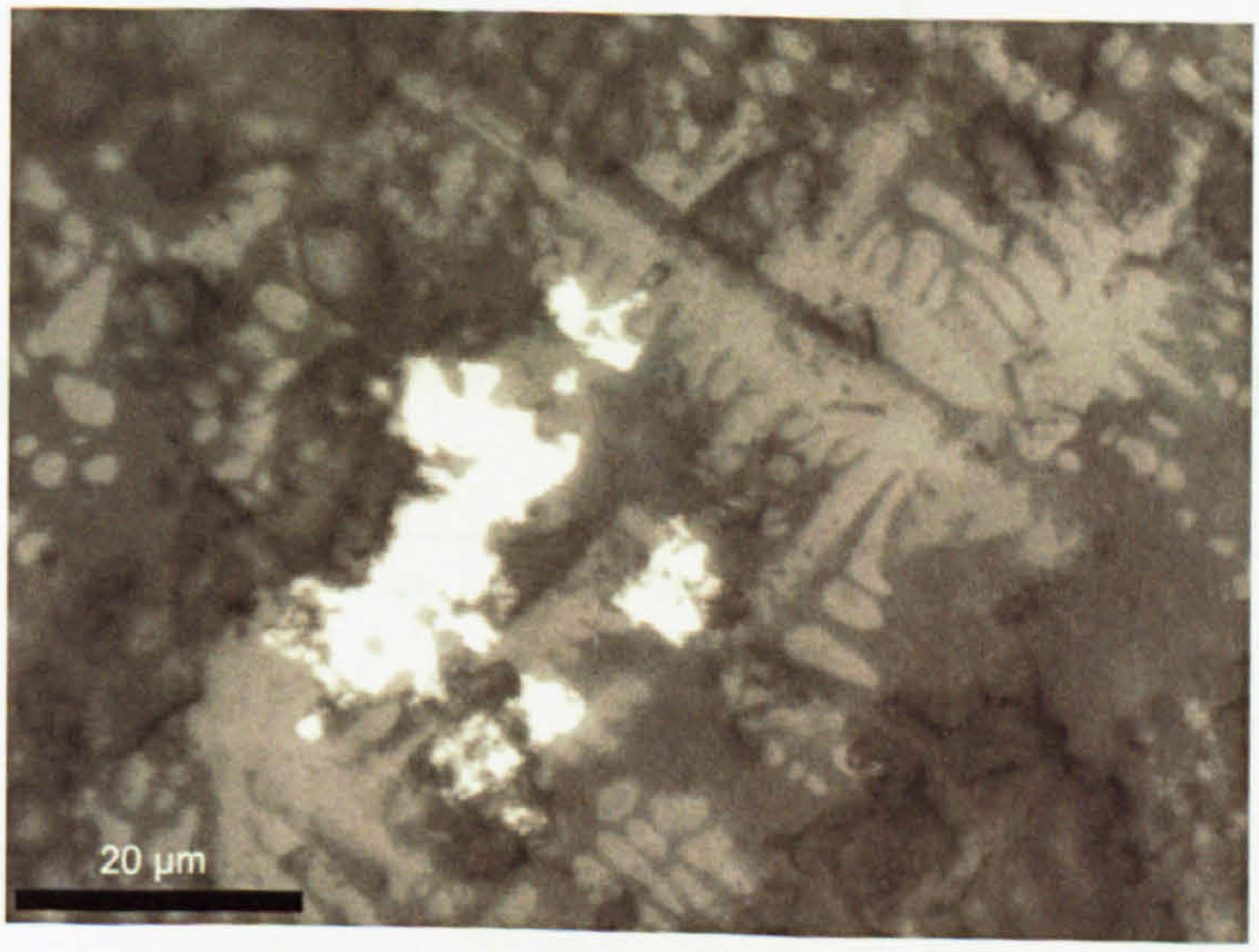
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO

Sample No. VTH04

Macroscopic features

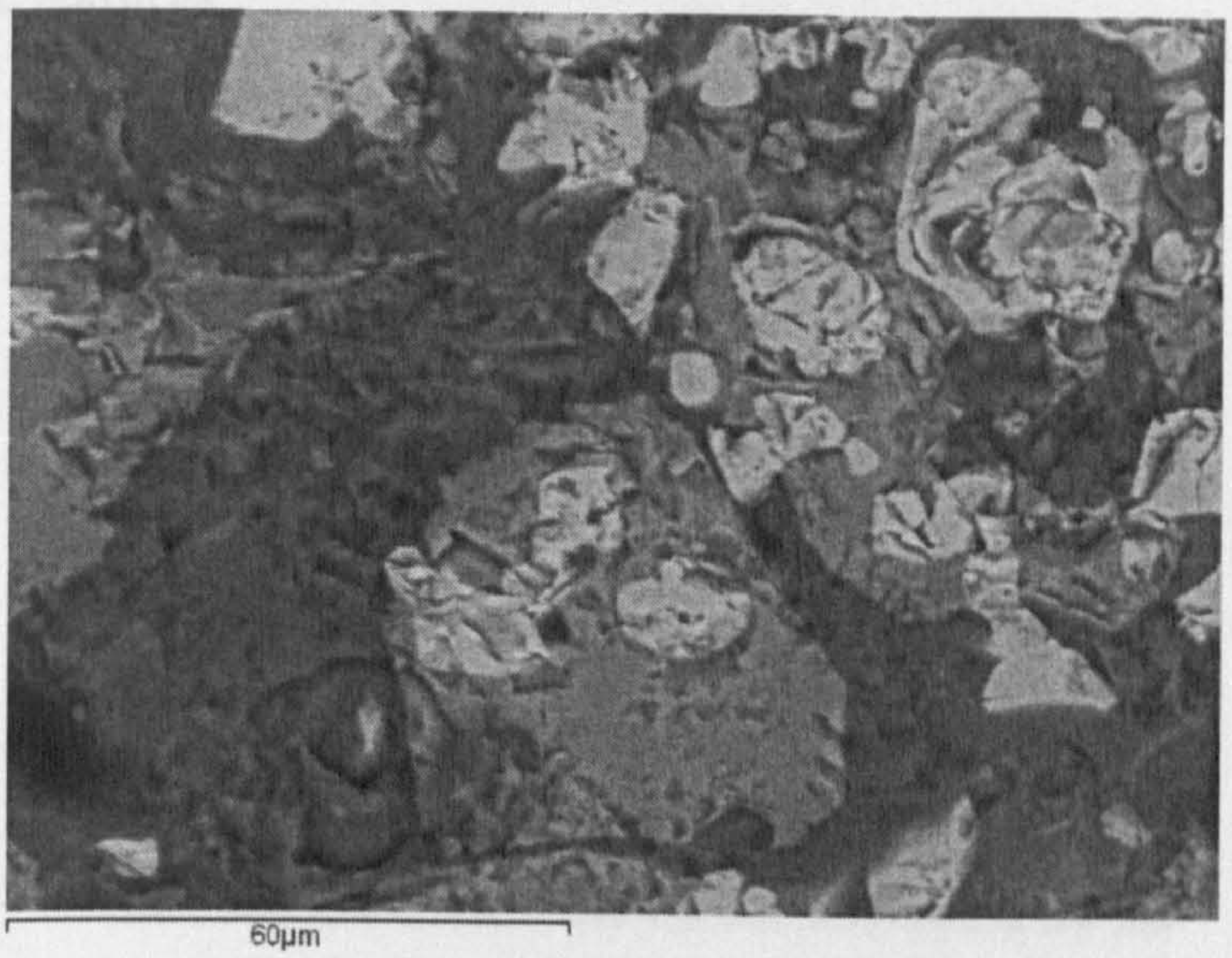
Size	5.00 cm
Weight	57.00 g
Colour	dark brown
Texture	flow
Porosity	high
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy



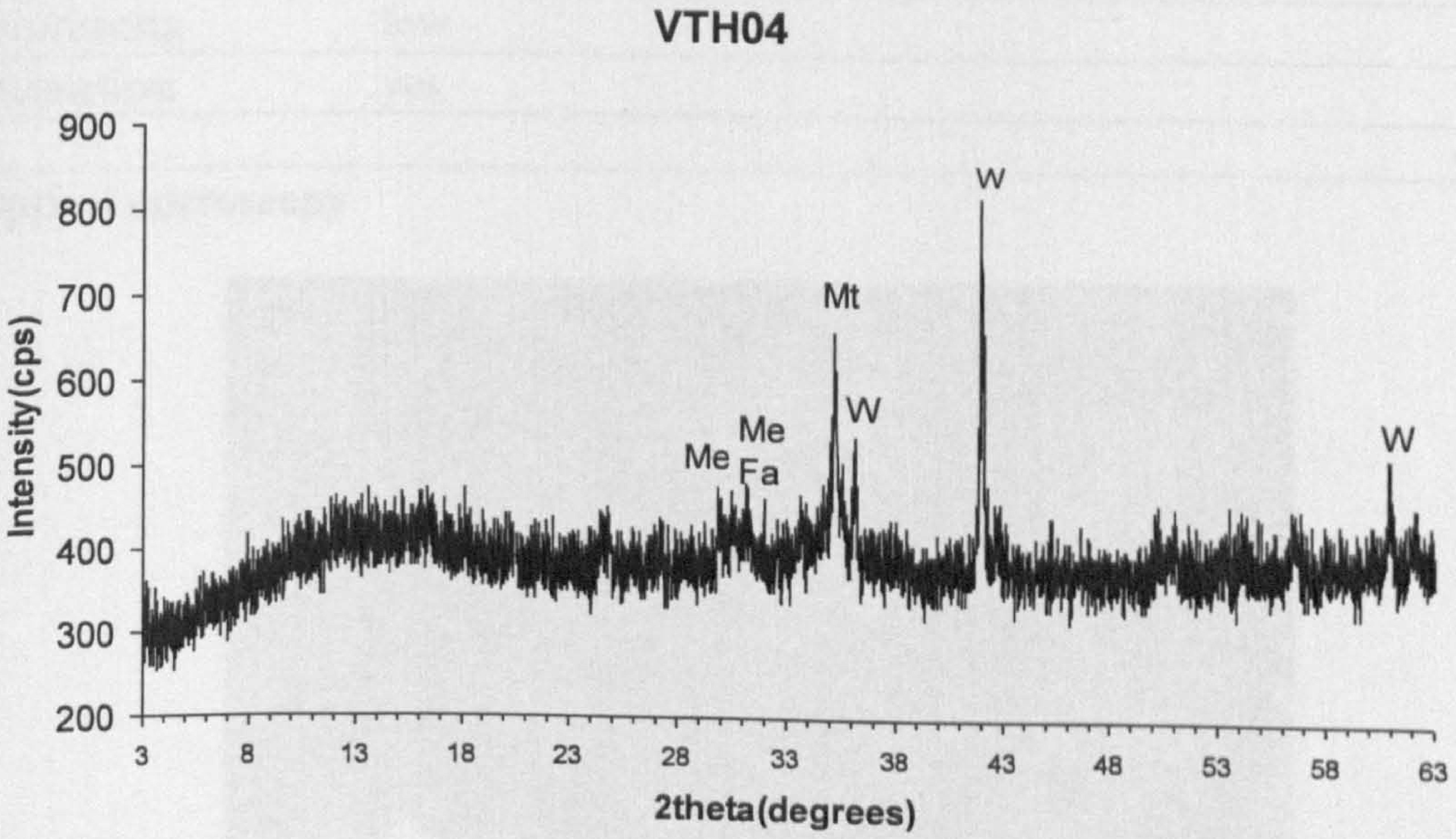
Vesicular matrix/Frequent wüstite dendrites/Occasional metallic prills in clusters (200x)

SEM image



Crystals of wustites (light grey) and magnetite (dark grey) abound on a siliceous matrix (grey-black).

XRD



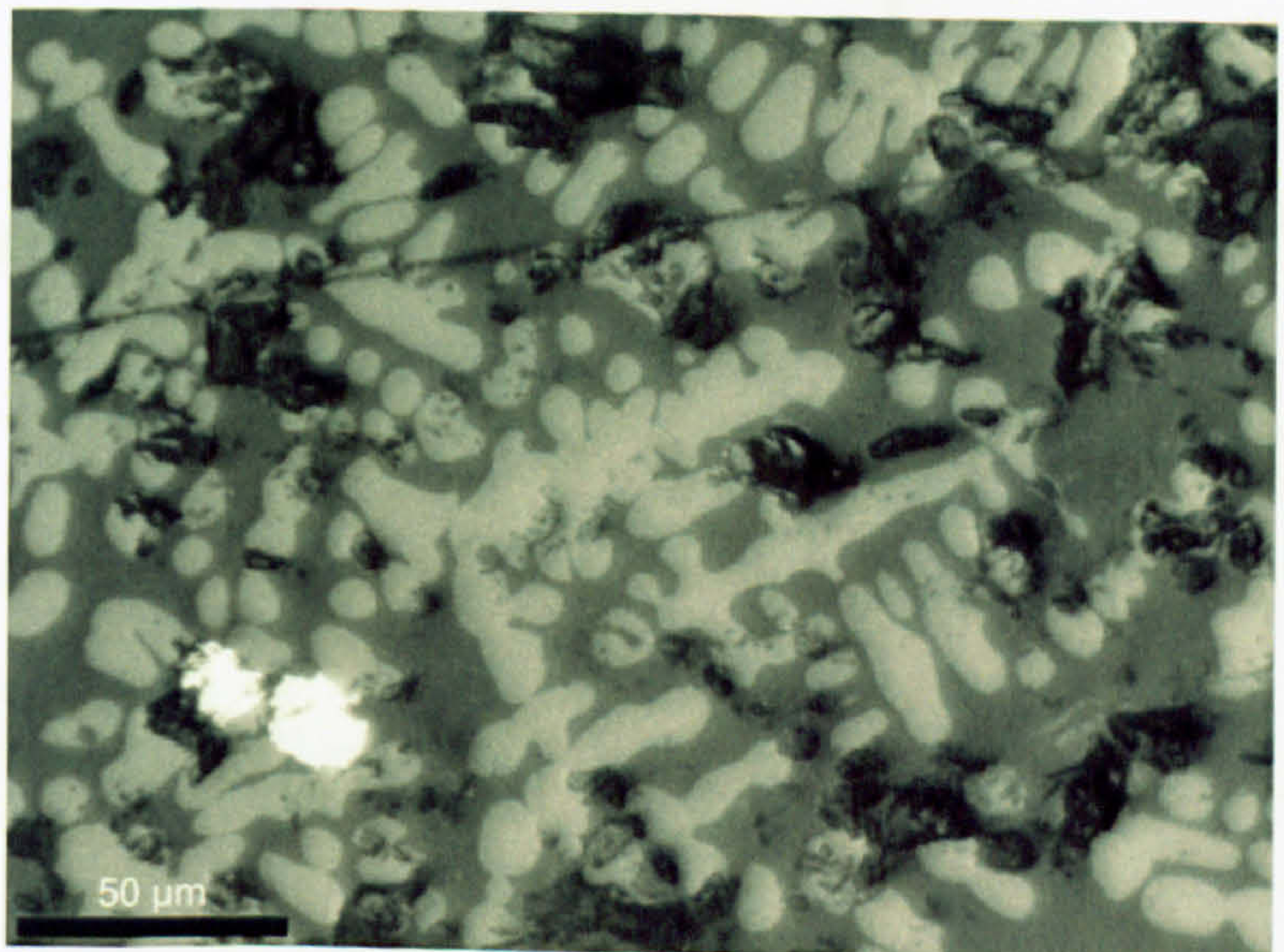
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO

Sample No. VTH05

Macroscopic features

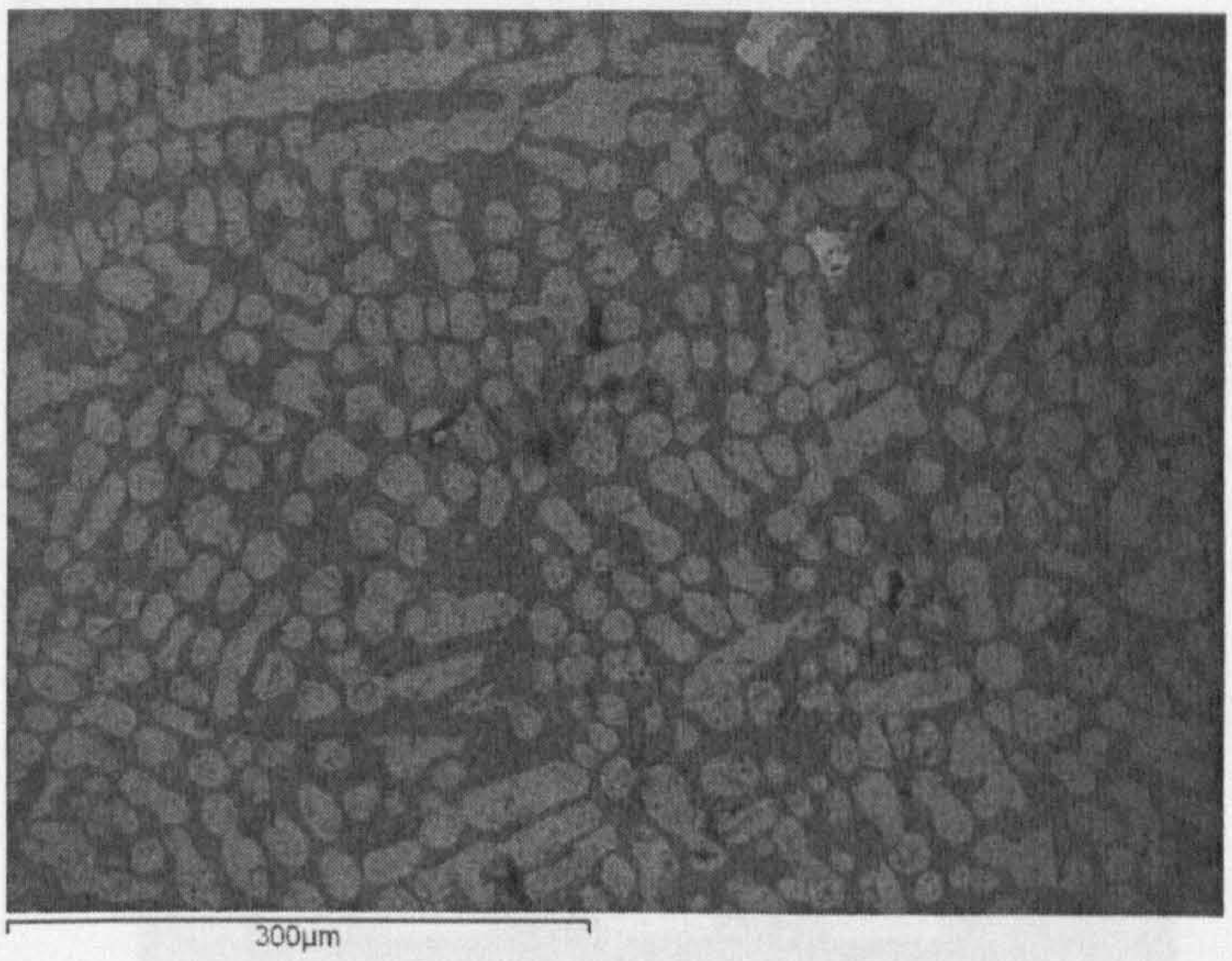
Size	5.00 cm
Weight	61.50 g
Colour	black
Texture	flow
Porosity	high
Inclusions	no
Weathering	low
Magnetism	yes

Optical microscopy



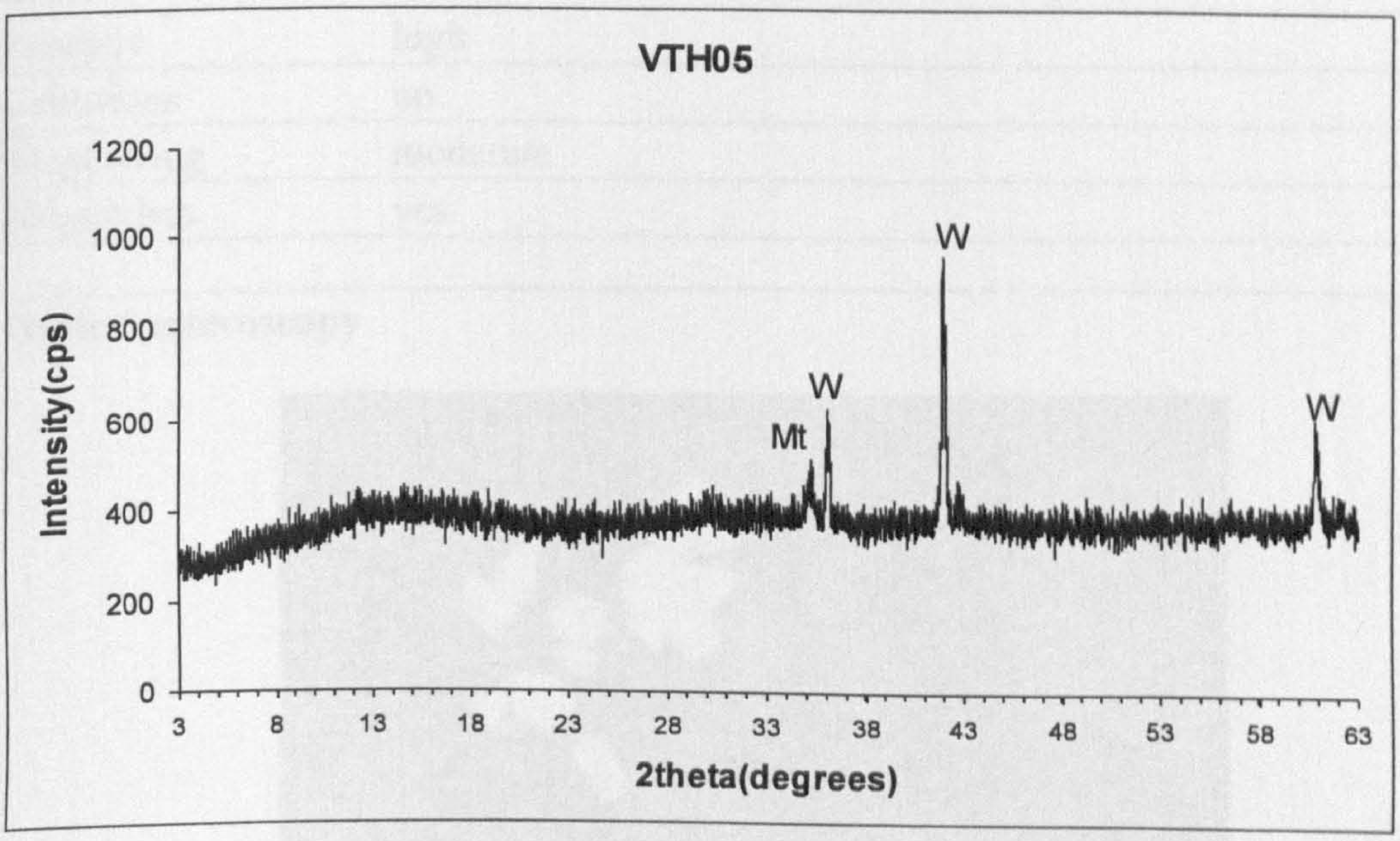
Vesicular matrix/Frequent wüstite dendrites/Frequent metallic prills (200x)

SEM image



Two major phases are present, a siliceous fayalitic matrix and a dendritic network of wustites.

XRD



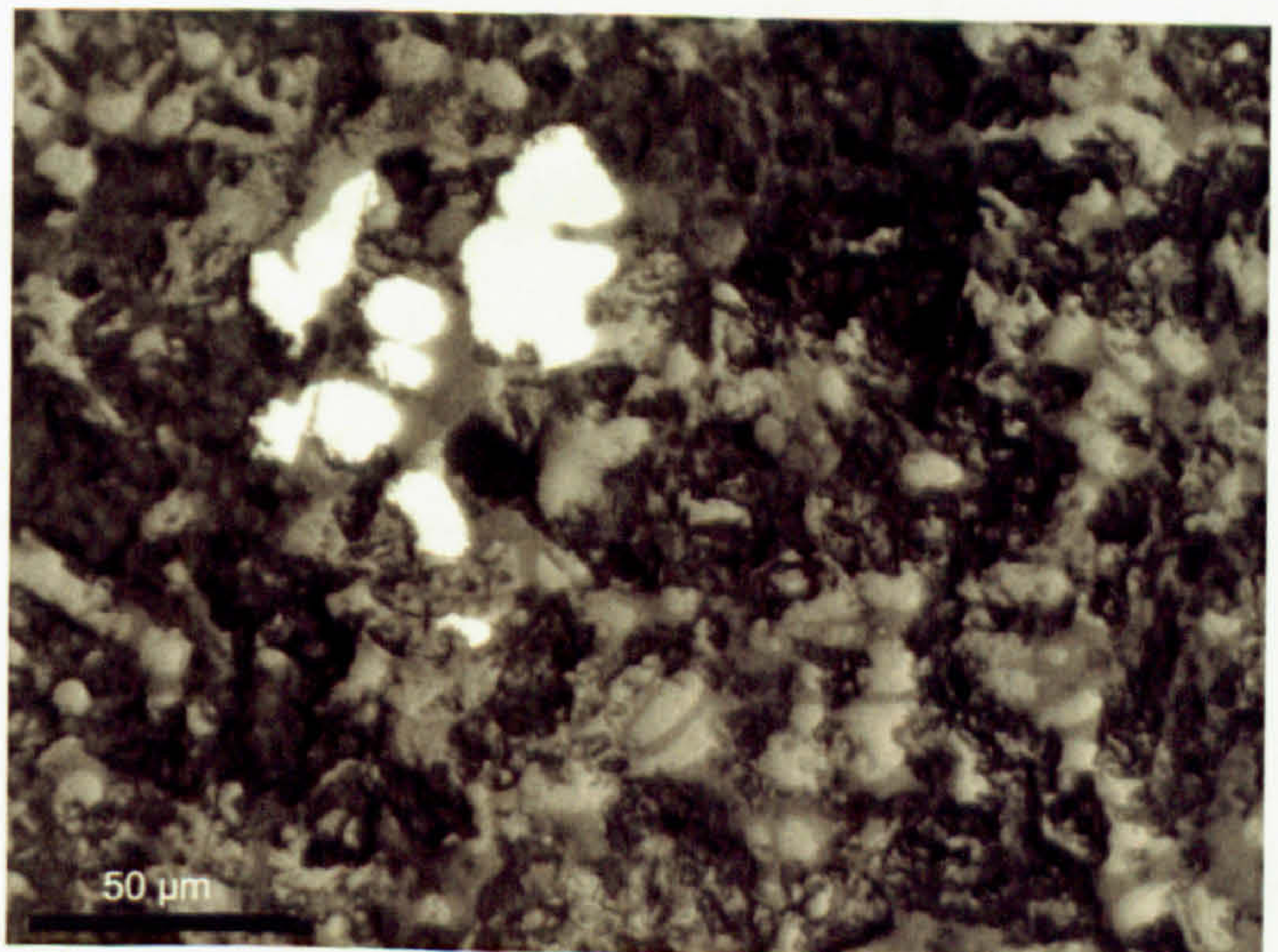
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO

Sample No. VTH06

Macroscopic features

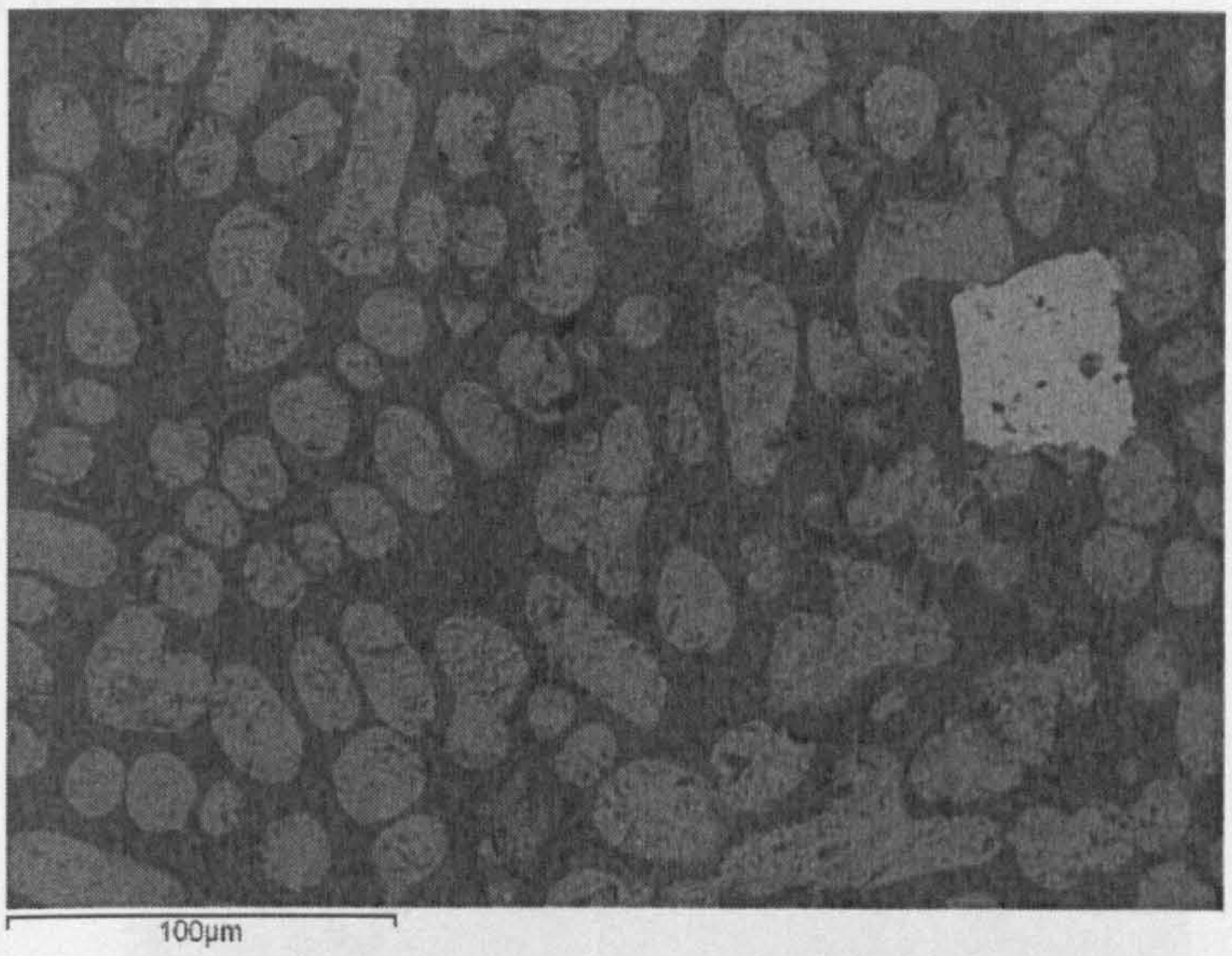
Size	4.50 cm
Weight	50.50 g
Colour	dark brown/black
Texture	spongy
Porosity	high
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy



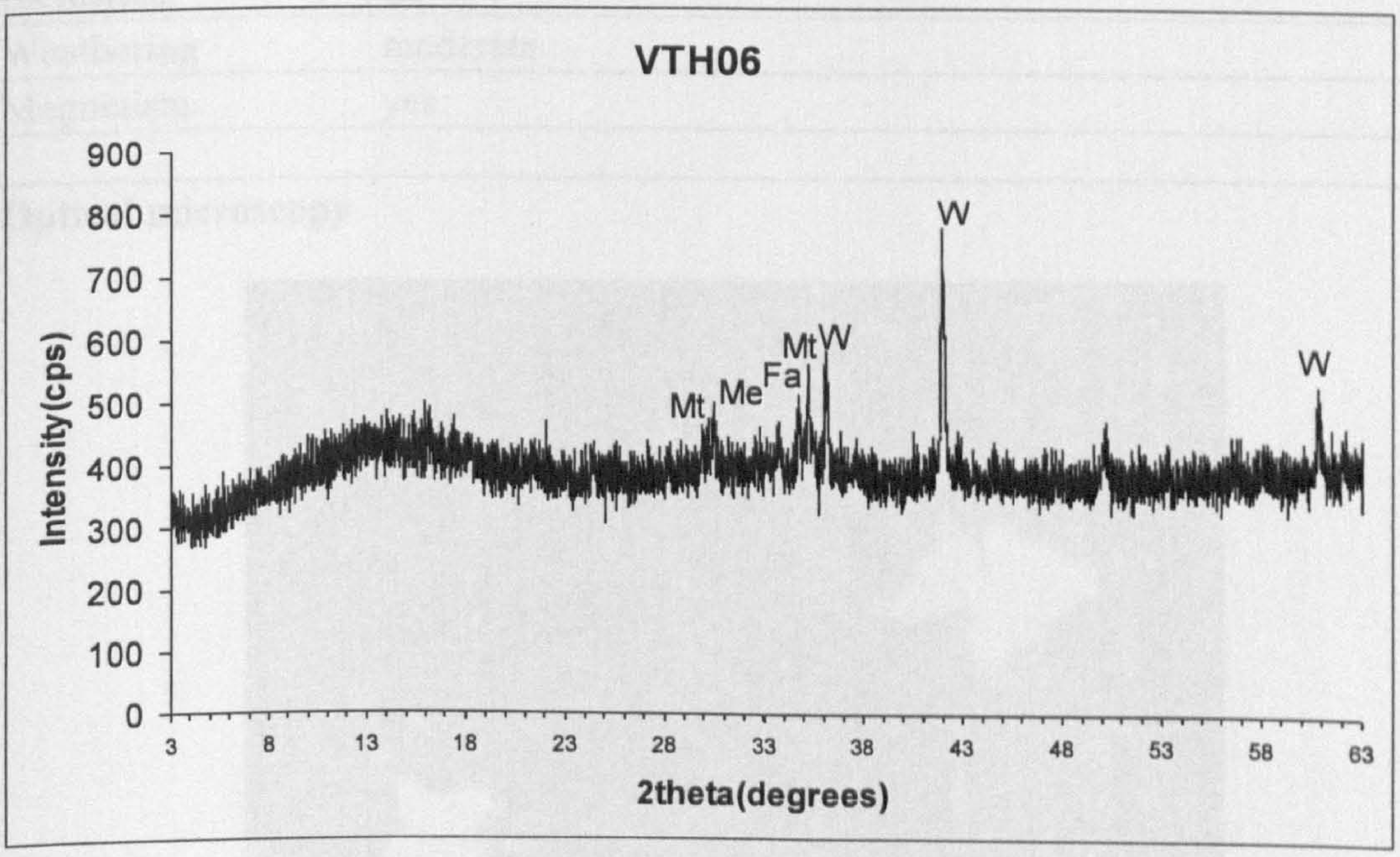
Vesicular matrix/Frequent wüstite dendrites/Occasional metallic prills in clusters (200x)

SEM image



The major phases are the darker in colour fayalitic matrix, the grey wustite dendrites and a brighter rhomboid metallic prill.

XRD



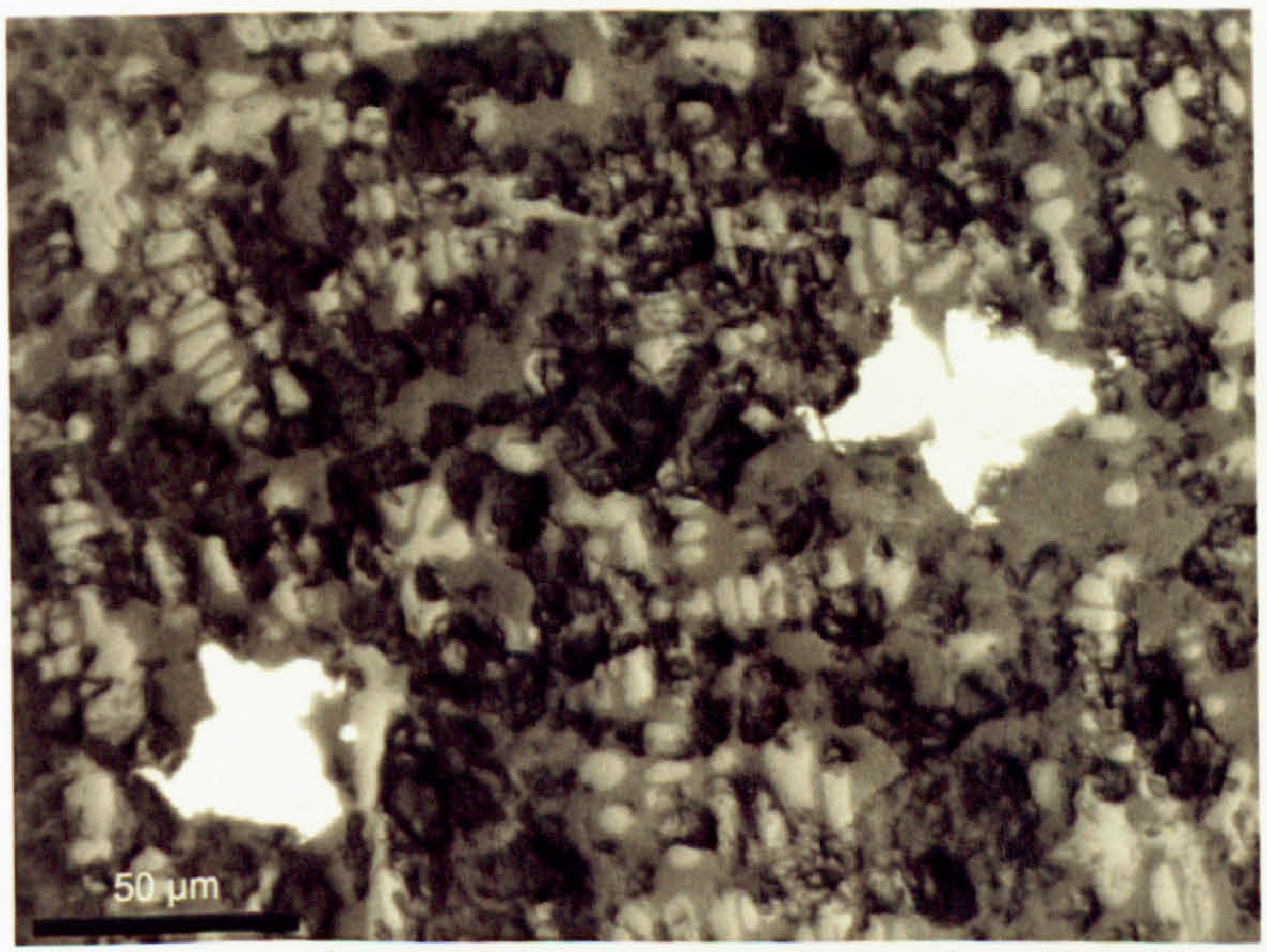
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$

Sample No.	VTH07

Macroscopic features

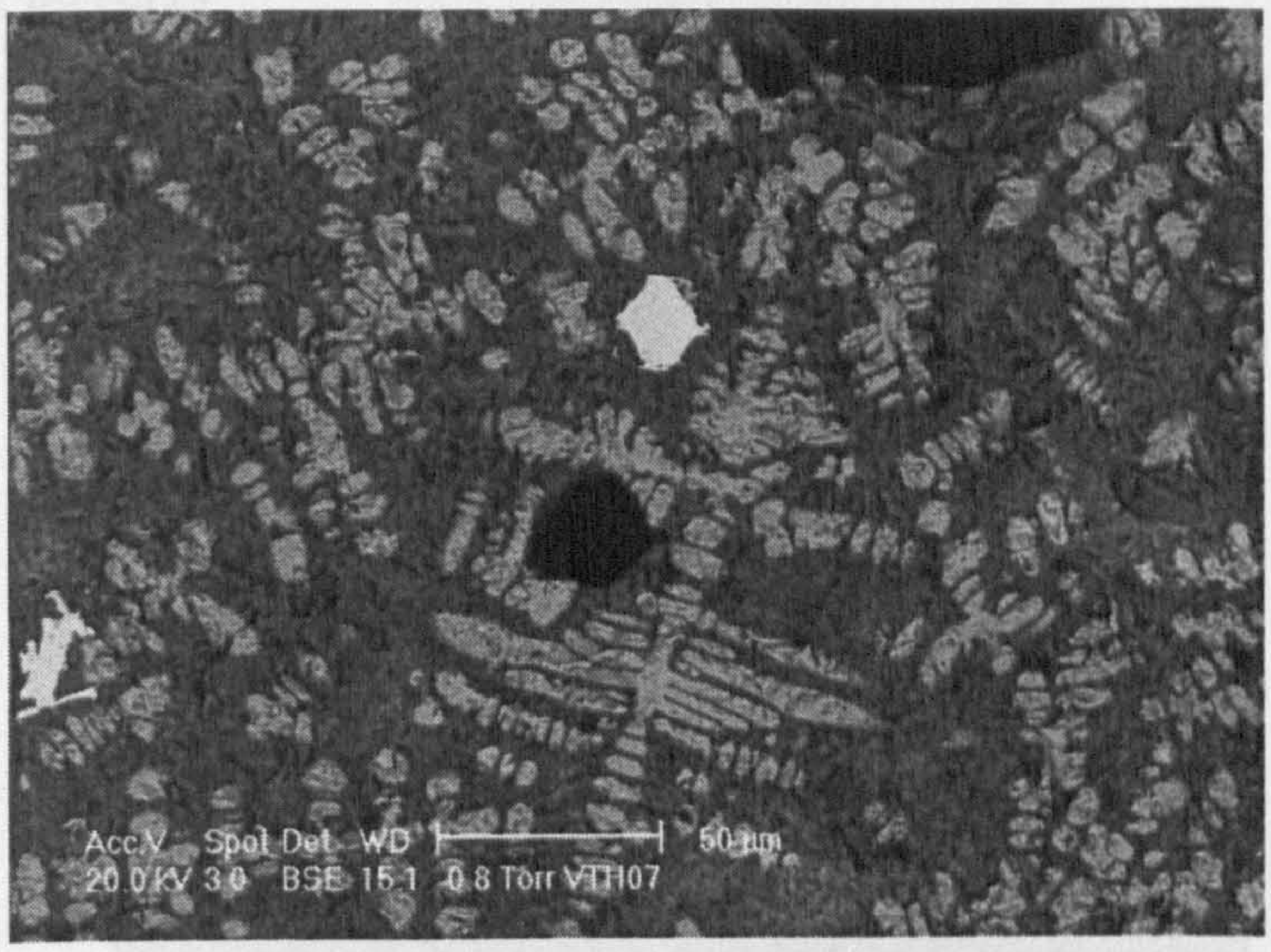
Size	4.50 cm
Weight	57.50 g
Colour	dark grey/black
Texture	spongy
Porosity	high
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy



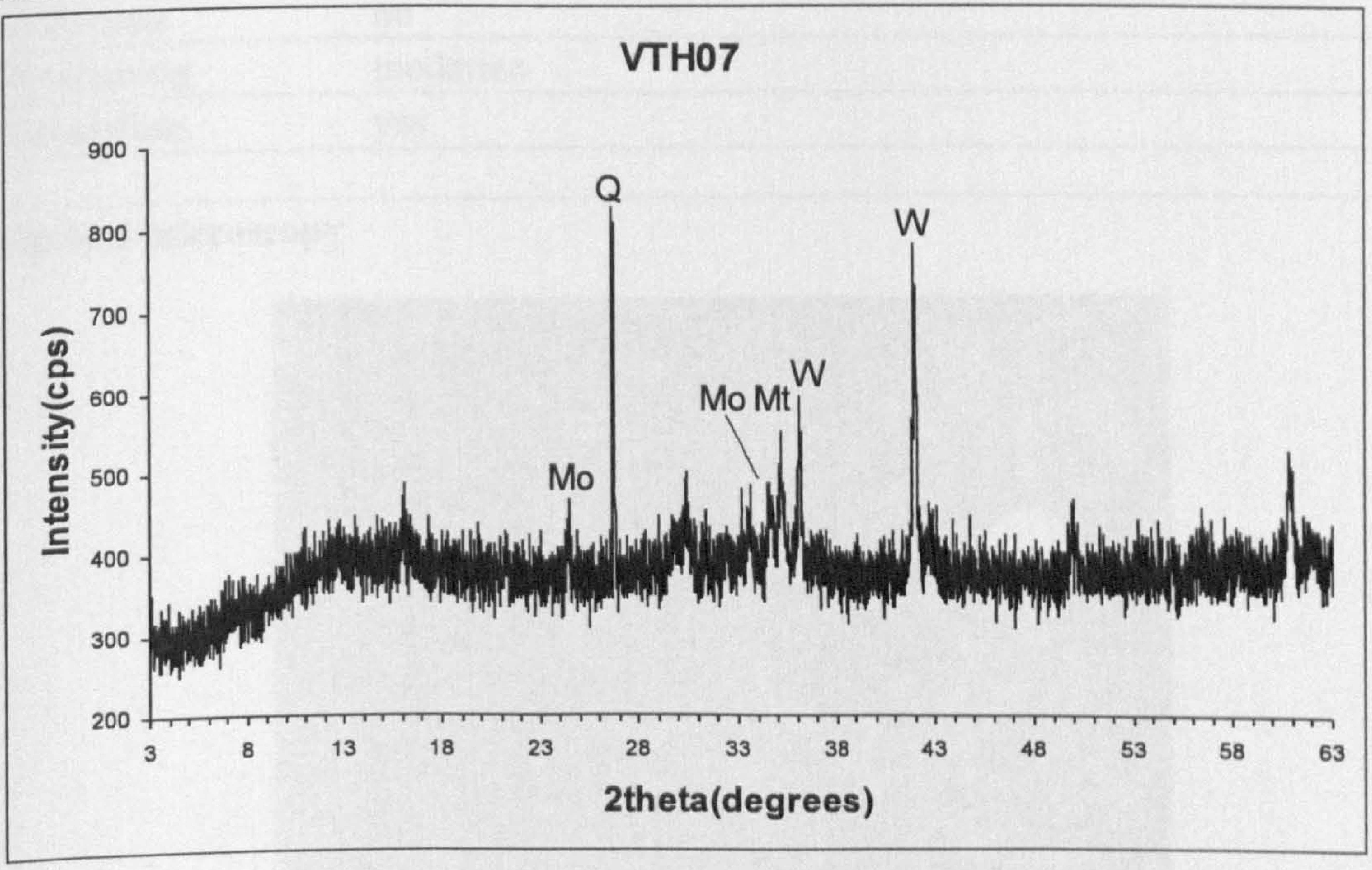
Glassy matrix/Frequent wüstite dendrites/Frequent metallic prills (200x)

SEM image



A dark siliceous, fayalitic matrix and a network of evenly distributed wüstite dendrites predominate. The bright white rhomboid crystal at the top centre is an iron-rich metallic prill.

XRD



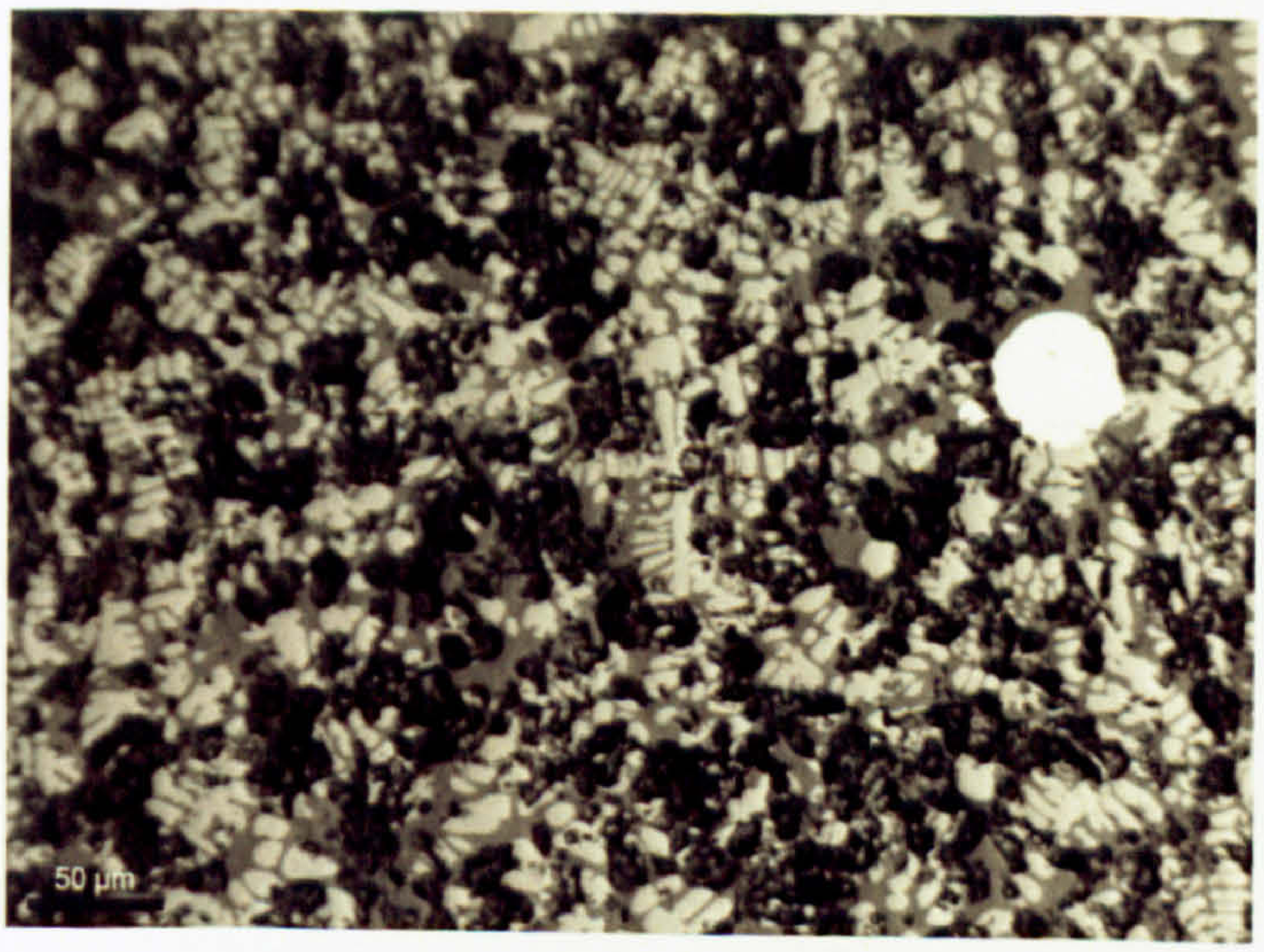
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Mo: Monticellite-$CaMgSiO_4$, Qz: Quartz-SiO_2

Sample No. VTH08

Macroscopic features

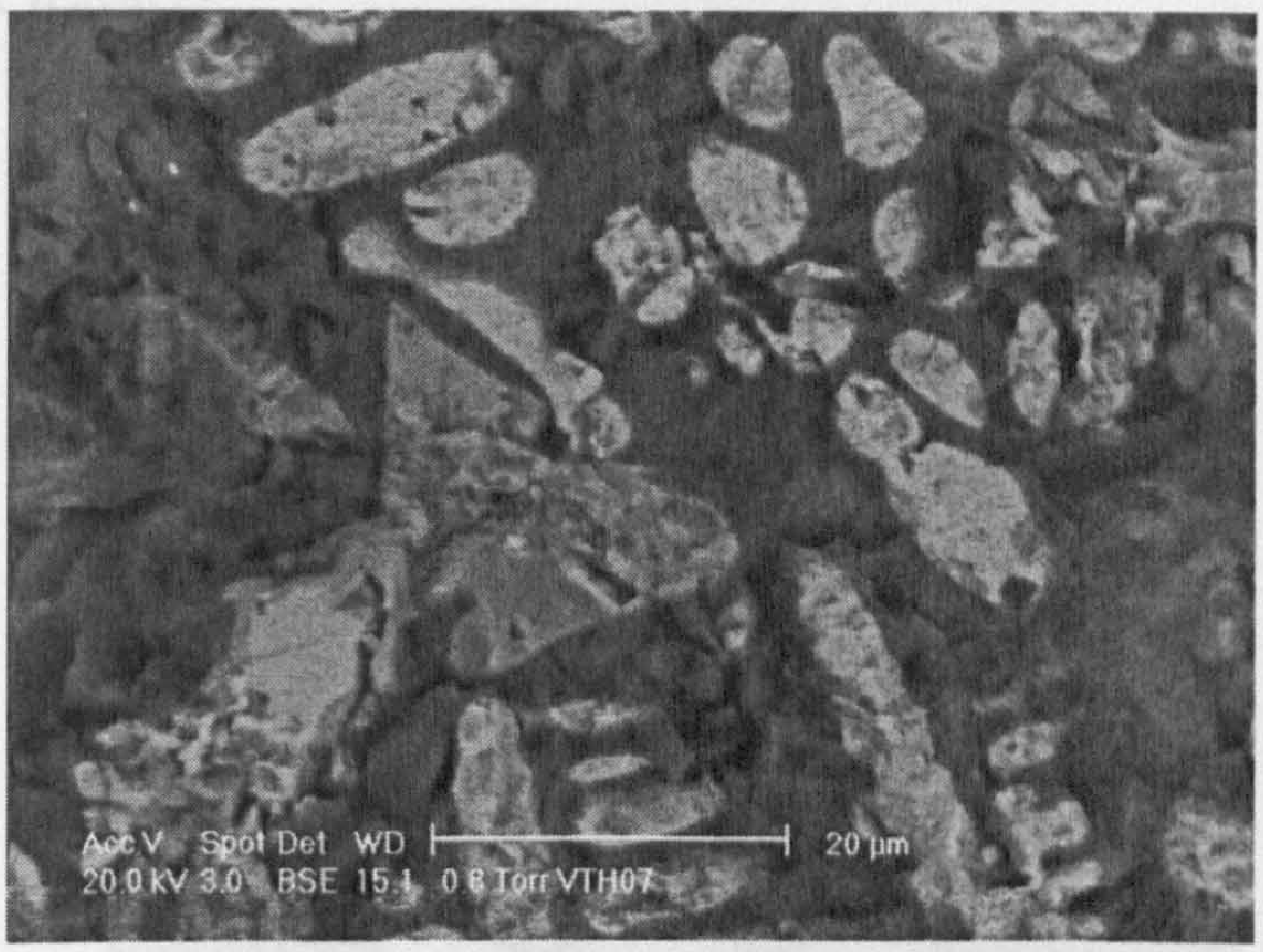
Size	4.00 cm
Weight	32.00 g
Colour	black
Texture	flow
Porosity	high
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy



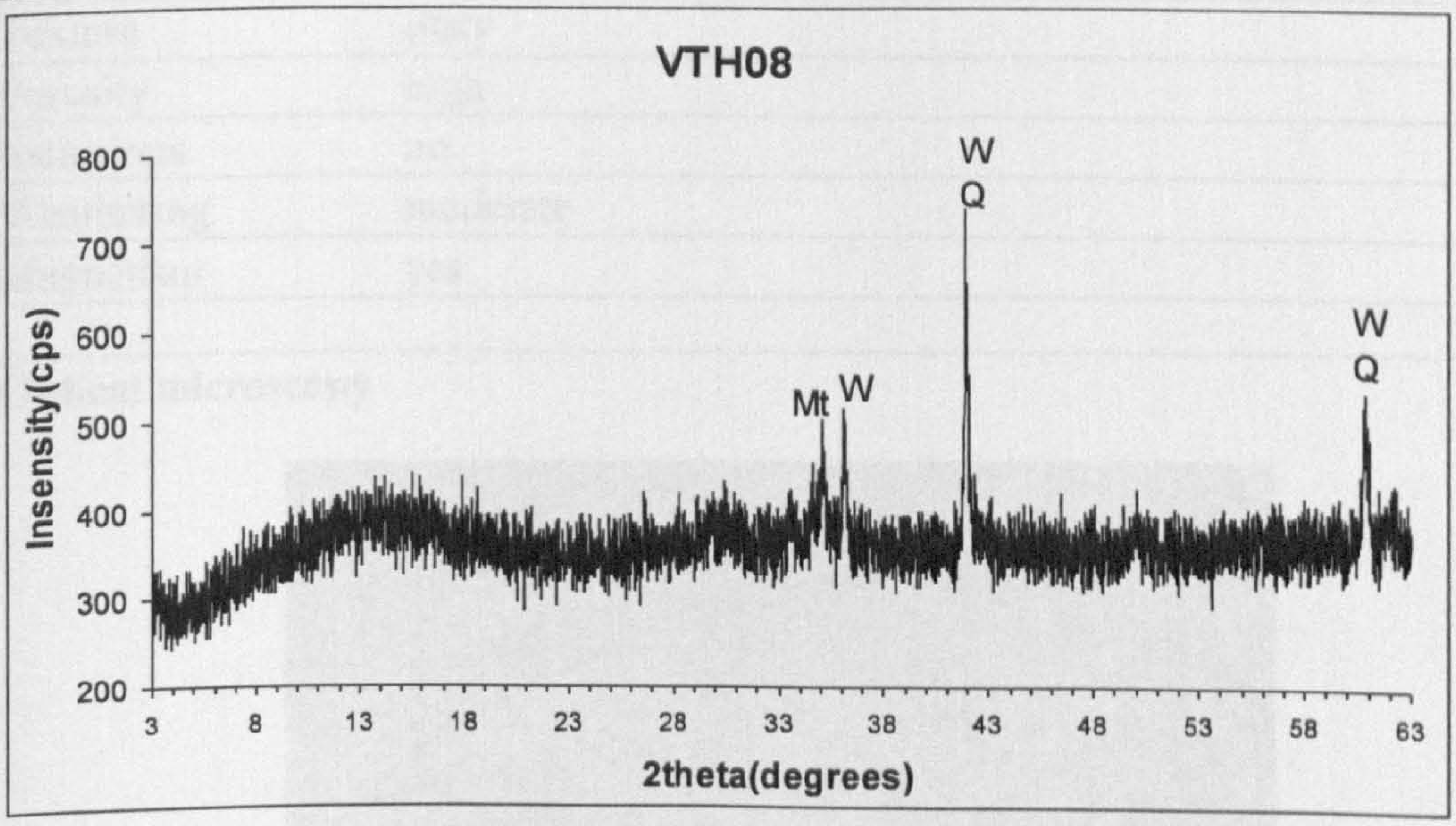
Vesicular matrix/Decomposed wüstite dendrites/Occasional metallic prills (200x)

SEM image



Three major phases are shown, namely the siliceous matrix appearing darker, rounded crystals of wüstite (bright grey) and pointed spinel crystal in the centre.

XRD



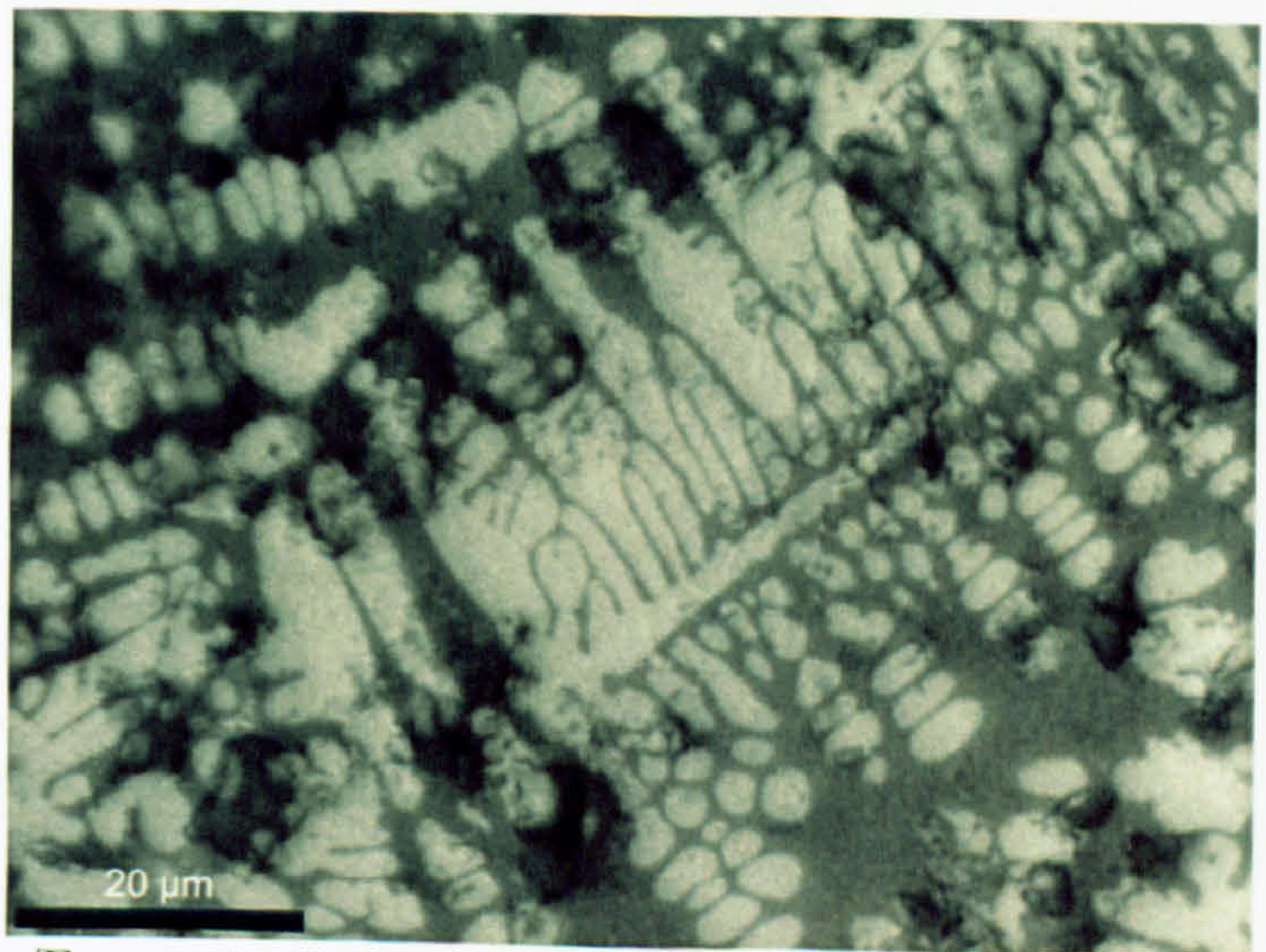
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Qz: Quartz-SiO_2

Sample No. VTH09

Macroscopic features

Size	5.50 cm
Weight	77.00 g
Colour	black
Texture	platy
Porosity	high
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy

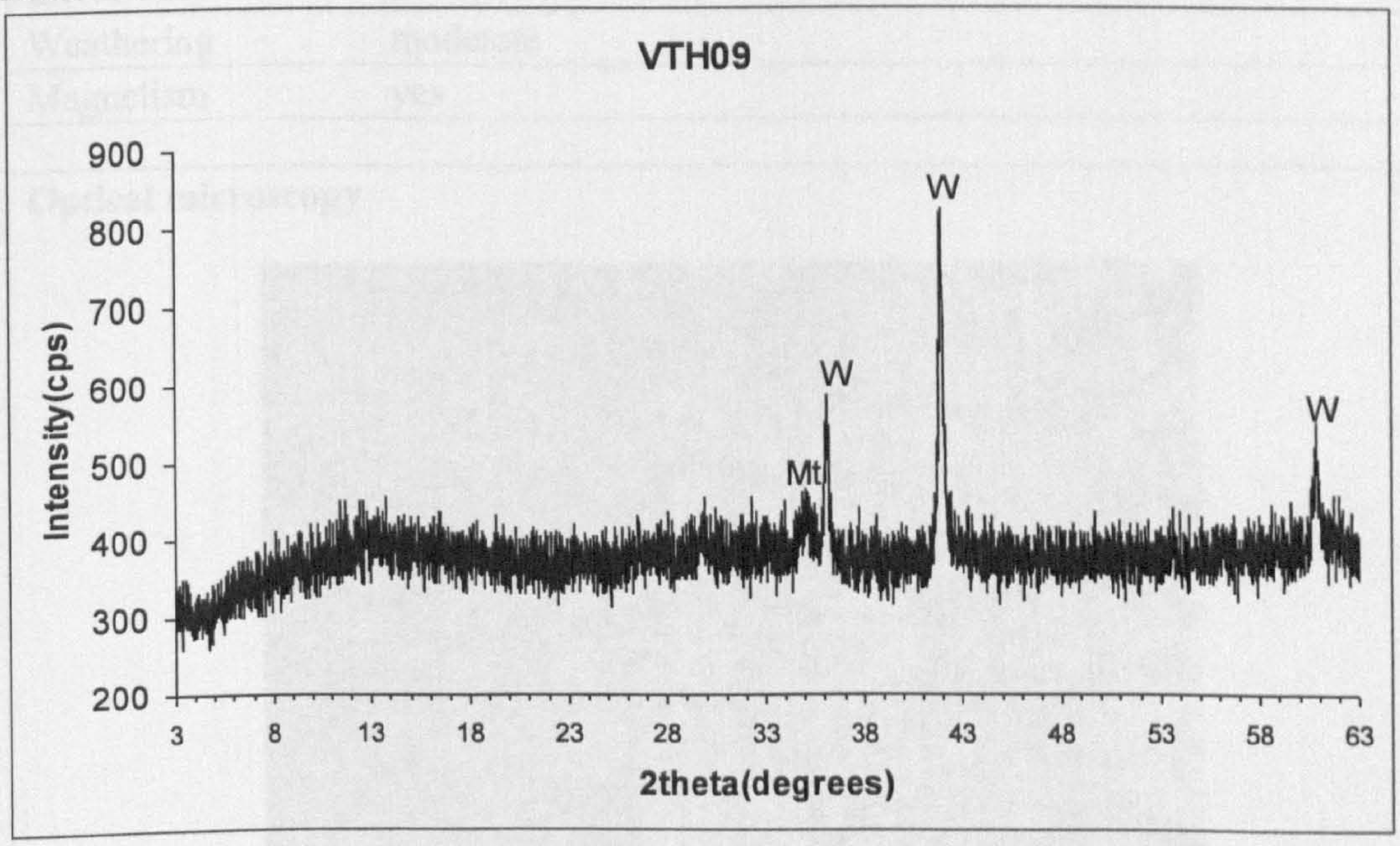


Vesicular matrix/Frequent wüstite dendrites (x 1000)

SEM image

A major characteristic of the micrograph is the fine network of wüstite dendrites spreading across its entire extent over a siliceous matrix. Occasional metallic prills form a small cluster at the top.

XRD



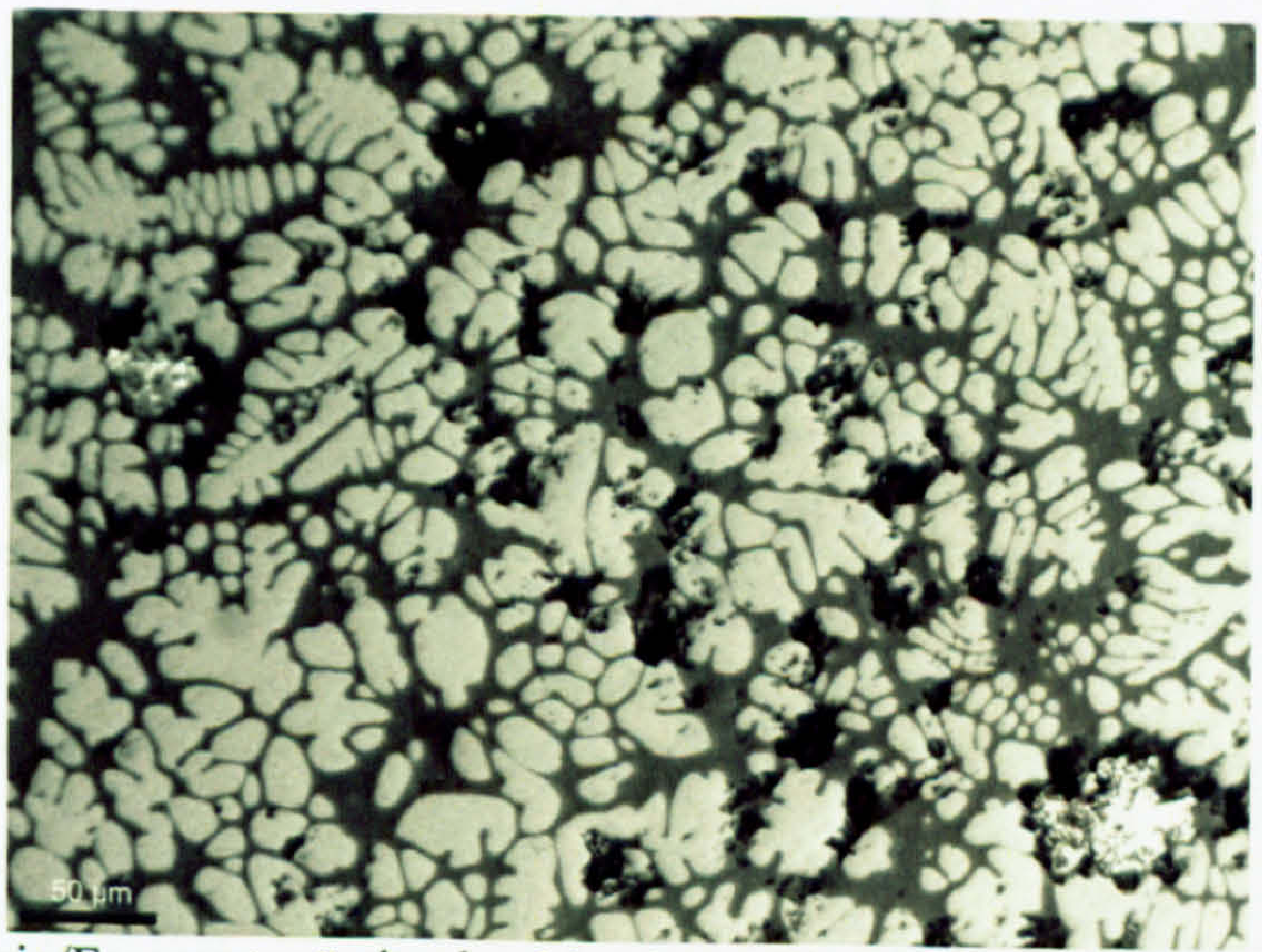
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO

Sample No. VTH10

Macroscopic features

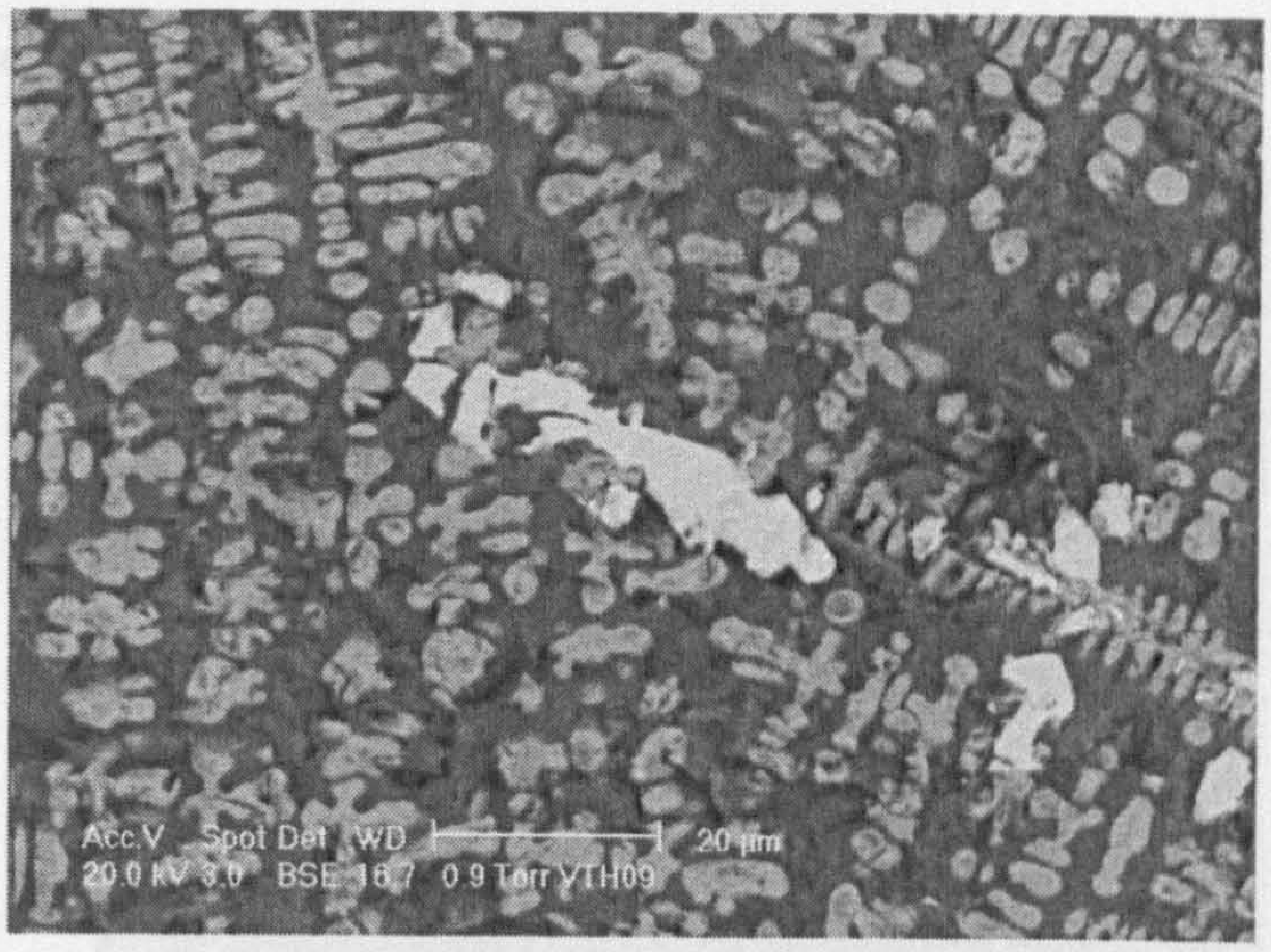
Size	6.50 cm
Weight	32.50 g
Colour	dark brown
Texture	flow
Porosity	high
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy



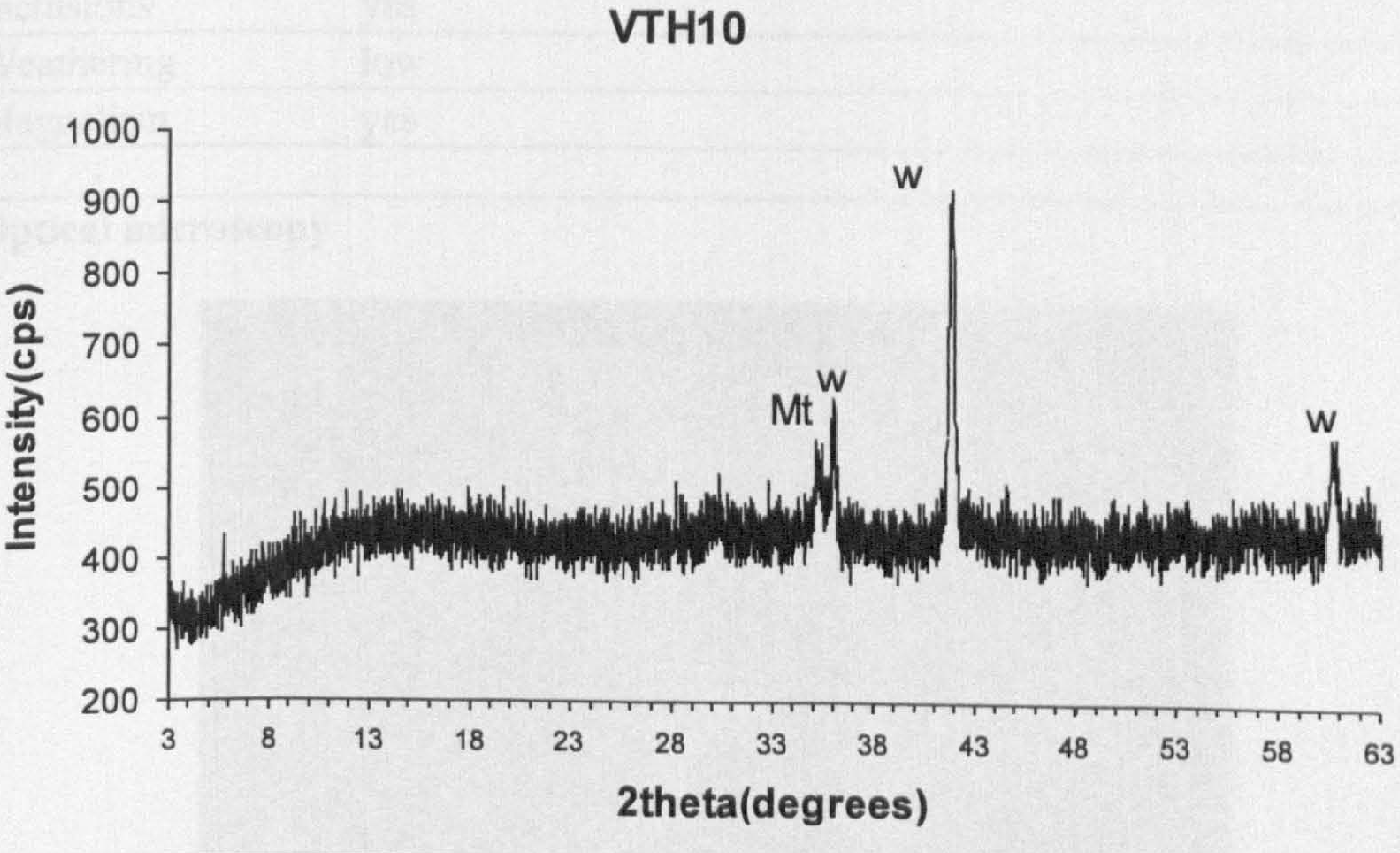
Vesicular matrix/Frequent wüstite dendrites/ metallic prills

SEM image



A siliceous matrix and a network of wustite dendrites of various sizes and orientation are the major phases while the central region is dominated by condensate iron appearing brighter in the micrograph.

XRD



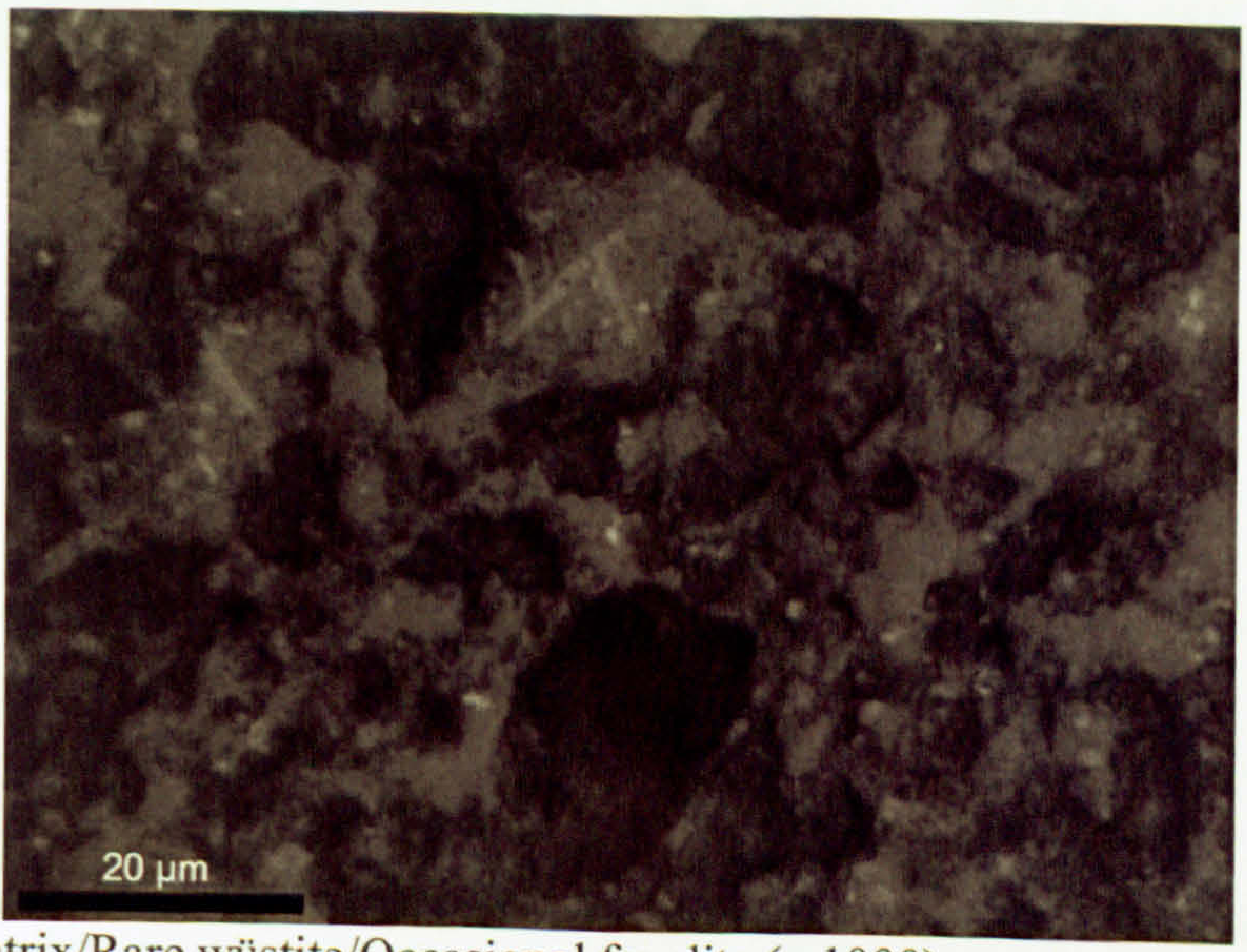
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO

Sample No. AGS01

Macroscopic features

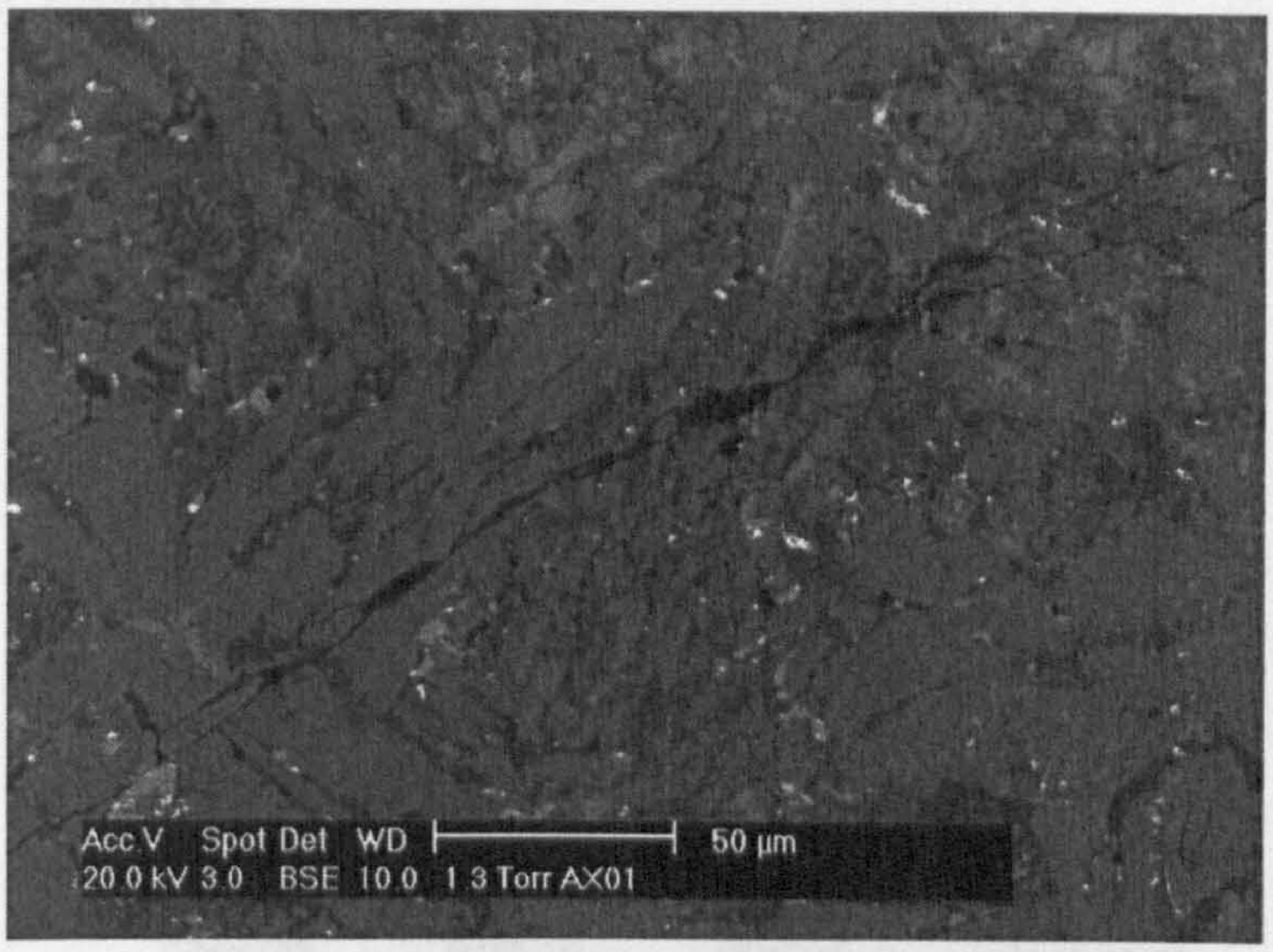
Size	8.50 cm
Weight	161.00 g
Colour	dark grey/black
Texture	concave
Porosity	moderate
Inclusions	yes
Weathering	low
Magnetism	yes

Optical microscopy



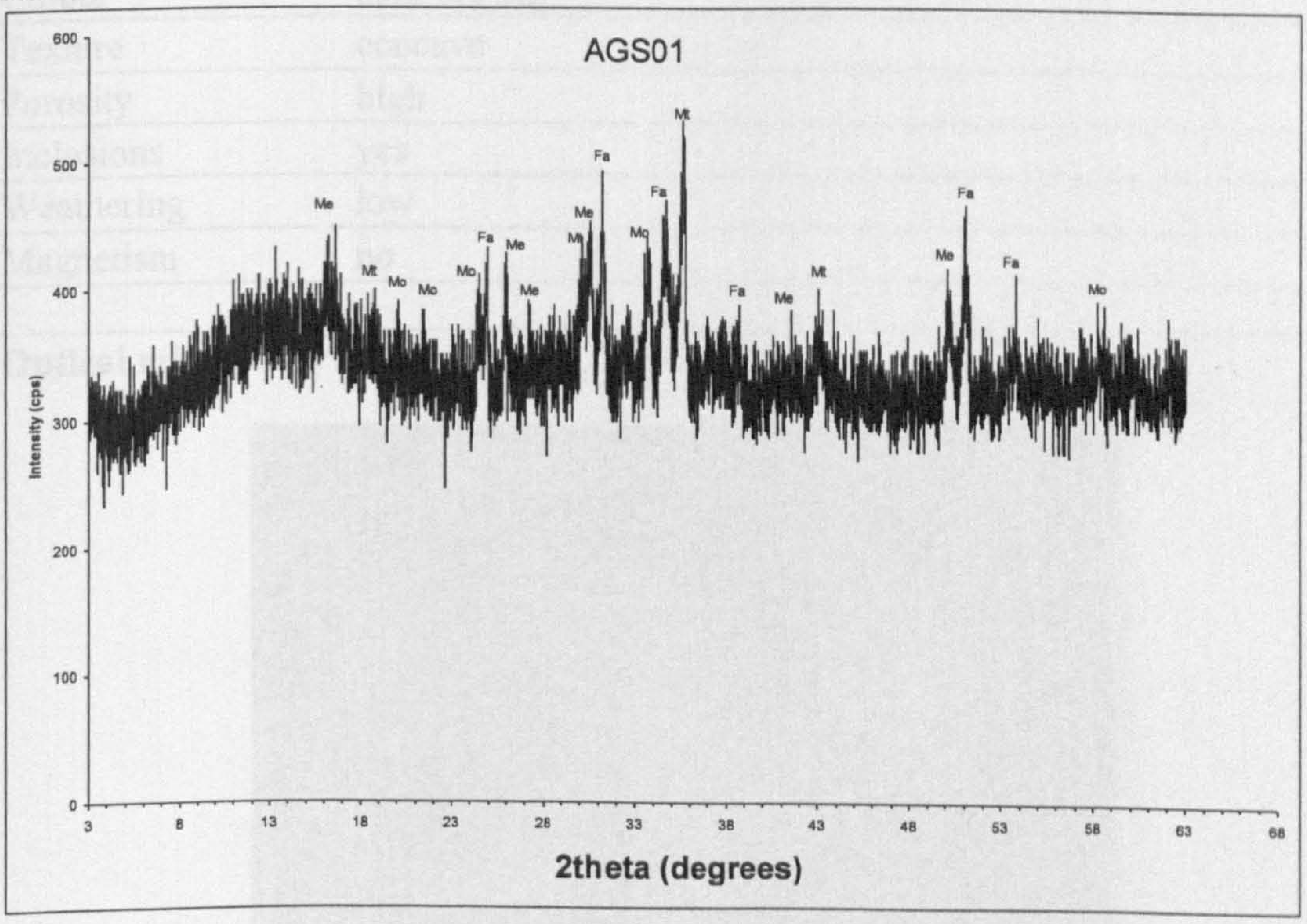
Vesicular matrix/Rare wüstite/Occasional fayalite (x 1000)

SEM image



Large fayalitic laths grey in colour, wüstite clusters in lighter grey and interstitial grey-black material are the major phases present. Frequent small iron-rich prills are evenly distributed across the sample's extent.

XRD



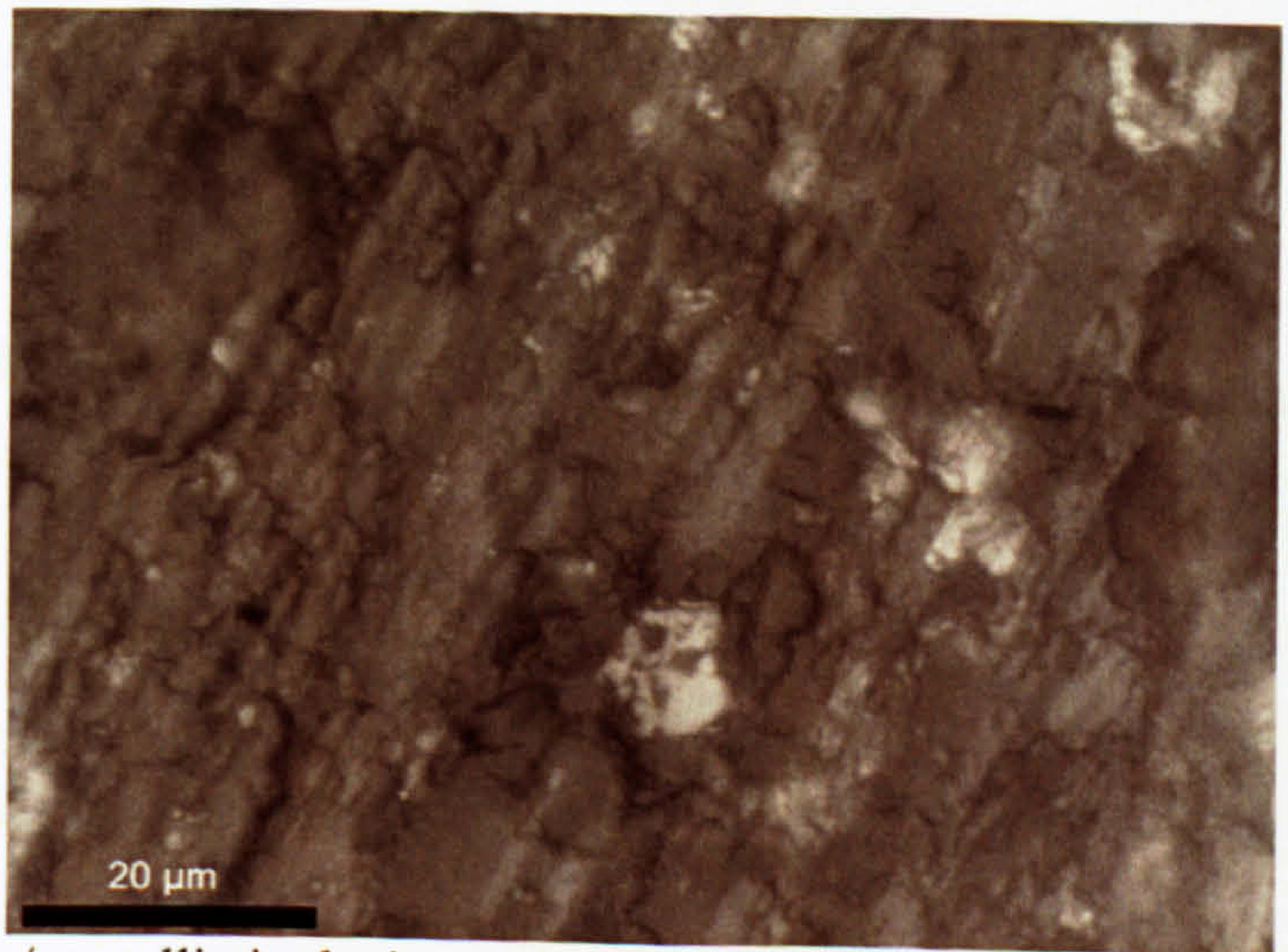
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$

Sample No. AGS02

Macroscopic features

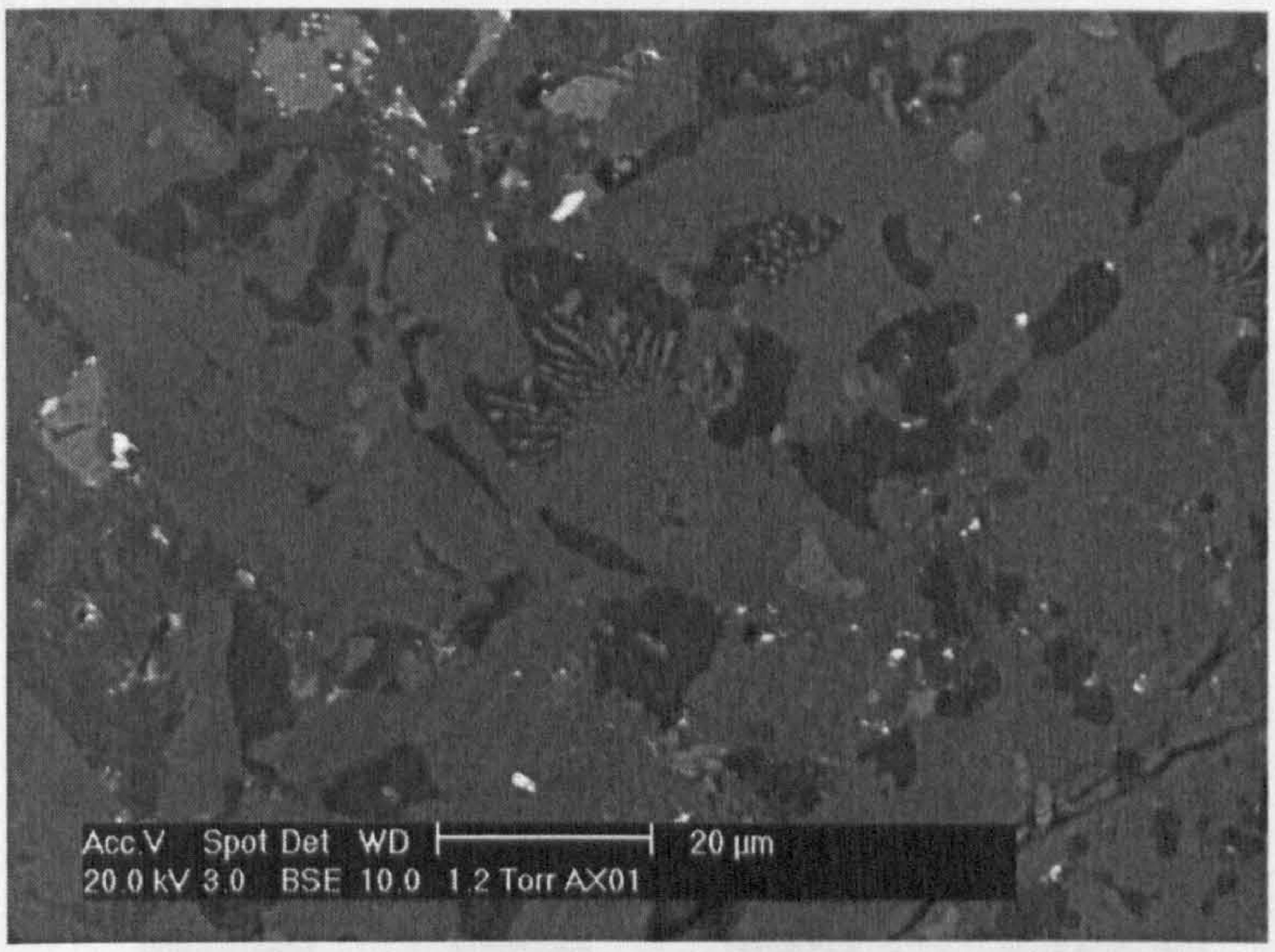
Size	4.50 cm
Weight	29.00 g
Colour	dark brown
Texture	concave
Porosity	high
Inclusions	yes
Weathering	low
Magnetism	no

Optical microscopy



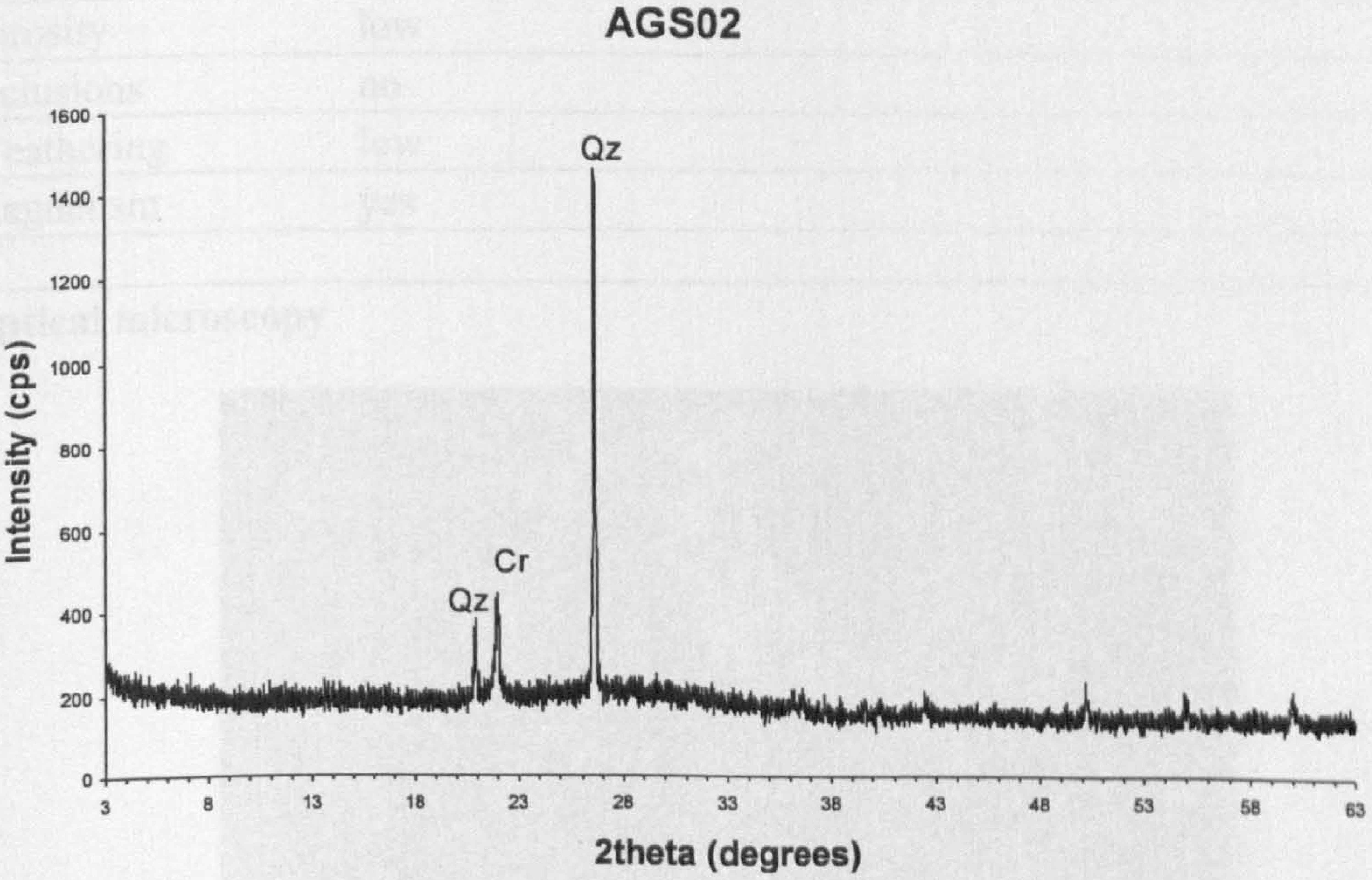
Laths of fayalite/ metallic inclusions and quartz (un-reacted ore) (x 1000)

SEM image



The matrix consists of fayalitic laths and interstitial glassy phases (grey-black) and mostly quartz while wüstite is rare. Metallic prills appear as brighter spots in clusters.

XRD



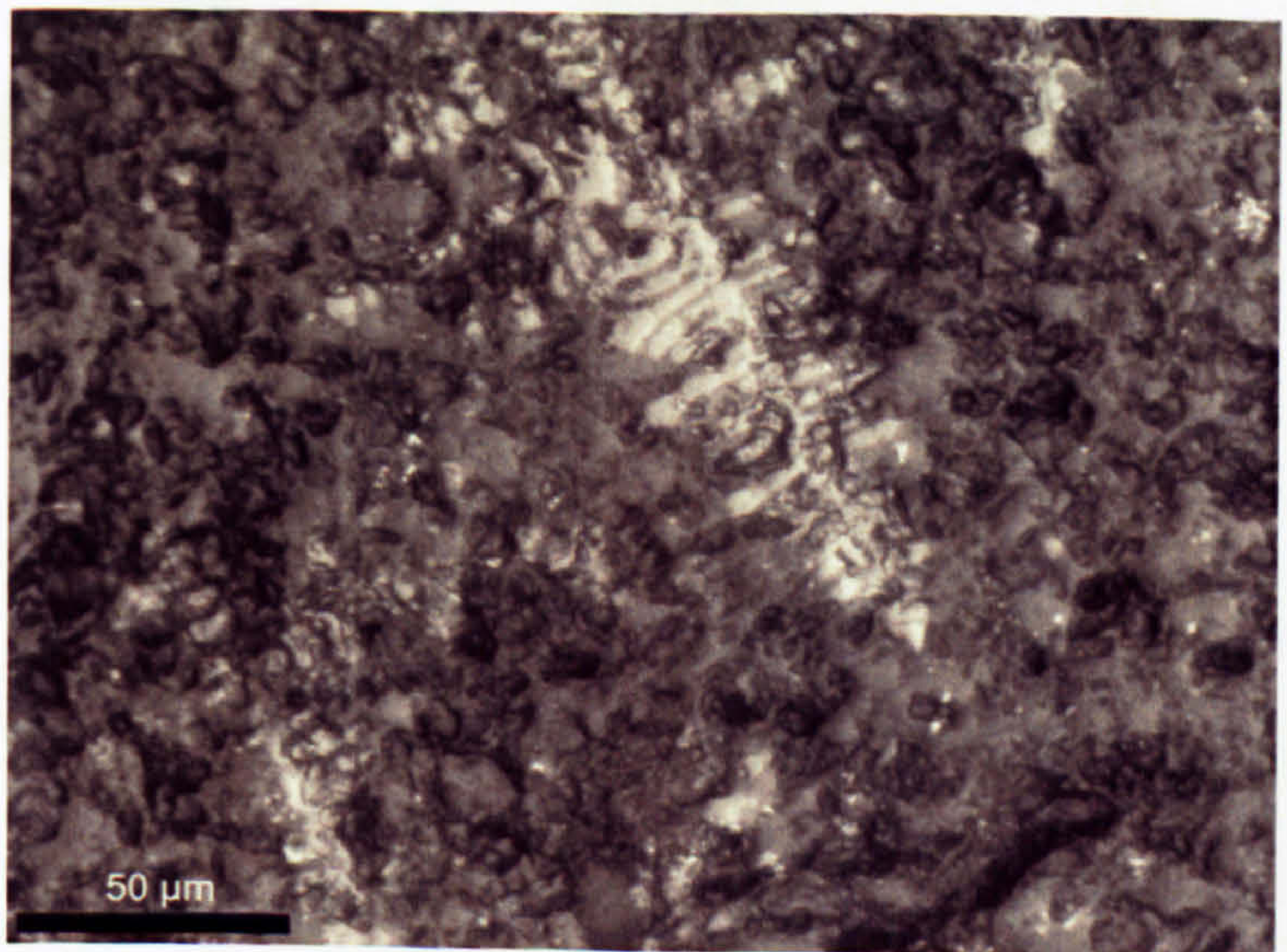
Intensity curve of sample:
Qz: Quartz-SiO_2, Cr: Cristobalite-SiO_2

Sample No. AGS03

Macroscopic features

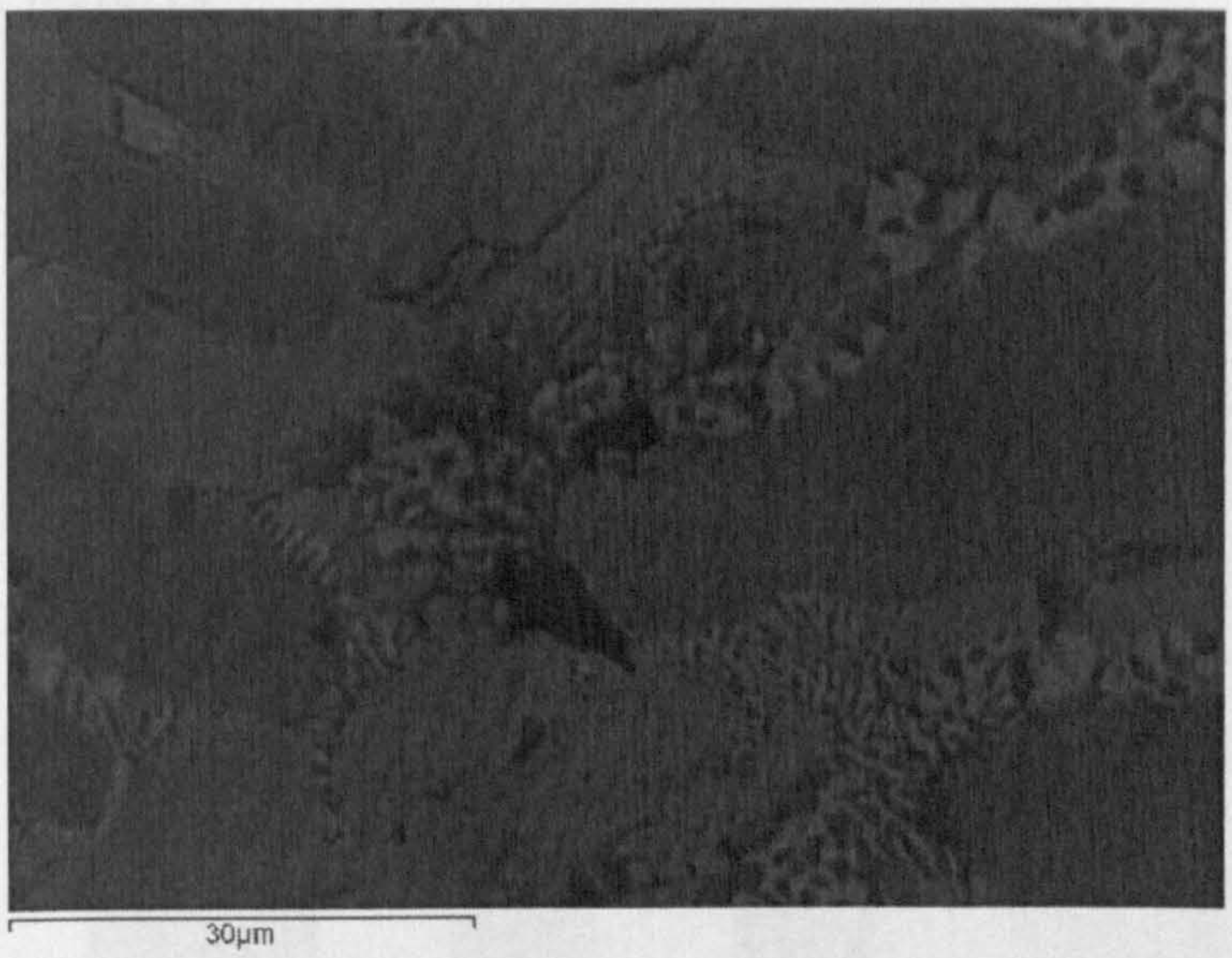
Size	4.50 cm
Weight	16.40 g
Colour	dark brown
Texture	platy
Porosity	low
Inclusions	no
Weathering	low
Magnetism	yes

Optical microscopy



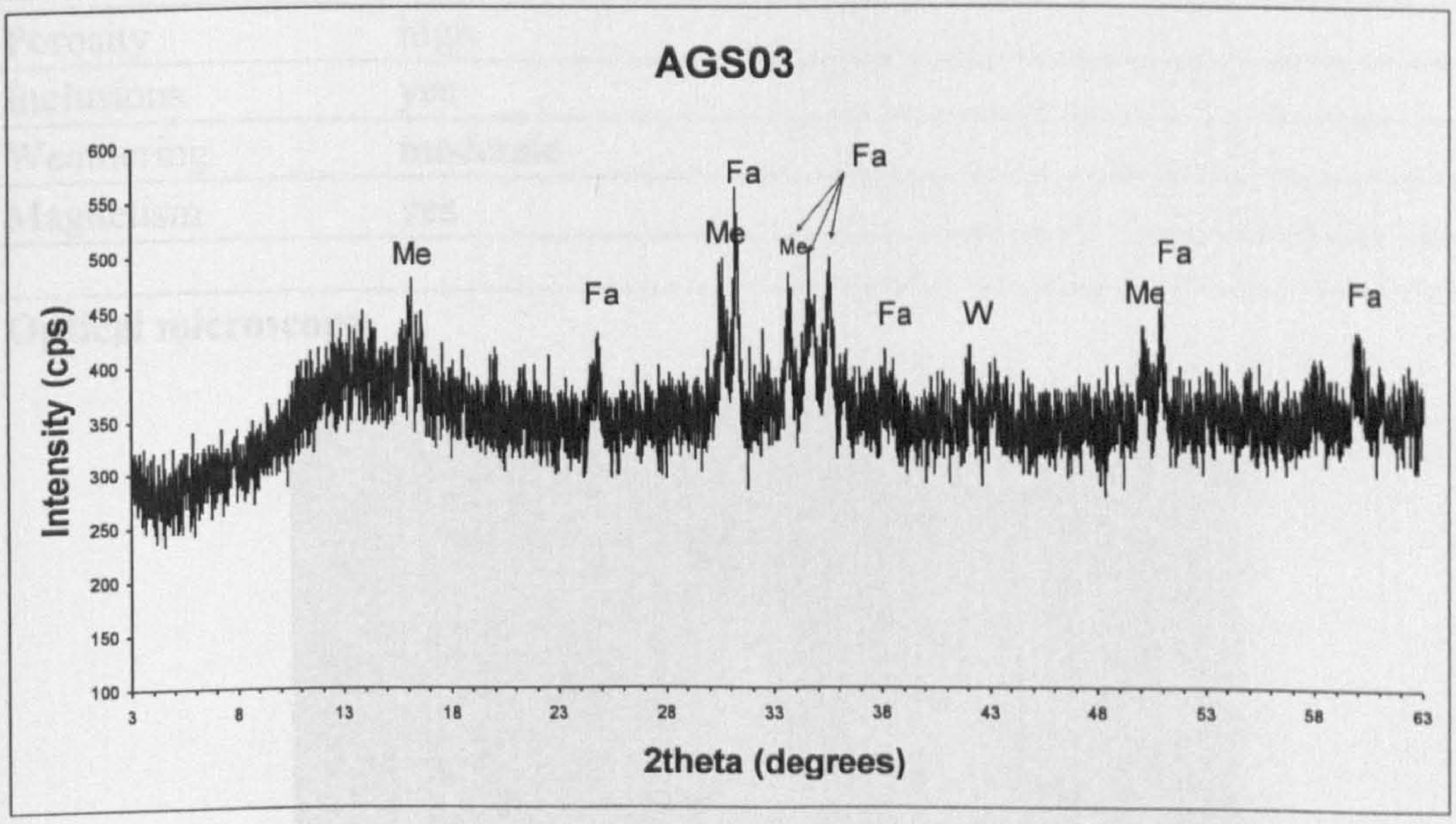
Vesicular matrix/Frequent wüstites/Occasional clusters of Fe prills/ (x 400)

SEM image



Large laths of fayalite are evident with interstitial glass and small crystals of wüstite present at the voids.

XRD



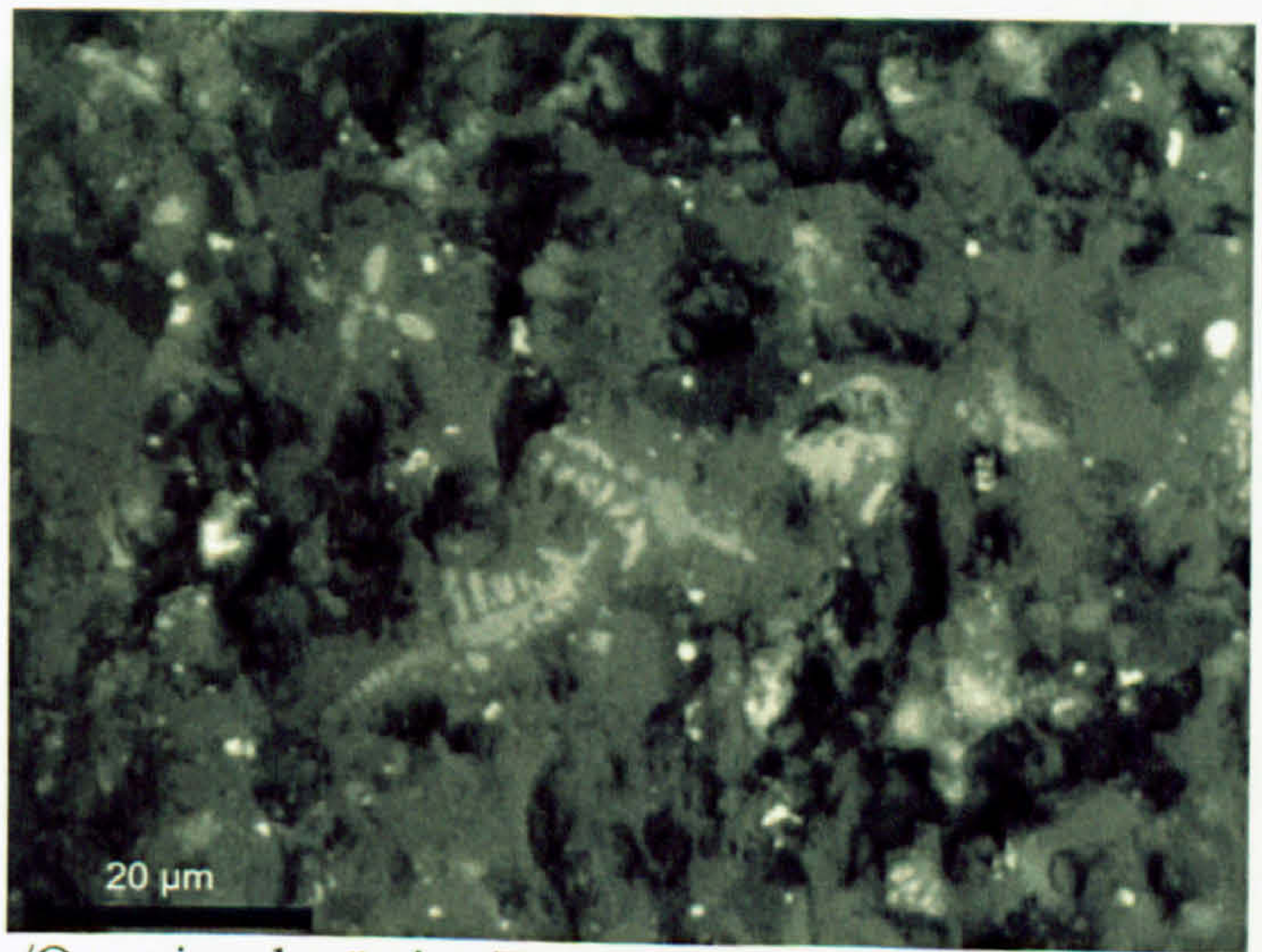
Intensity curve of sample:
Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$,

Sample No. AGS04

Macroscopic features

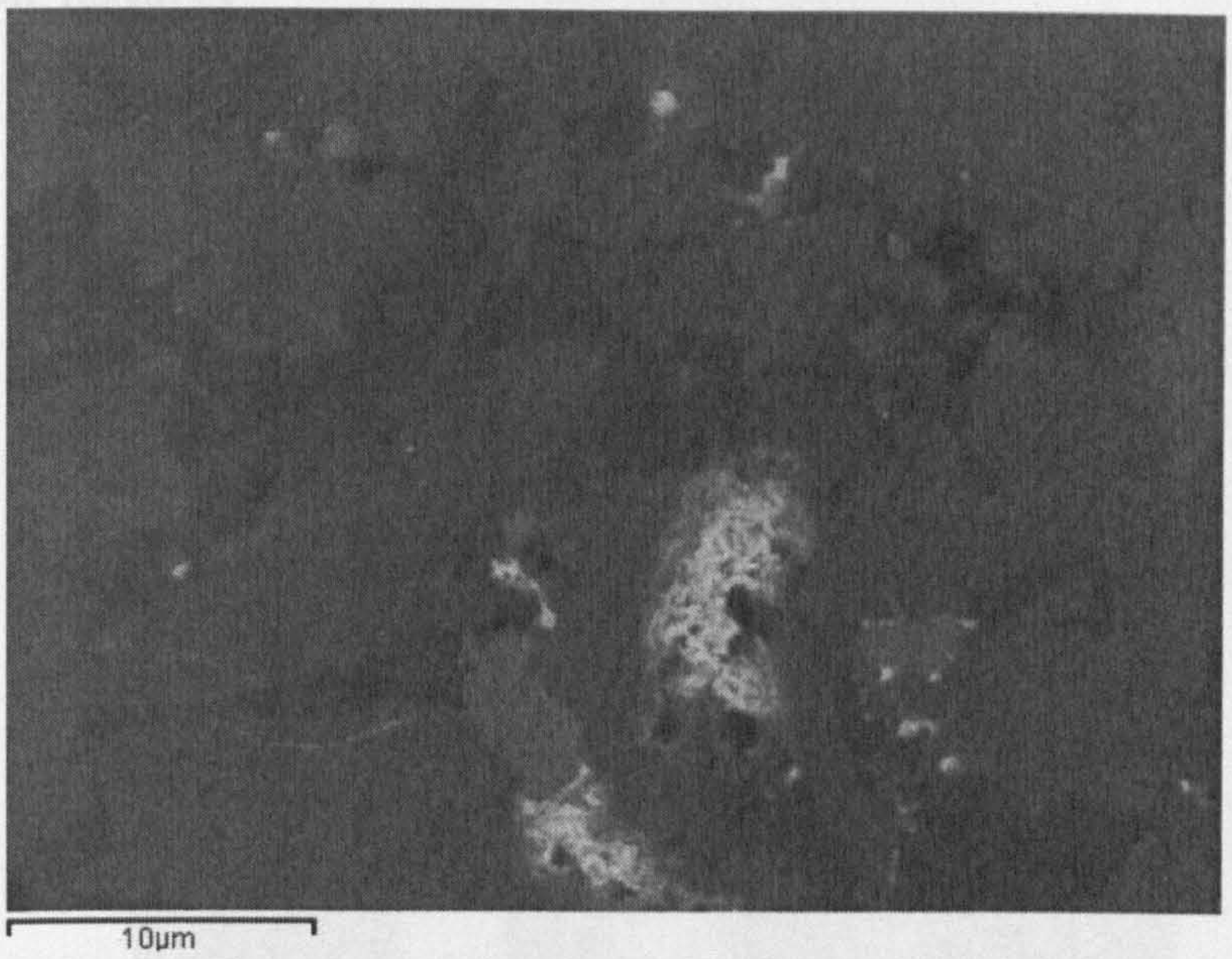
Size	5.00 cm
Weight	42.00 g
Colour	dark brown
Texture	spongy
Porosity	high
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



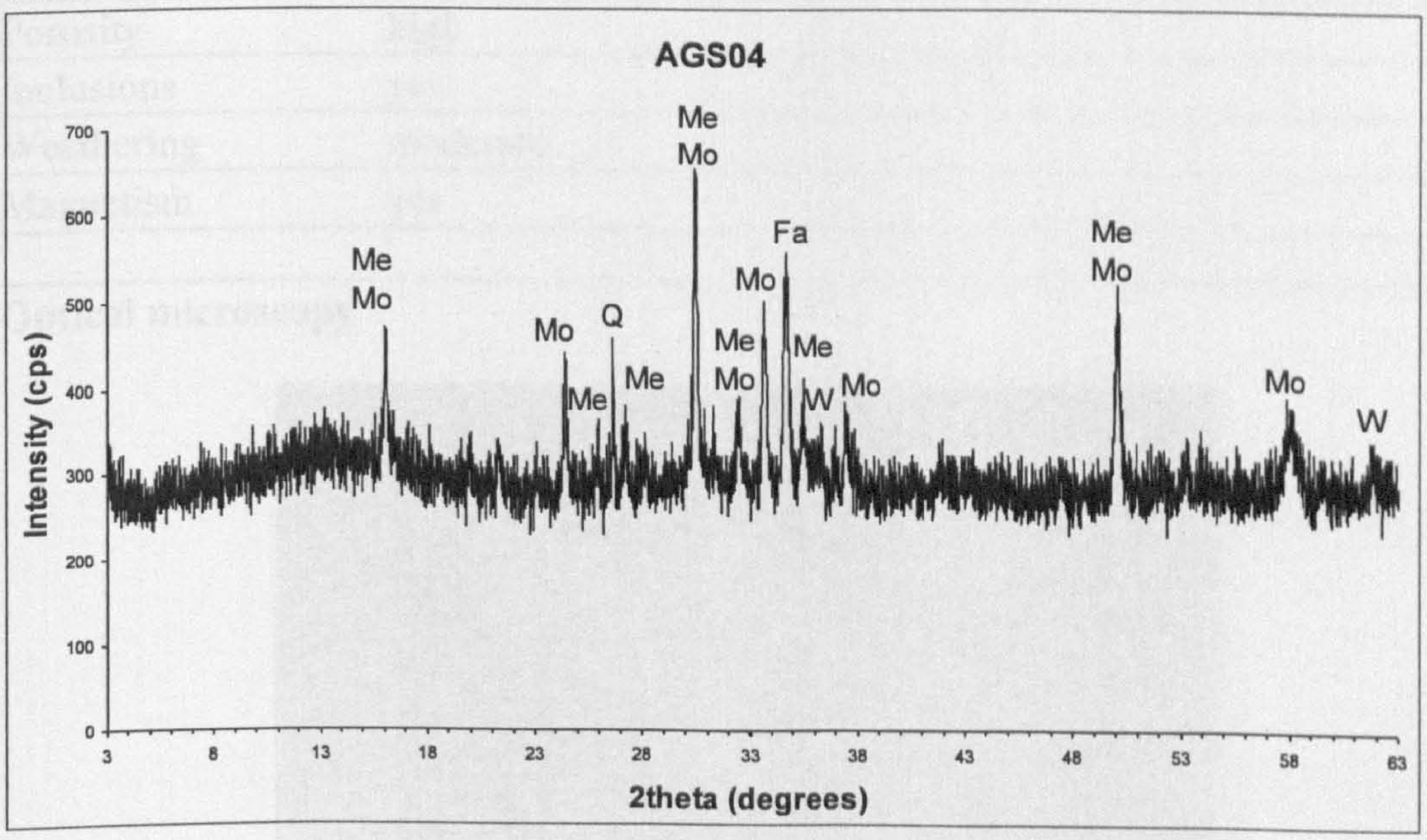
Vesicular matrix/Occasional wüstite /Fayalite laths/Occasional iron prills (x 1000)

SEM image



The structure in mainly glassy with some fayalites and occasional brighter metallic spots distributed across.

XRD



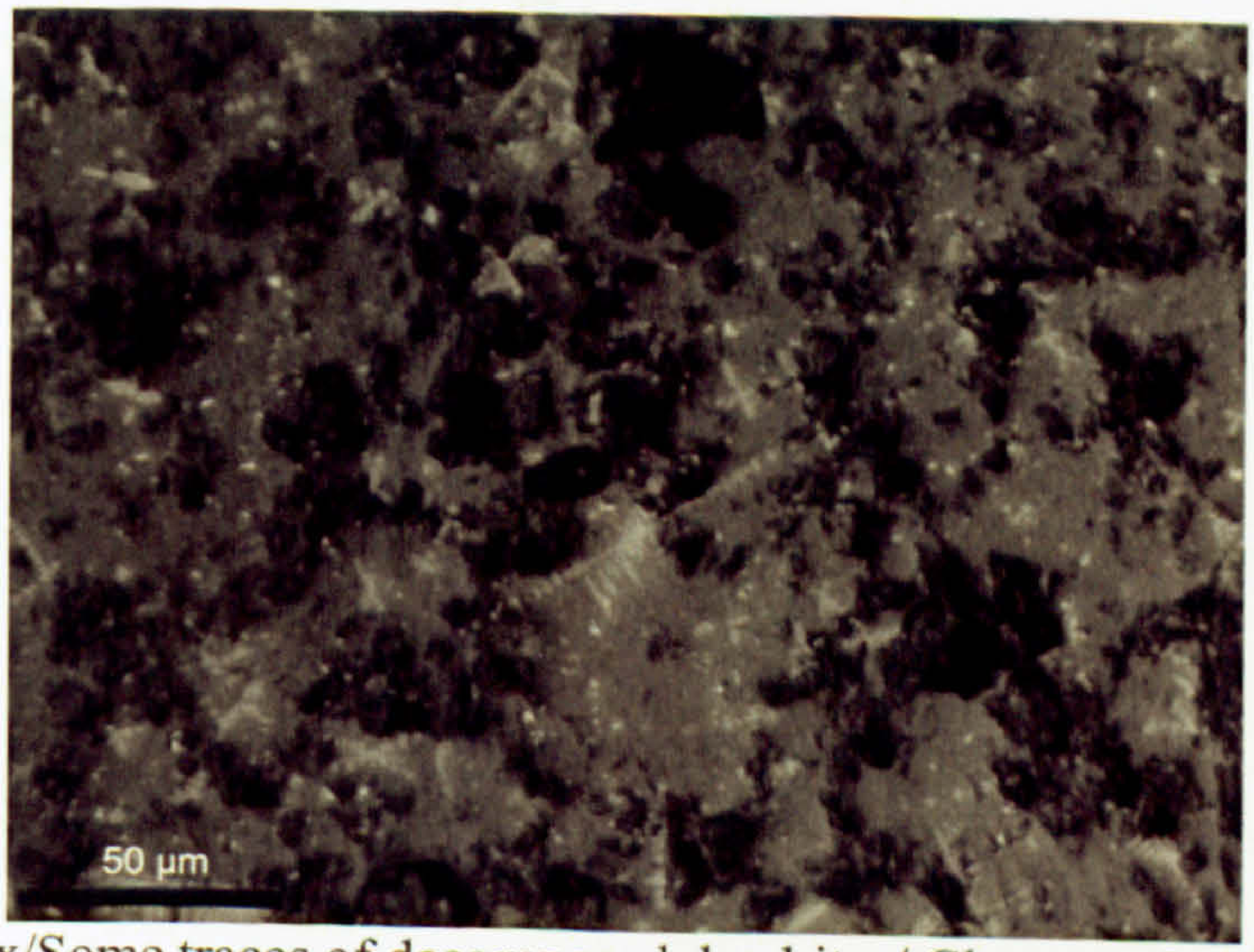
Intensity curve of sample:
Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$, Qz: Quartz-$SiO_2$

Sample No. AGS05

Macroscopic features

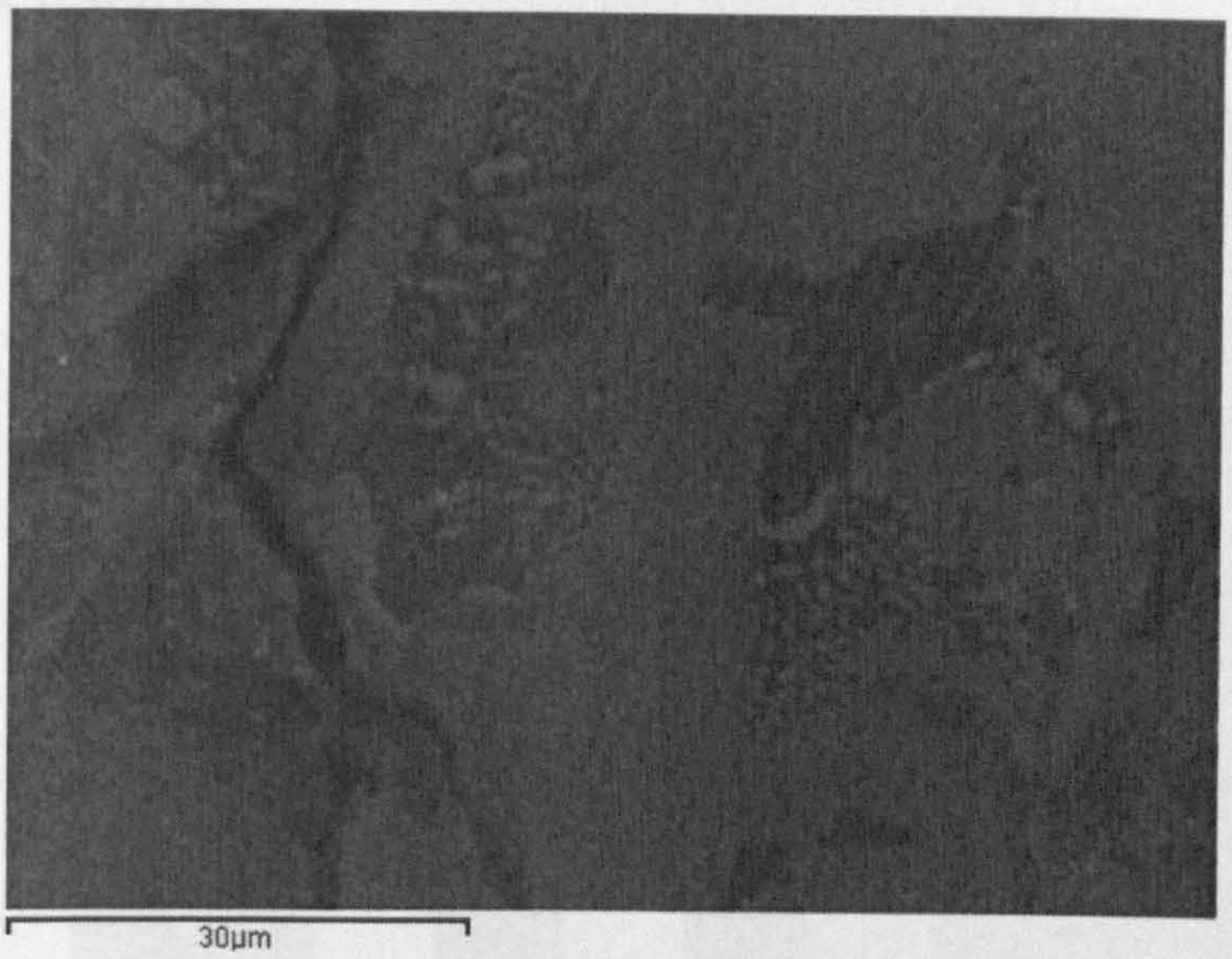
Size	6.50 cm
Weight	80.00 g
Colour	dark brown/black
Texture	spongy
Porosity	high
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



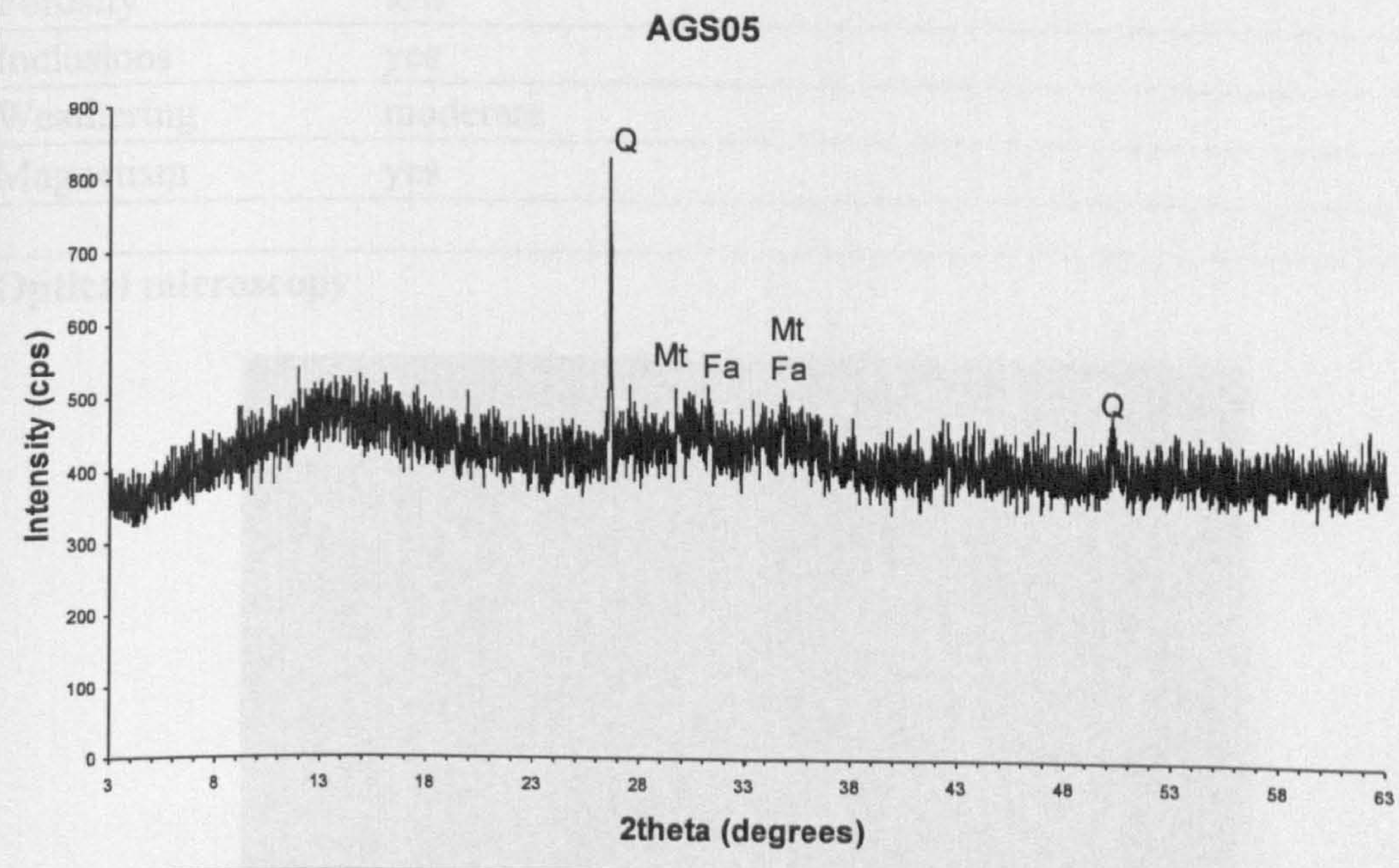
Vesicular matrix/Some traces of decomposed dendrites/ Clusters of metallic prills (x 400)

SEM image



Fayalite is present forming dark grey laths and also quartz and glassy material. There are also occasional magnetite crystals.

XRD



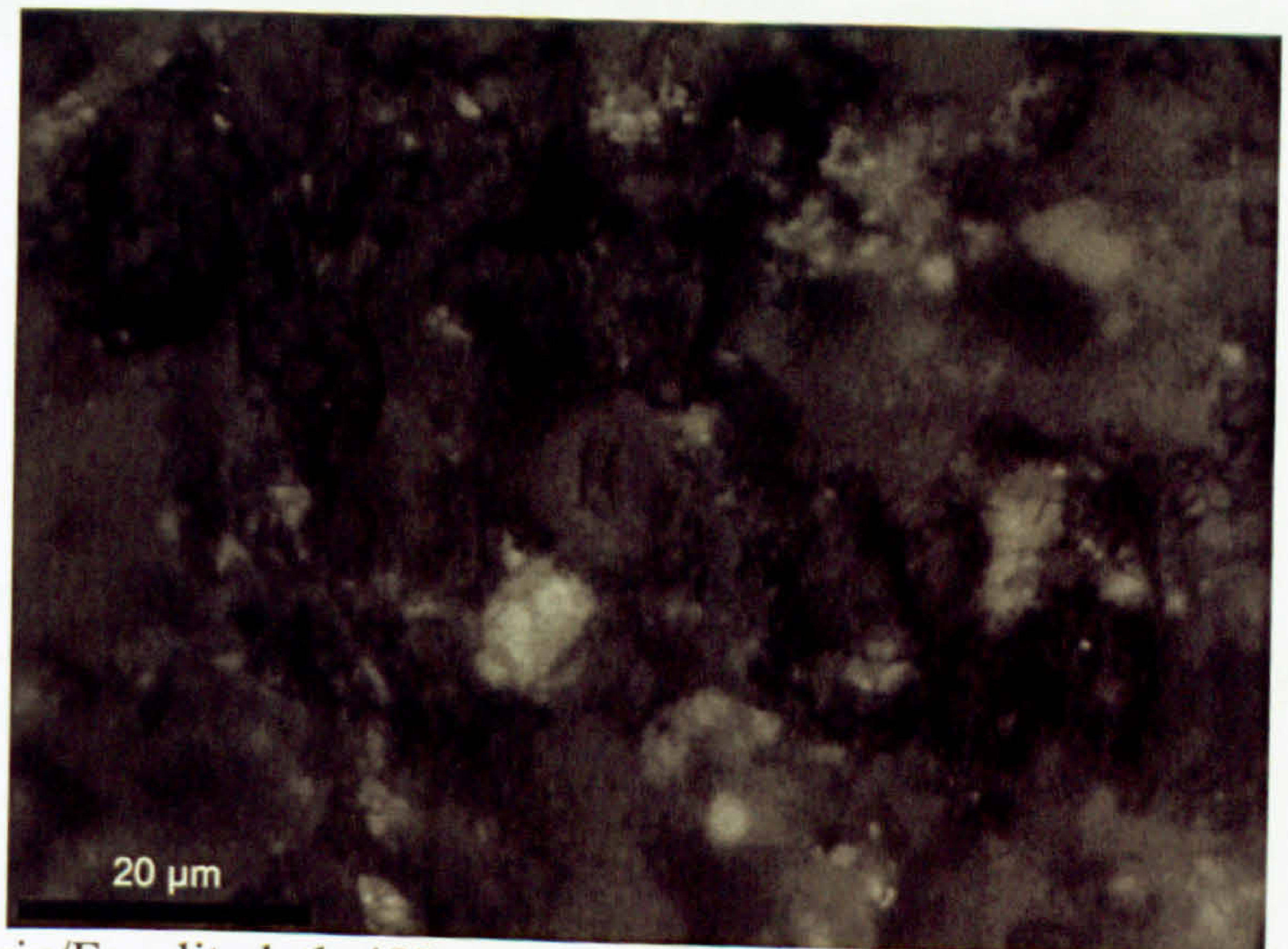
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Fa: Fayalite-Fe_2SiO_4, Qz: Quartz-SiO_2

Sample No. AGS06

Macroscopic features

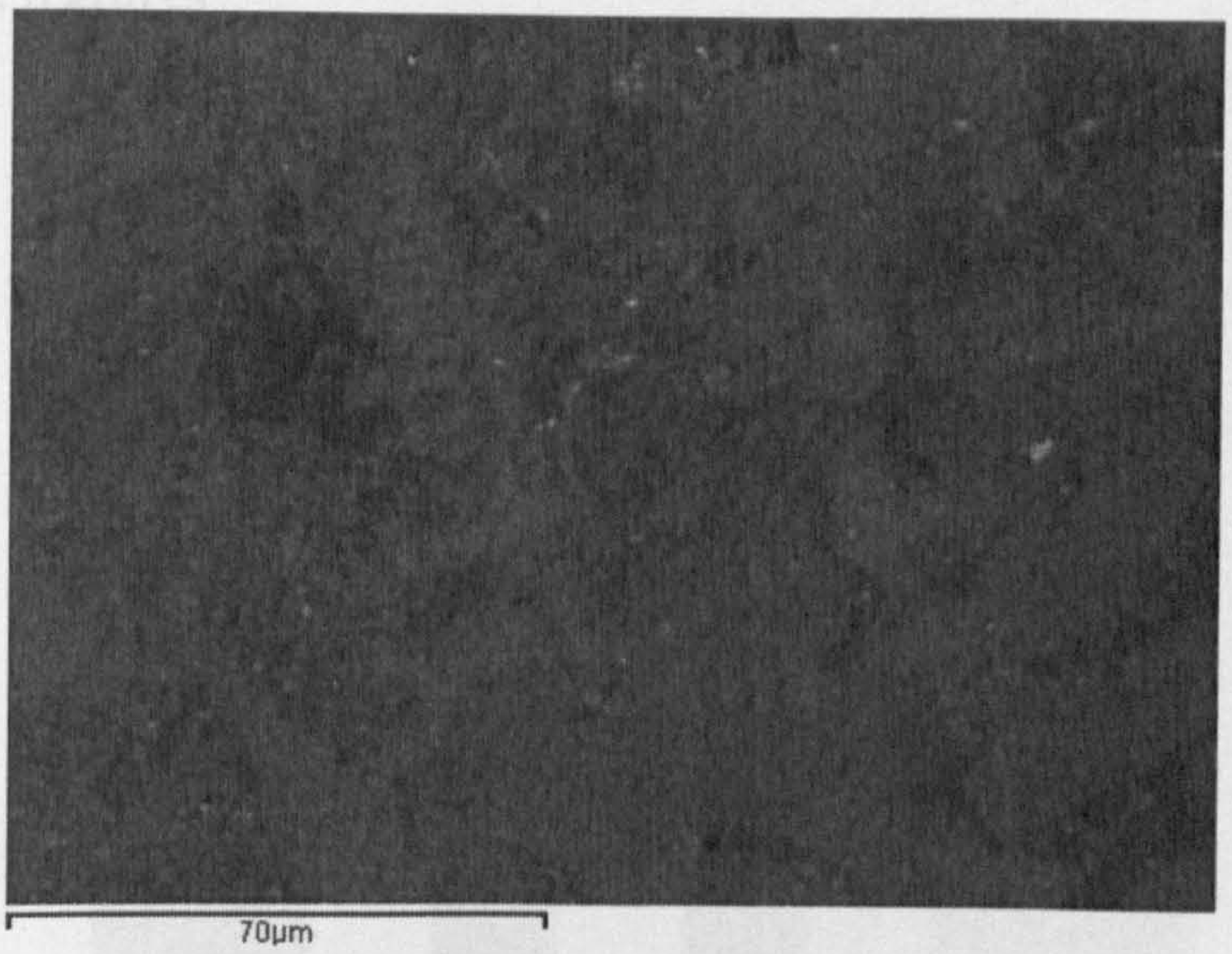
Size	7.00 cm
Weight	71.50 g
Colour	dark grey/black
Texture	flow
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



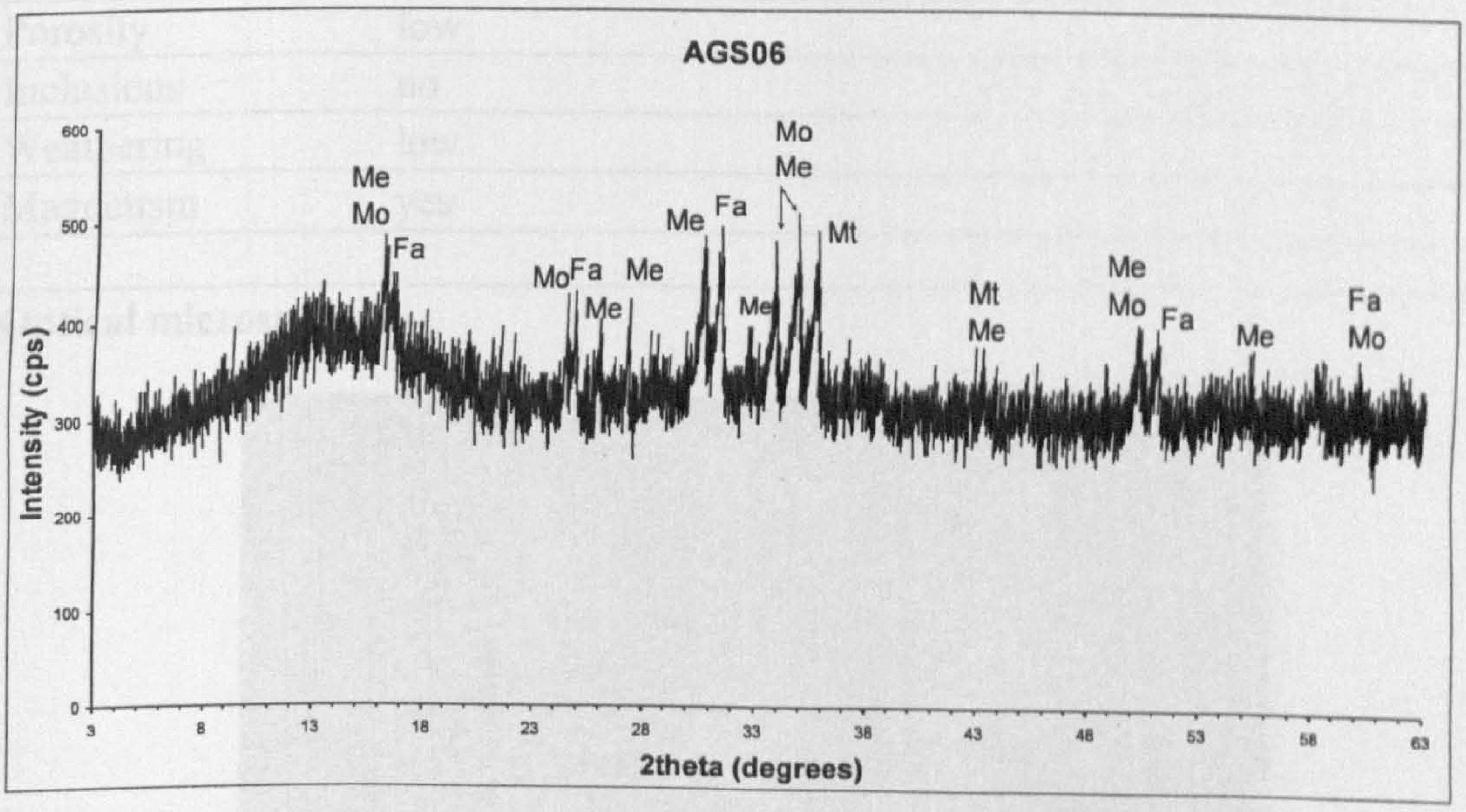
Vesicular matrix/Fayalite laths/ Un-reacted ore inclusions (x 1000)

SEM image



The matrix is mainly fayalitic with areas of interstitial glass. Some dendrites of wüstite are present and bright metallic prills are also a common occurrence.

XRD



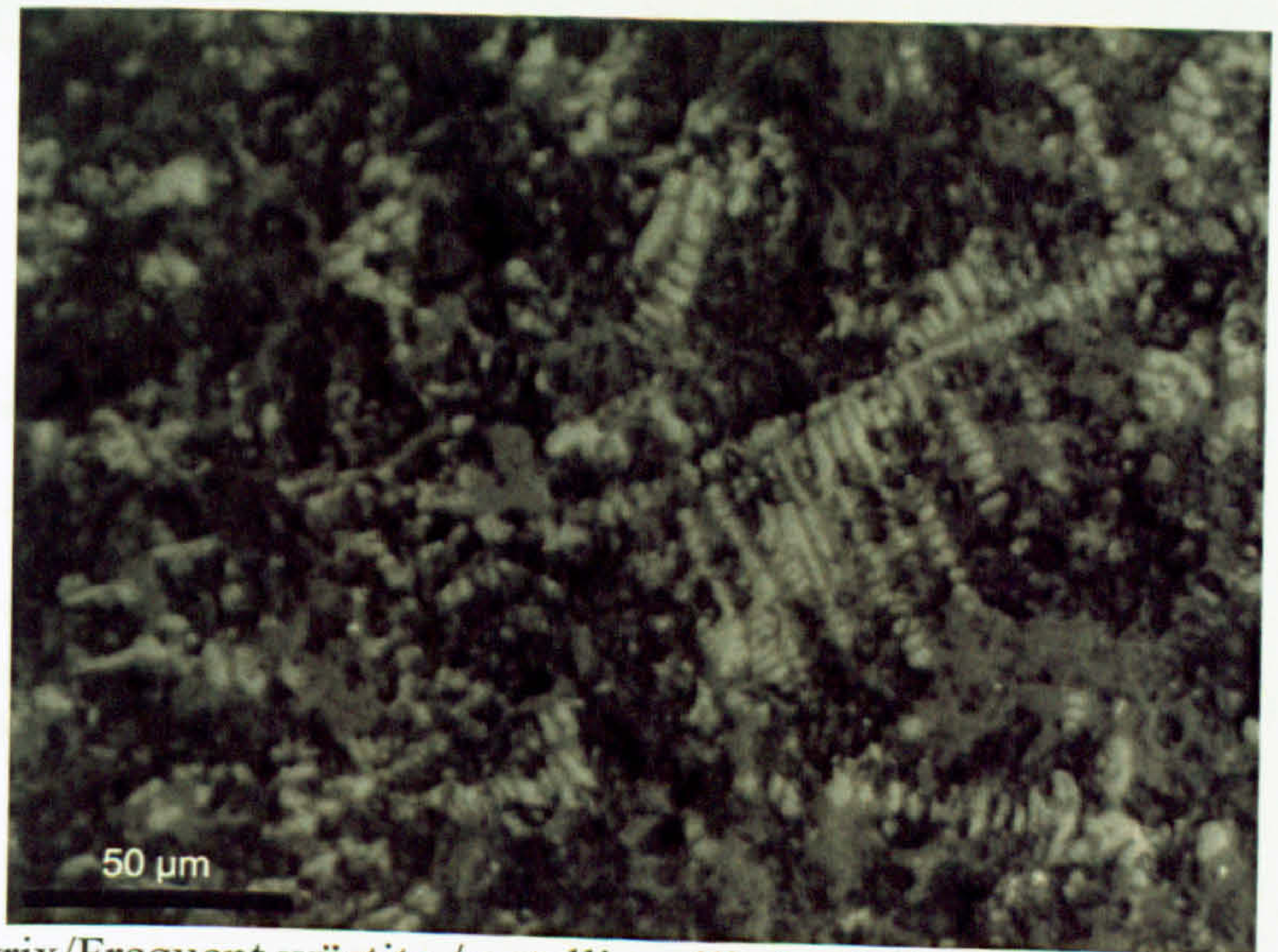
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$

Sample No. AGS07

Macroscopic features

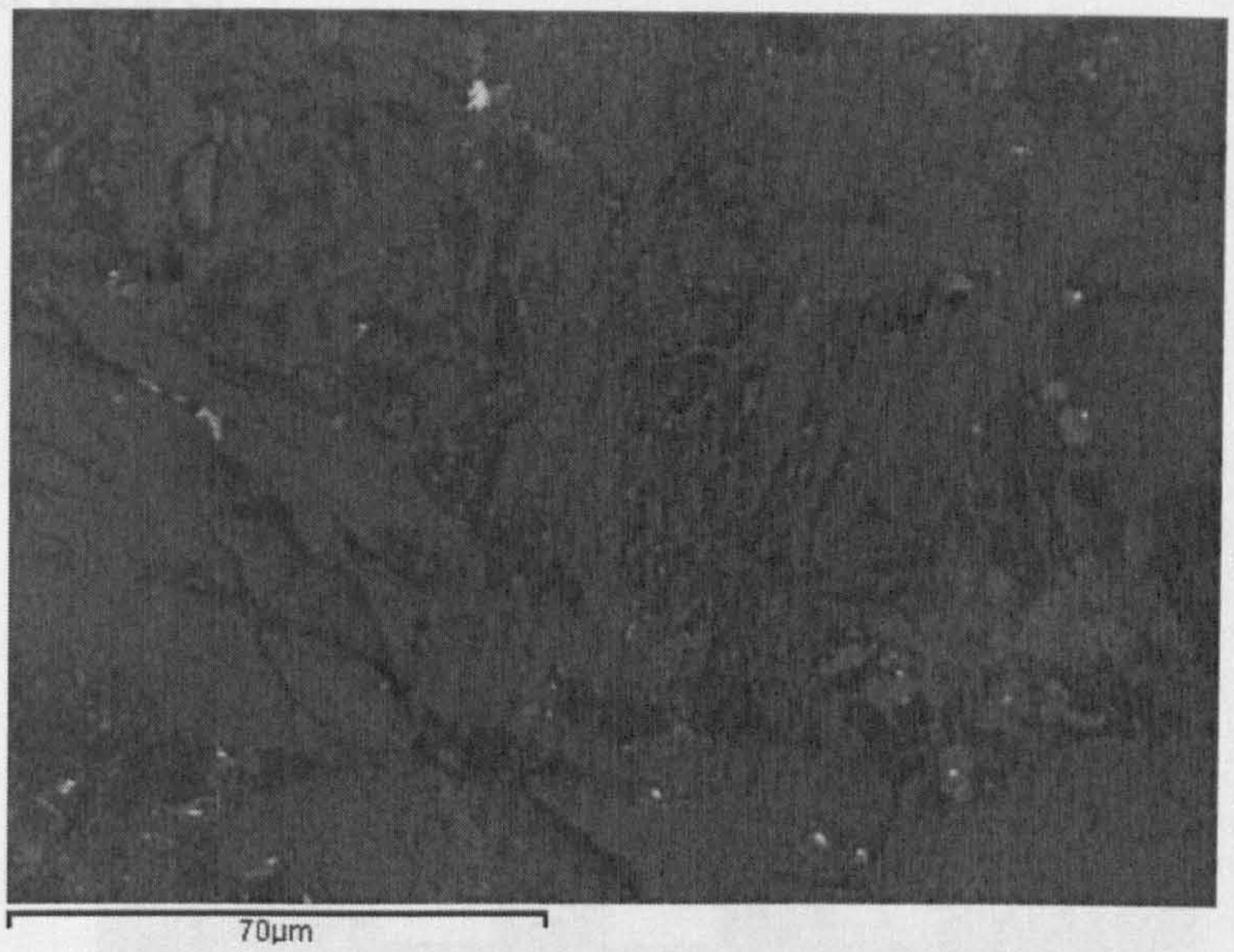
Size	6.00 cm
Weight	72.00 g
Colour	dark grey/black
Texture	flow
Porosity	low
Inclusions	no
Weathering	low
Magnetism	yes

Optical microscopy



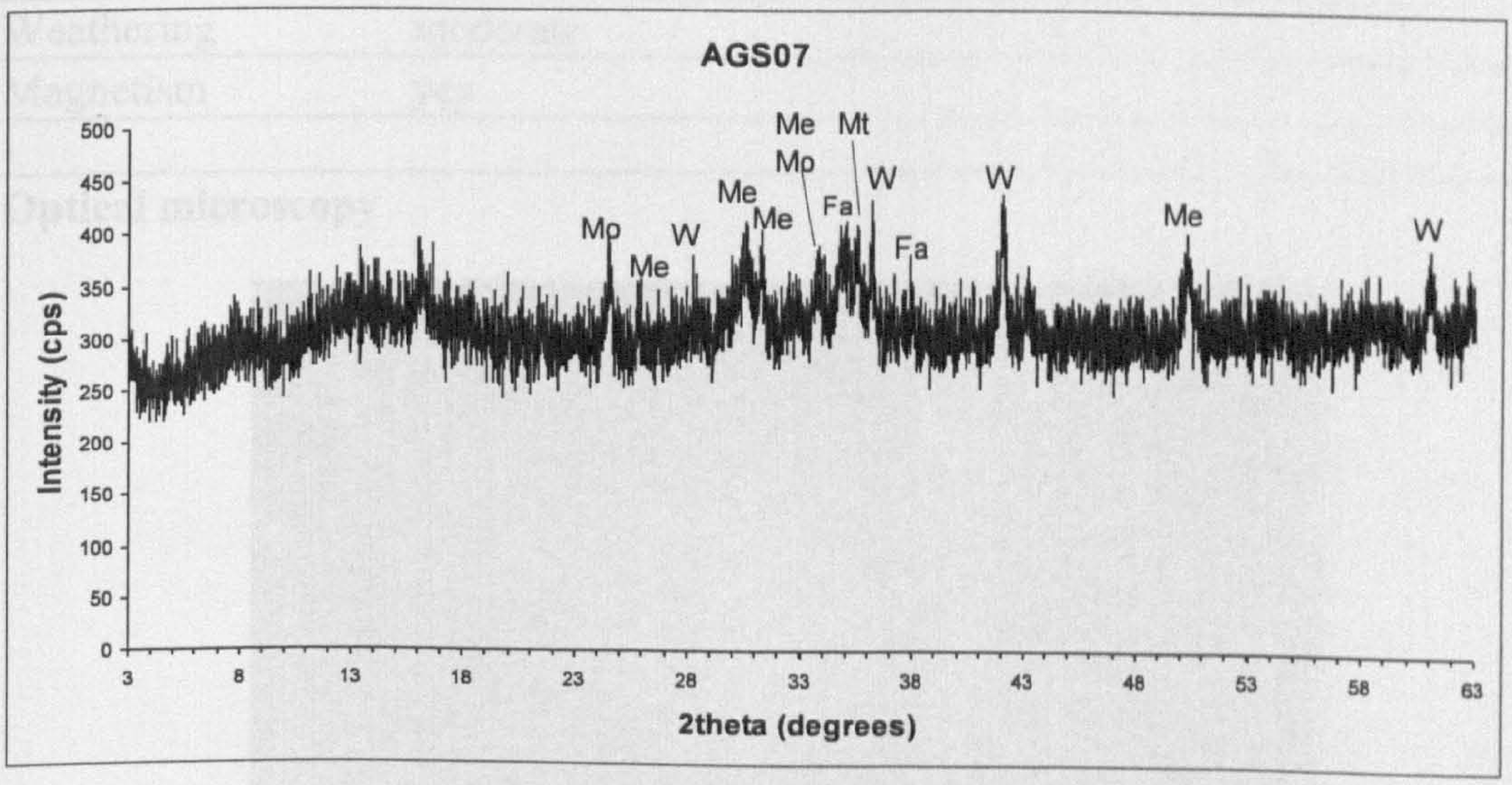
Vesicular matrix/Frequent wüstite /metallic prills (x 400)

SEM image



The matrix is mainly fayalitic with areas of interstitial glass. Wüstites are rare and metallic prills more frequent as is magnetite clustering in form of crystals at certain regions.

XRD



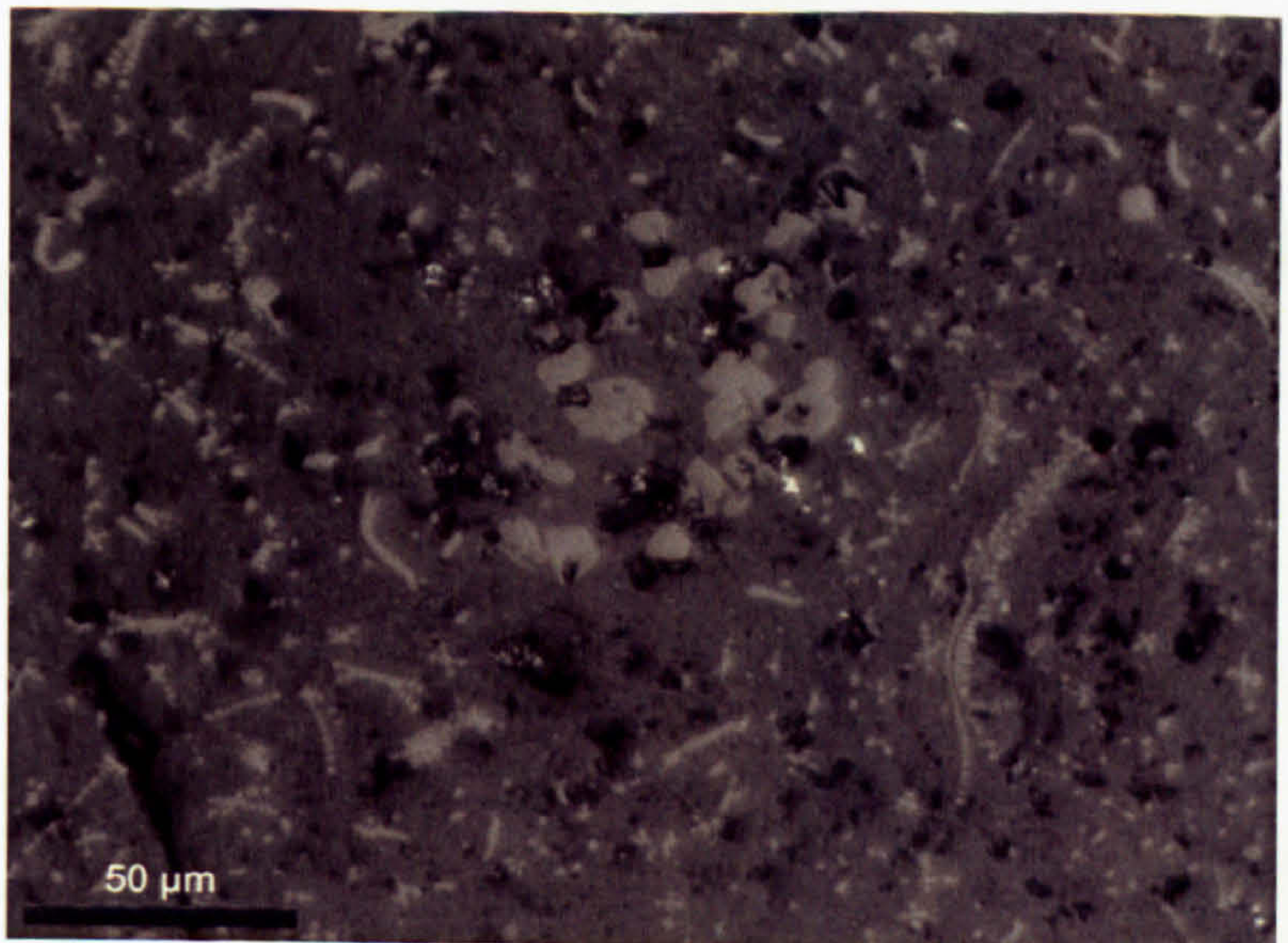
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$

Sample No. AGS08

Macroscopic features

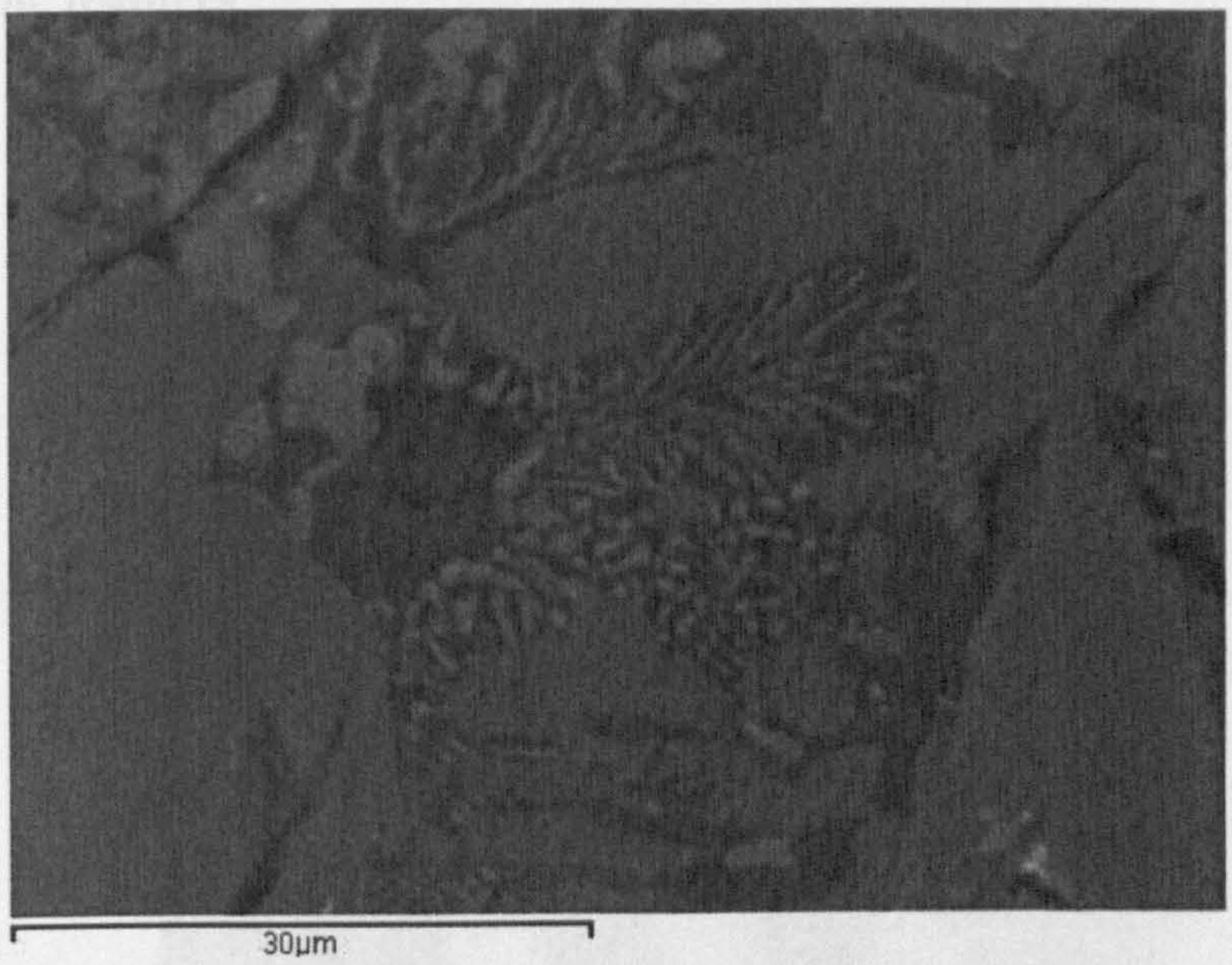
Size	6.50 cm
Weight	82.00 g
Colour	dark brown
Texture	angular
Porosity	low
Inclusions	yes
Weathering	moderate
Magnetism	yes

Optical microscopy



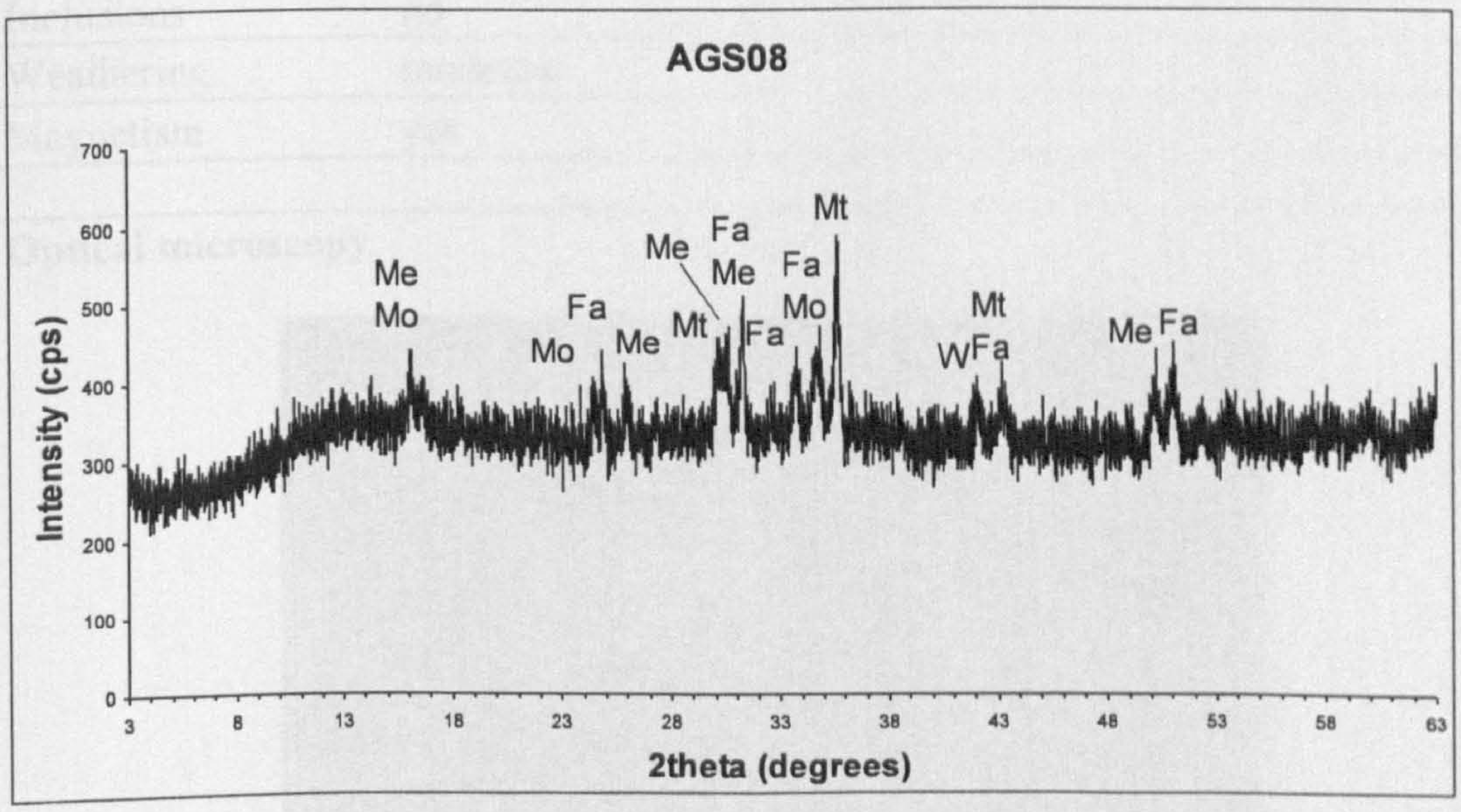
Vesicular matrix/Magnetite crystals /Wüstite dendrites/Rare metallic prills (x 400)

SEM image



Laths of fayalite and substantial glassy phases are present in the matrix. Angular crystals of magnetite also occur while decomposed wüstite dendrites are frequent.

XRD



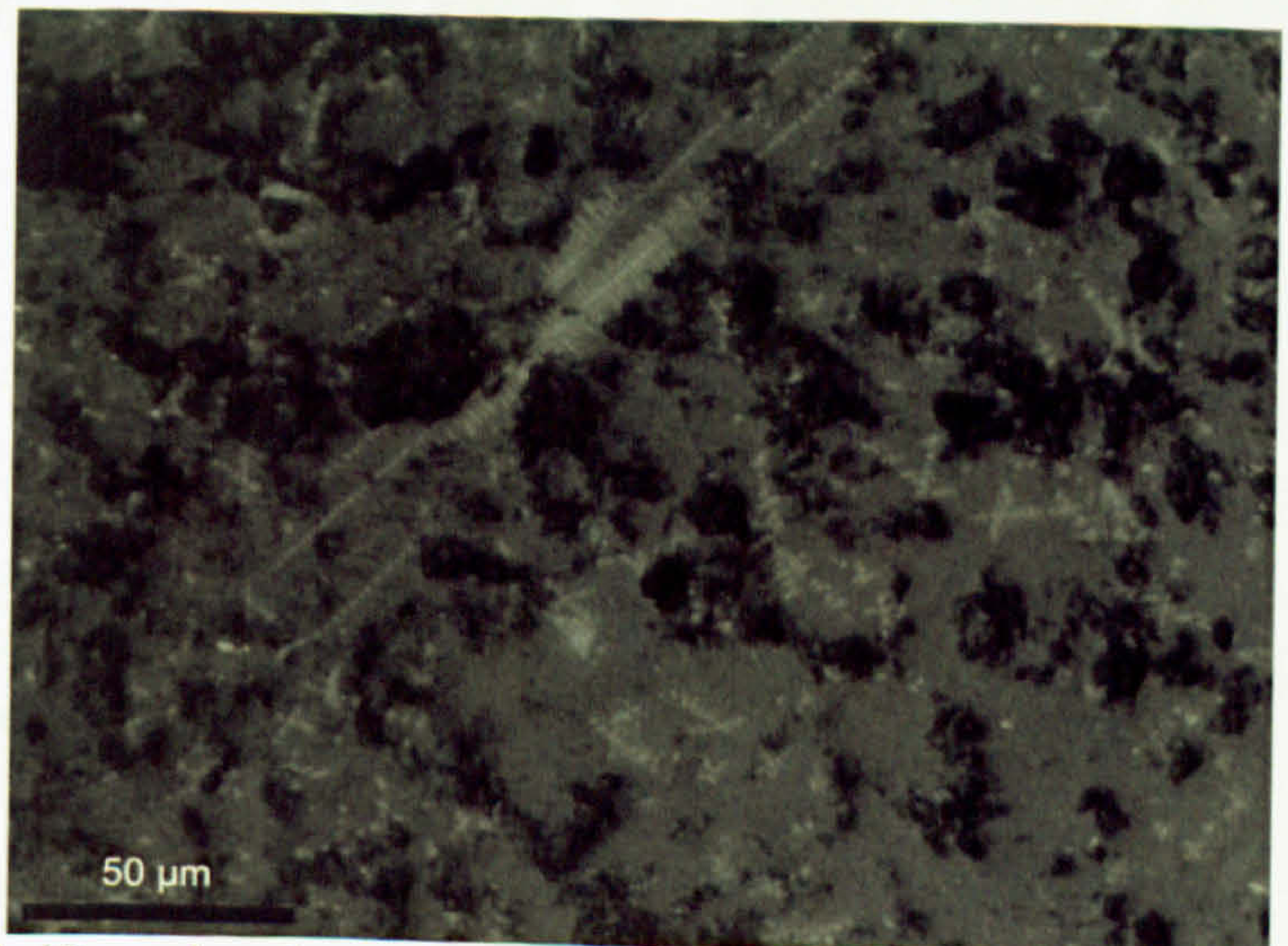
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$

Sample No. AGS09

Macroscopic features

Size	7.00 cm
Weight	100.50 g
Colour	dark brown/black
Texture	flow
Porosity	low
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy

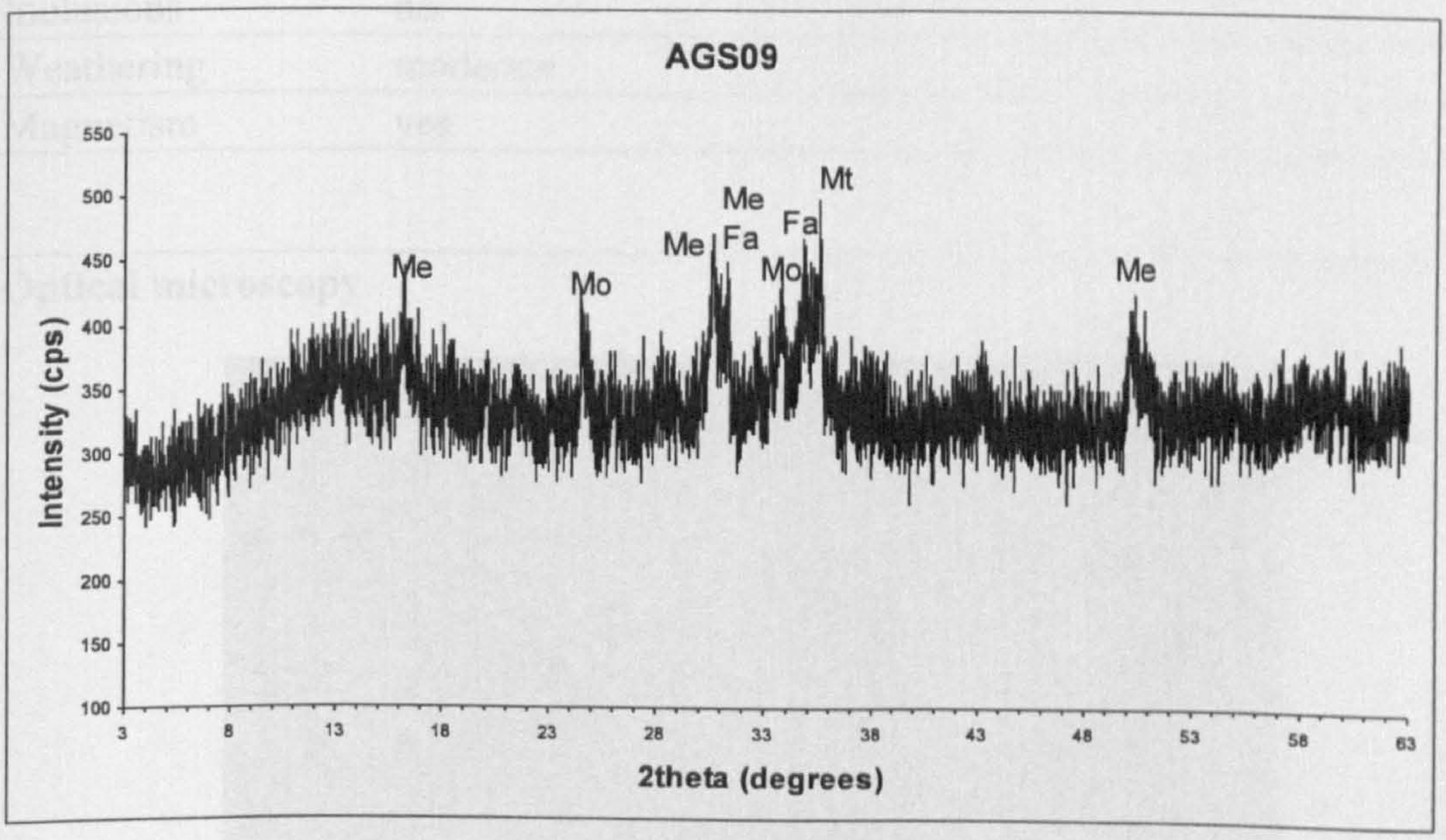


Vesicular matrix/Occasional wüstite dendrites /Fayalite phase (dark grey) (x 400)

SEM image

Laths of fayalite and wüstite dendrites predominate with occasional occurrence of magnetite crystals. Rare metallic prills also exist.

XRD



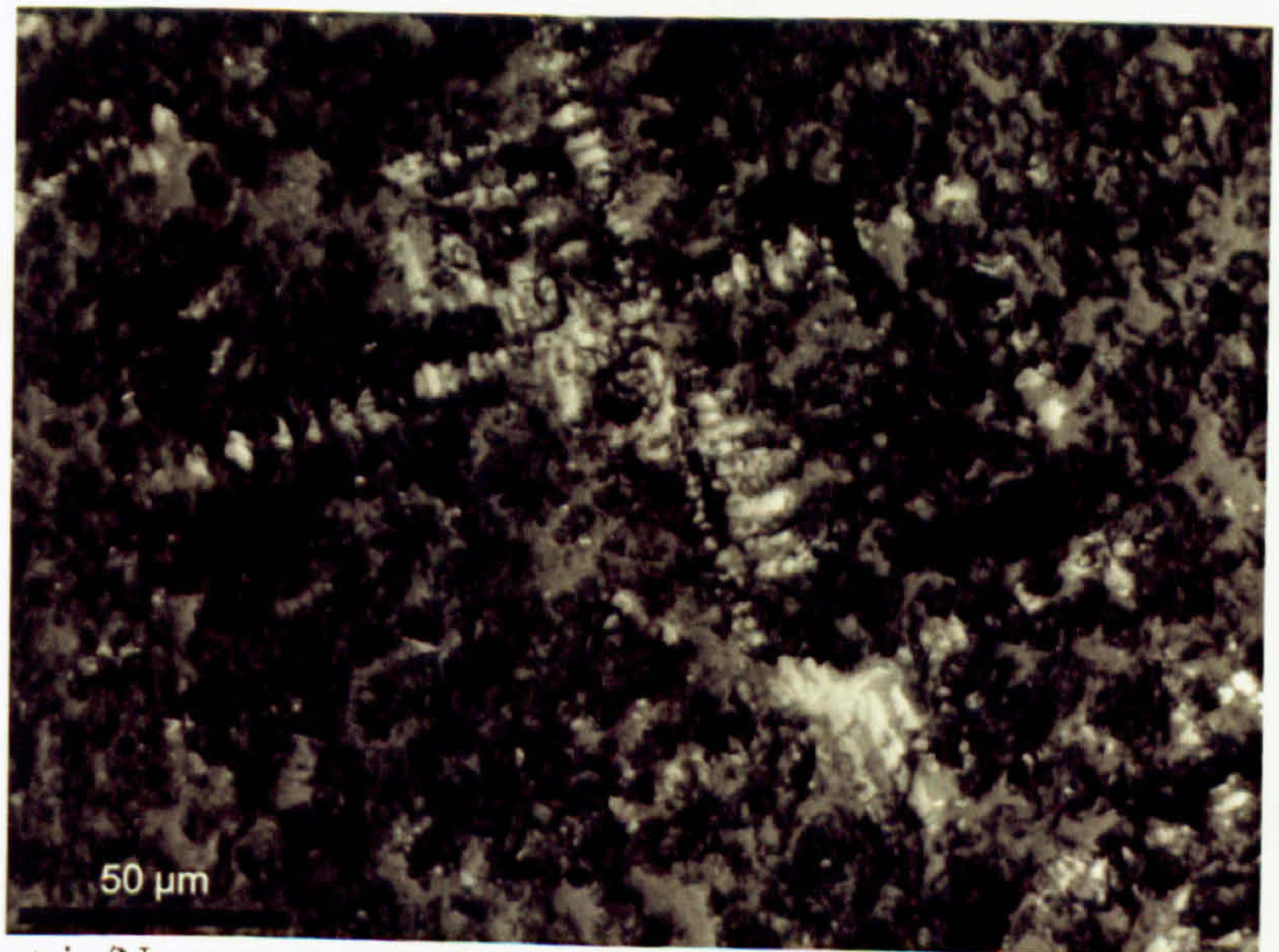
Intensity curve of sample:
Mt: Magnetite-Fe_3O_4, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$

Sample No. AGS10

Macroscopic features

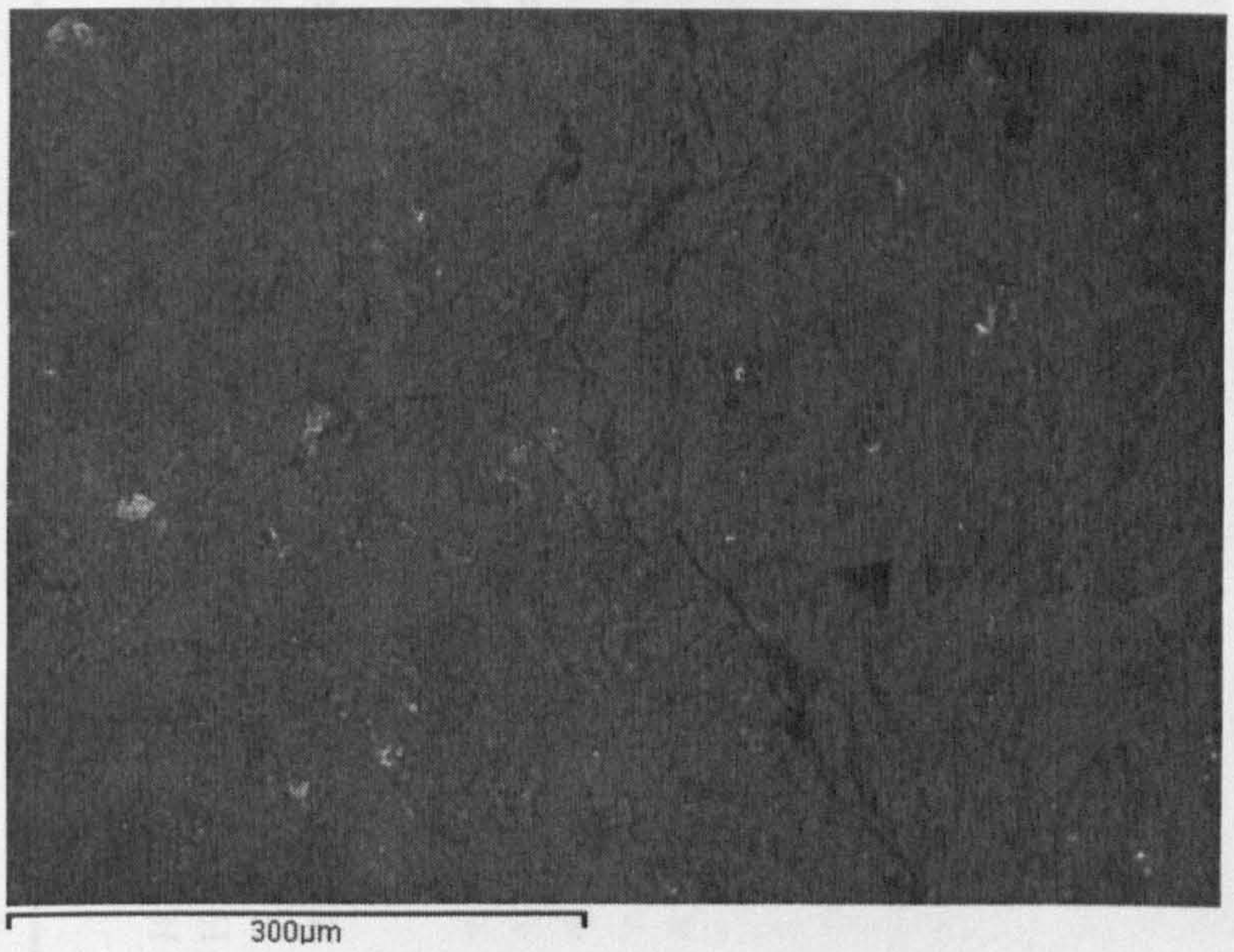
Size	7.50 cm
Weight	59.00 g
Colour	dark brown/black
Texture	angular
Porosity	low
Inclusions	no
Weathering	moderate
Magnetism	yes

Optical microscopy



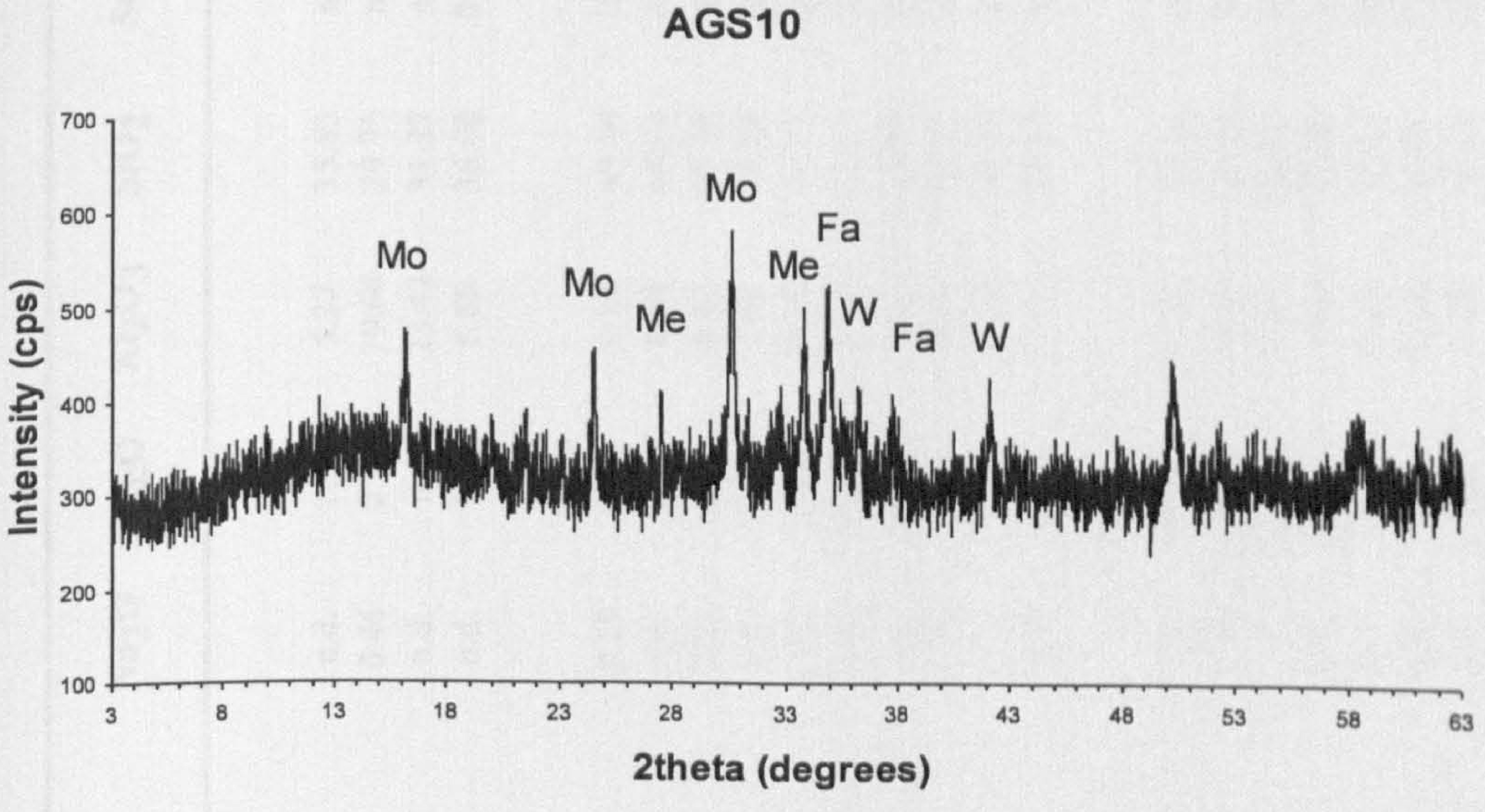
Vesicular matrix/Numerous wüstite dendrites /Fayalite phase (dark grey)/ Large cluster of Fe- prills (x 400)

SEM image



The matrix is fayalite-rich, wüstite is rare and there are also regions were small metallic prills abound in form of clusters. Separate larger prills also exist.

XRD



Intensity curve of sample:
Wu: Wustite-FeO, Fa: Fayalite-Fe_2SiO_4, Me: Melanotekite-$Pb_2Fe_2^{+3}(Si_2O_7)O_2$, Mo: Monticellite-$CaMgSiO_4$

APPENDIX II

Scanning Electron Microscopy/Energy Dispersive X-ray data: area and point analysis on mineral phases in slag

(percentages normalized to wt.%)

	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	MnO	FeO	ZnO	PbO	CuO	As_2O_3	Sb_2O_3
MAK01														
matrix (area 1)	n.d.	1.32	5.37	35.83	n.d.	1.58	19.52	18.58	12.37	2.33	3.05	n.d.	n.d.	n.d.
matrix (spot 1)	0.46	0.79	19.66	29.75	n.d.	0.56	18.50	19.30	10.16	n.d.	0.79	n.d.	n.d.	n.d.
matrix (spot 2)	n.d.	n.d.	23.42	31.27	n.d.	1.67	15.31	12.09	9.47	2.44	4.28	n.d.	n.d.	n.d.
matrix (area 2)	n.d.	1.38	6.66	36.08	0.59	1.20	20.55	19.87	12.34	1.29	n.d.	n.d.	n.d.	n.d.
MAK02														
matrix (area 1)	0.79	1.41	8.15	49.14	n.d.	2.05	16.89	4.13	15.05	n.d.	2.35	n.d.	n.d.	n.d.
matrix (spot 1)	n.d.	1.43	8.04	49.91	n.d.	49.91	16.31	4.48	14.93	n.d.	2.67	n.d.	n.d.	n.d.
matrix (spot 2)	0.62	1.35	8.52	50.19	n.d.	2.25	16.22	4.49	14.40	n.d.	1.92	n.d.	n.d.	n.d.
metallic prill	n.d.	n.d.	3.58	22.38	n.d.	0.86	6.77	1.62	6.17	n.d.	8.28	n.d.	17.47	32.82
matrix (area 2)	1.09	1.05	8.78	49.77	n.d.	2.18	15.69	4.75	14.57	n.d.	2.08	n.d.	n.d.	n.d.
metallic prill	n.d.	n.d.	3.11	21.15	3.91	0.89	6.06	2.01	6.87	n.d.	35.63	4.88	15.46	n.d.
metallic prill	n.d.	n.d.	3.34	21.58	n.d.	0.71	7.26	1.96	6.72	n.d.	22.20	1.43	10.74	24.00
metallic prill	0.78	n.d.	9.04	31.97	n.d.	5.44	1.93	n.d.	4.79	n.d.	1.00	n.d.	1.51	n.d.
glassy phase	1.53	0.62	17.01	57.19	n.d.	11.20	4.67	2.27	5.47	n.d.	n.d.	n.d.	n.d.	n.d.
matrix (area 3)	1.69	1.91	21.24	51.89	n.d.	8.13	3.30	1.08	8.60	n.d.	n.d.	n.d.	2.11	n.d.
MAK08														
metallic prill	n.d.	n.d.	8.26	35.56	n.d.	1.74	5.04	1.68	32.78	n.d.	12.86	n.d.	2.03	n.d.
matrix (area 1)	1.95	n.d.	26.24	52.45	n.d.	1.55	12.88	n.d.	4.90	n.d.	n.d.	n.d.	n.d.	n.d.
fayalite	n.d.	1.26	5.93	32.42	n.d.	1.47	1.82	n.d.	15.09	n.d.	n.d.	n.d.	n.d.	n.d.
fayalite	0.98	n.d.	7.50	33.80	n.d.	1.48	2.09	n.d.	12.02	n.d.	n.d.	n.d.	n.d.	n.d.
metallic prill	n.d.	n.d.	2.76	10.81	16.89	n.d.	1.00	n.d.	18.19	n.d.	50.31	n.d.	n.d.	n.d.
matrix (area 2)	n.d.	n.d.	17.56	45.26	2.28	1.50	8.89	0.82	23.66	n.d.	n.d.	n.d.	n.d.	n.d.
wüstite	n.d.	n.d.	4.17	15.64	n.d.	0.48	0.85	n.d.	78.82	n.d.	n.d.	n.d.	n.d.	n.d.
metallic prill	n.d.	1.19	0.61	39.23	n.d.	1.10	2.66	1.61	32.23	n.d.	21.33	n.d.	n.d.	n.d.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	V_2O_5	FeO	ZrO	MnO
KAT01												
magnetite	0.54	0.69	2.72	11.74	n.d.	1.00	3.58	2.51	n.d.	37.20	n.d.	0.86
matrix (area 1)	n.d.	n.d.	9.26	50.24	n.d.	3.55	13.10	n.d.	n.d.	23.82	n.d.	n.d.
matrix (area 2)	1.09	1.12	7.22	35.19	n.d.	2.56	9.53	3.69	n.d.	36.59	2.97	n.d.
metallic prill	n.d.	n.d.	3.84	15.38	n.d.	1.00	3.79	4.76	n.d.	69.72	1.47	n.d.
magnetite	n.d.	0.91	2.84	11.12	n.d.	0.61	0.71	4.55	n.d.	76.67	1.07	1.49
magnetite	n.d.	0.61	2.96	11.22	n.d.	0.63	4.26	2.00	n.d.	77.01	n.d.	1.27
wüstite	n.d.	1.24	3.77	17.98	n.d.	n.d.	12.44	1.07	n.d.	61.98	n.d.	1.48
wüstite	n.d.	0.86	7.53	29.77	1.51	2.63	11.43	2.62	1.20	41.21	n.d.	1.19
wüstite	n.d.	n.d.	7.95	28.16	1.66	3.02	9.80	2.70	n.d.	45.58	n.d.	1.07
matrix (area 3)	1.46	n.d.	10.51	44.68	3.49	3.36	14.80	1.56	2.05	18.06	n.d.	n.d.
magnetite	0.71	n.d.	3.38	28.01	n.d.	0.87	24.06	6.97	n.d.	32.41	3.54	n.d.
magnetite	n.d.	1.46	4.44	14.39	n.d.	0.94	5.29	2.05	n.d.	69.65	n.d.	1.74
metallic prill	n.d.	n.d.	5.70	22.15	n.d.	1.31	8.34	2.44	n.d.	56.83	1.99	1.21
matrix (area 4)	1.09	n.d.	6.74	29.41	1.47	2.85	9.24	3.03	1.24	43.88	n.d.	0.99
KAT02												
matrix (area 1)	1.11	n.d.	9.81	37.21	n.d.	2.44	6.23	0.72	n.d.	40.23	2.21	n.d.
matrix (area 1)	1.09	n.d.	11.13	49.85	2.91	3.27	11.17	0.63	n.d.	19.91	n.d.	n.d.
magnetite	n.d.	n.d.	8.43	12.68	n.d.	0.90	2.18	1.20	n.d.	74.57	n.d.	n.d.
magnetite	n.d.	0.99	6.96	14.22	n.d.	0.76	1.84	1.23	n.d.	73.97	n.d.	n.d.
KAT06												
wüstite	0.26	0.88	2.59	9.19	n.d.	0.63	3.35	1.43	n.d.	81.63	n.d.	n.d.
wüstite	n.d.	1.28	0.49	10.80	n.d.	0.52	3.21	1.58	1.14	80.93	n.d.	n.d.
matrix (spot 1)	n.d.	n.d.	5.95	36.04	2.03	2.76	15.21	1.81	n.d.	34.76	n.d.	1.40
spinel	n.d.	n.d.	5.52	9.19	n.d.	0.51	3.41	15.43	4.87	60.26	n.d.	0.77
metallic prill	n.d.	0.52	2.36	8.02	n.d.	0.59	2.68	1.61	n.d.	84.19	n.d.	n.d.
matrix (spot 2)	0.52	1.20	6.92	33.92	2.06	3.19	15.54	1.74	n.d.	33.51	n.d.	1.33
wüstite	n.d.	1.08	2.25	10.47	n.d.	0.45	3.22	1.06	n.d.	81.43	n.d.	n.d.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	V_2O_5	FeO	ZrO	MnO	Cr_2O_3
KAT07													
spinel	n.d.	1.21	6.80	6.58	n.d.	0.65	1.96	15.50	8.44	58.82	n.d.	n.d.	n.d.
fayalite	0.51	n.d.	15.67	40.61	3.34	12.24	5.28	2.25	n.d.	20.07	n.d.	n.d.	n.d.
fayalite	0.29	2.25	1.99	30.25	1.13	0.63	11.59	1.50	n.d.	49.44	n.d.	0.89	n.d.
wüstite	n.d.	0.70	2.47	9.38	n.d.	0.65	2.79	2.17	n.d.	81.35	n.d.	0.46	n.d.
matrix (area 1)	0.83	0.94	6.14	23.21	1.92	2.12	6.91	5.95	1.61	50.33	n.d.	n.d.	n.d.
wüstite	n.d.	0.65	2.60	8.39	0.67	0.39	2.56	2.66	n.d.	82.04	n.d.	n.d.	n.d.
matrix (spot 1)	n.d.	2.84	1.40	29.19	n.d.	0.46	7.70	2.26	n.d.	55.17	n.d.	0.93	n.d.
fayalite	0.45	0.36	15.76	42.44	0.69	12.74	3.83	1.96	n.d.	21.72	n.d.	n.d.	n.d.
wüstite	n.d.	0.50	2.23	6.55	n.d.	0.39	1.50	3.38	1.35	84.05	n.d.	n.d.	n.d.
spinel	n.d.	0.89	5.98	7.13	n.d.	0.69	2.19	15.47	7.50	59.13	n.d.	0.97	n.d.
metallic prill	n.d.	n.d.	2.10	5.45	n.d.	0.40	1.04	1.14	n.d.	89.85	n.d.	n.d.	n.d.
metallic prill	n.d.	n.d.	1.88	5.62	n.d.	0.40	1.12	0.83	n.d.	90.12	n.d.	n.d.	n.d.
metallic prill	n.d.	n.d.	1.72	5.90	n.d.	0.42	1.04	1.14	n.d.	89.76	n.d.	n.d.	n.d.
matrix (spot 2)	n.d.	n.d.	1.44	6.47	n.d.	0.54	0.95	1.09	n.d.	89.47	n.d.	n.d.	n.d.
spinel	0.12	0.46	5.71	6.83	n.d.	0.50	1.70	16.44	7.56	60.64	n.d.	n.d.	n.d.
KAT09													
metallic prill	0.65	1.02	4.02	17.80	n.d.	1.76	4.79	1.15	n.d.	66.89	1.50	0.37	n.d.
wüstite	n.d.	0.71	3.12	12.12	n.d.	0.92	2.71	3.14	n.d.	75.72	0.94	0.57	n.d.
matrix (spot 1)	0.87	1.65	6.31	35.03	1.80	3.68	8.67	2.17	n.d.	38.97	n.d.	0.82	n.d.
spinel	n.d.	1.16	6.04	14.05	0.61	0.97	3.42	8.93	4.68	58.67	1.13	n.d.	0.28
magnetite	0.55	1.27	6.60	33.36	n.d.	3.03	9.92	1.99	n.d.	40.06	2.17	1.00	n.d.
magnetite	0.53	0.49	5.67	30.04	n.d.	4.13	9.11	1.92	n.d.	44.39	2.48	1.20	n.d.
magnetite	1.39	1.35	6.55	33.40	1.86	3.69	9.79	1.76	n.d.	39.17	n.d.	0.99	n.d.
wüstite	n.d.	0.60	3.78	6.24	n.d.	n.d.	1.06	2.69	1.65	82.96	n.d.	0.95	n.d.
wüstite	0.23	0.827	3.18	5.98	0.63	0.73	1.14	1.91	0.97	83.60	n.d.	0.74	n.d.
metallic prill	n.d.	n.d.	2.65	5.49	0.44	0.34	1.54	0.85	n.d.	88.66	n.d.	n.d.	n.d.
wüstite	0.31	0.50	3.82	5.49	0.90	0.67	1.40	2.39	1.42	82.10	n.d.	0.94	n.d.
magnetite	0.61	1.54	7.71	26.05	n.d.	2.65	7.00	4.21	1.26	45.69	2.52	0.71	n.d.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	V_2O_5	FeO	ZrO	MnO
VTH01												
metallic prill	n.d.	n.d.	0.90	4.50	n.d.	0.37	1.55	n.d.	n.d.	92.64	n.d.	n.d.
wüstite	0.54	0.81	2.30	5.76	n.d.	n.d.	2.34	2.22	1.86	83.20	n.d.	0.93
matrix (spot 1)	n.d.	1.07	6.70	28.76	1.82	2.60	16.90	1.63	n.d.	40.48	n.d.	n.d.
matrix (spot 2)	n.d.	n.d.	7.83	31.73	2.69	2.55	16.83	1.72	n.d.	36.61	n.d.	n.d.
wüstite	0.05	0.86	1.84	5.67	n.d.	0.42	2.68	1.85	1.57	84.10	n.d.	0.91
metallic prill	n.d.	n.d.	1.22	6.54	n.d.	0.34	1.92	0.73	n.d.	89.22	n.d.	n.d.
matrix (area 1)	n.d.	n.d.	3.59	12.73	0.83	1.11	6.13	1.69	n.d.	45.01	n.d.	0.38
matrix (area 2)	n.d.	1.09	4.84	19.53	n.d.	2.11	8.60	2.20	1.13	58.67	1.78	n.d.
wüstite	n.d.	n.d.	1.67	5.76	n.d.	n.d.	2.62	n.d.	n.d.	89.93	n.d.	n.d.
wüstite	n.d.	n.d.	2.49	6.68	n.d.	0.47	3.32	4.24	2.47	79.27	n.d.	1.03
matrix (spot 3)	0.34	0.84	7.05	33.63	2.68	2.80	16.23	1.10	n.d.	35.29	n.d.	n.d.
wüstite	0.33	0.69	2.71	8.07	n.d.	0.81	2.96	3.56	1.83	78.37	n.d.	0.62
VTH02												
wüstite	n.d.	0.42	1.75	7.01	n.d.	n.d.	1.78	2.52	1.89	83.90	n.d.	0.69
matrix (spot 1)	0.81	1.02	7.26	34.10	n.d.	3.03	7.85	1.21	n.d.	41.95	2.09	0.64
metallic prill	n.d.	n.d.	0.86	5.30	n.d.	n.d.	1.19	n.d.	n.d.	92.26	n.d.	0.37
wüstite	n.d.	0.28	2.18	6.66	n.d.	n.d.	1.57	2.55	1.33	84.79	n.d.	0.60
matrix (spot 2)	n.d.	n.d.	n.d.	39.78	n.d.	n.d.	n.d.	n.d.	n.d.	60.21	n.d.	n.d.
matrix (area 1)	n.d.	1.13	4.31	20.55	n.d.	1.58	6.18	1.77	1.16	61.59	1.69	n.d.
metallic prill	n.d.	n.d.	0.98	4.95	n.d.	n.d.	1.24	0.48	0.25	92.07	n.d.	n.d.
wüstite	n.d.	1.09	1.75	7.03	n.d.	0.58	1.99	1.60	0.94	84.98	n.d.	n.d.
matrix (spot 3)	1.05	0.45	6.32	32.08	1.65	3.14	10.16	1.13	n.d.	43.97	n.d.	n.d.
matrix (area 2)	n.d.	n.d.	4.32	20.77	n.d.	1.46	6.12	1.67	1.00	63.23	1.40	n.d.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	V_2O_5	FeO	ZrO	MnO
VTH07												
metallic prill	n.d.	n.d.	2.05	8.70	n.d.	n.d.	2.96	n.d.	n.d.	86.28	n.d.	n.d.
matrix (spot 1)	1.26	1.33	5.96	35.90	n.d.	3.10	14.78	1.37	n.d.	34.53	1.73	n.d.
matrix (spot 2)	1.12	0.86	6.32	33.80	n.d.	2.93	16.53	1.30	n.d.	34.65	2.45	n.d.
wüstite	0.87	0.90	3.06	9.91	n.d.	1.21	3.48	4.52	1.44	73.32	1.24	n.d.
matrix (area 1)	0.83	1.49	5.35	26.88	n.d.	2.42	11.34	2.81	n.d.	47.67	1.17	n.d.
matrix (area 2)	0.30	0.79	4.78	26.00	n.d.	2.44	11.16	3.25	n.d.	51.25	n.d.	n.d.
matrix (area 3)	0.71	1.79	4.79	27.03	n.d.	2.53	10.74	3.15	n.d.	46.86	2.36	n.d.
magnetite	1.06	0.90	4.58	10.78	n.d.	1.20	4.67	12.46	5.39	57.98	0.93	n.d.
wüstite	1.08	0.49	3.64	10.76	n.d.	0.58	4.28	3.65	n.d.	75.42	n.d.	n.d.
fayalite	0.75	0.72	6.64	33.75	n.d.	3.78	14.12	1.68	n.d.	34.88	2.77	0.86
matrix (area 4)	1.03	0.69	5.00	21.66	n.d.	2.12	9.52	4.19	n.d.	53.65	2.08	n.d.
VTH09												
matrix (area 1)	n.d.	n.d.	4.29	25.12	n.d.	1.87	9.52	3.64	n.d.	55.53	n.d.	n.d.
metallic prill	0.45	0.83	2.57	9.23	n.d.	0.67	4.57	1.49	0.06	78.36	1.71	n.d.
wüstite	0.59	1.35	2.78	12.99	n.d.	1.66	5.07	4.38	1.58	68.88	1.87	n.d.
matrix (spot 1)	0.65	1.34	5.17	32.84	n.d.	3.17	12.22	1.75	0.48	40.52	1.83	n.d.
matrix (spot 2)	1.27	1.95	6.25	33.15	n.d.	2.96	13.06	n.d.	0.55	40.76	n.d.	n.d.
matrix (area 2)	0.20	1.96	3.67	23.36	2.57	2.92	7.46	4.36	0.54	53.14	0.07	0.15

APPENDIX III

X-Ray Fluorescence data: bulk chemical composition

Table 1. Makrychori and Katafyto samples

Sample no.	SiO_2	Al_2O_3	CaO	Cl	FeO	K_2O	MgO	MnO	S	P_2O_5	Pb	W	TiO_2	Sr
MAK01	39.17	6.80	19.20	0.57	14.14	n.d.	n.d.	19.74	n.d.	0.48	1.63	n.d.	0.28	0.13
MAK02	61.24	9.35	12.23	n.d.	11.99	0.42	n.d.	3.37	n.d.	0.15	0.96	n.d.	0.26	0.05
MAK03	52.80	11.13	12.88	0.39	14.53	n.d.	n.d.	6.05	n.d.	0.30	3.72	n.d.	0.31	0.08
MAK04	68.93	12.33	1.11	0.43	5.06	n.d.	9.06	0.20	n.d.	n.d.	2.24	0.020	0.36	0.00
MAK05	59.27	16.88	5.50	n.d.	6.16	n.d.	11.86	0.14	n.d.	n.d.	2.71	n.d.	0.44	0.04
MAK06	38.03	7.09	19.48	0.45	12.54	n.d.	9.85	10.28	n.d.	0.23	0.58	n.d.	0.23	0.06
MAK07	47.21	9.48	21.80	0.06	10.92	n.d.	n.d.	9.18	0.18	0.41	1.09	n.d.	0.31	0.11
MAK08	68.64	18.49	1.29	0.31	8.01	n.d.	n.d.	0.35	0.24	n.d.	2.04	n.d.	0.77	0.07
MAK09	41.41	8.44	20.48	0.53	15.00	n.d.	n.d.	12.83	n.d.	0.23	0.78	n.d.	0.30	0.10
MAK10	38.87	8.51	20.64	0.53	8.29	n.d.	9.89	10.94	n.d.	0.39	0.04	n.d.	0.25	0.06
KAT01	25.63	10.71	7.78	0.23	52.95	n.d.	n.d.	1.12	0.14	n.d.	n.d.	n.d.	2.31	0.15
KAT02	26.30	8.61	4.39	0.68	55.35	n.d.	n.d.	0.47	0.20	n.d.	n.d.	n.d.	1.94	0.08
KAT03	26.30	5.45	5.86	0.65	56.97	n.d.	n.d.	0.65	0.22	n.d.	n.d.	0.026	2.13	0.05
KAT04	11.97	2.93	3.17	0.74	77.18	n.d.	n.d.	0.32	0.11	n.d.	0.006	n.d.	1.32	0.05
KAT05	43.14	9.32	1.12	0.85	41.44	n.d.	5.15	0.07	0.11	n.d.	0.003	0.010	0.30	0.10
KAT06	21.17	6.18	6.78	1.05	60.40	n.d.	n.d.	0.95	0.25	n.d.	0.004	0.023	2.63	0.07
KAT07	21.18	7.63	4.21	0.39	50.26	n.d.	13.25	0.57	0.15	n.d.	0.006	n.d.	3.59	0.08
KAT08	32.63	7.04	5.43	0.95	49.10	n.d.	n.d.	0.72	0.27	n.d.	n.d.	0.032	1.97	0.05
KAT09	25.49	7.69	5.47	0.53	54.74	n.d.	n.d.	0.71	0.15	n.d.	n.d.	0.037	2.90	0.07
KAT10	23.51	9.47	5.73	0.31	56.27	n.d.	n.d.	0.55	0.08	n.d.	n.d.	0.035	2.08	0.12

Sample no.	Rb	As	Sb	Sn	Cu	Zn	Mo (ppm)	Zr (ppm)	Bi (ppm)	Ni (ppm)	Cr (ppm)	V (ppm)	Ba (ppm)	Ag (ppm)	TOTAL
MAK01	0.002	0.41	0.51	n.d.	0.069	0.793	n.d.	16.07	n.d.	130.46	n.d.	235.78	718.82	29.2	103.52
MAK02	0.002	0.08	0.05	n.d.	0.012	0.232	n.d.	24.32	n.d.	n.d.	n.d.	165.93	n.d.	n.d.	100.35
MAK03	0.004	0.38	0.40	0.015	0.048	0.715	n.d.	29.43	n.d.	n.d.	n.d.	150.89	505.35	23.21	103.41
MAK04	0.003	0.51	0.04	n.d.	0.007	0.212	n.d.	32.87	n.d.	n.d.	n.d.	90.67	n.d.	37.01	100.48
MAK05	0.004	0.87	0.14	n.d.	0.029	0.023	n.d.	57.36	n.d.	n.d.	n.d.	190	n.d.	n.d.	103.94
MAK06	n.d.	0.12	0.17	n.d.	0.034	0.433	25.04	22.29	n.d.	80.74	n.d.	173.46	n.d.	n.d.	99.42
MAK07	0.002	0.12	0.34	n.d.	0.051	0.689	n.d.	43.52	n.d.	n.d.	n.d.	272.64	412.09	18.28	101.69
MAK08	0.012	0.78	0.10	0.006	0.012	0.069	n.d.	200.98	n.d.	n.d.	121.63	285.61	239.97	57.32	101.17
MAK09	0.002	0.25	0.35	n.d.	0.027	0.572	25.39	28.24	n.d.	n.d.	101.65	163.68	268.39	26.61	101.01
MAK10	n.d.	0.08	0.19	n.d.	0.025	0.353	n.d.	26.25	n.d.	83.77	99.88	195.57	n.d.	n.d.	98.90
KAT01	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9197.02	1454.48	n.d.	257.21	5830.67	501.68	28.22	102.75
KAT02	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	38.16	6223.44	894.94	n.d.	266.9	3428.1	326.69	n.d.	99.14
KAT03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	50.43	4340.59	687.63	140.49	213.53	2795.71	n.d.	n.d.	99.10
KAT04	0.002	n.d.	n.d.	n.d.	0.013	n.d.	n.d.	3369.97	872.72	n.d.	n.d.	1460.04	292.78	n.d.	98.40
KAT05	0.007	n.d.	n.d.	n.d.	0.004	n.d.	36.21	350.79	51.27	n.d.	176.14	463.47	178.84	n.d.	101.74
KAT06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	61.93	4428.35	798.81	148.02	218.65	3244.68	239.71	17.47	100.38
KAT07	0.003	n.d.	n.d.	n.d.	n.d.	n.d.	45.04	6696.37	1337.41	n.d.	267.62	6580.47	613.14	n.d.	102.87
KAT08	0.003	n.d.	n.d.	n.d.	0.012	n.d.	n.d.	3185.59	441.74	124.06	203.65	1428.98	n.d.	n.d.	98.70
KAT09	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	47.81	6703.88	639.82	n.d.	266.95	4557.98	238.26	n.d.	98.98
KAT10	0.003	n.d.	n.d.	n.d.	n.d.	n.d.	43.11	6611.14	637.61	n.d.	831.04	6486.38	417.46	19	99.63

Table 2. Vathytopos and Angistro samples

Sample no.	SiO_2	Al_2O_3	CaO	Cl	FeO	K_2O	MgO	MnO	S	P_2O_5	Pb	W	TiO_2	Sr
VTH01	18.10	8.23	6.71	0.23	62.82	n.d.	n.d.	0.59	0.08	n.d.	n.d.	0.043	1.99	0.13
VTH02	18.03	6.49	6.84	0.22	63.00	n.d.	n.d.	0.58	0.11	n.d.	n.d.	0.056	2.00	0.13
VTH03	17.96	4.52	3.75	0.70	71.77	n.d.	n.d.	0.36	0.20	n.d.	n.d.	0.026	1.52	0.04
VTH04	19.46	4.47	5.66	0.84	66.48	n.d.	n.d.	0.66	0.23	n.d.	n.d.	0.003	2.46	0.12
VTH05	23.97	4.29	6.24	0.93	60.14	n.d.	n.d.	0.64	0.27	n.d.	n.d.	0.027	2.79	0.05
VTH06	19.48	6.74	6.78	0.37	64.90	n.d.	n.d.	0.64	0.12	n.d.	0.003	0.003	1.96	0.07
VTH07	16.82	4.47	6.76	1.23	70.21	n.d.	n.d.	0.44	0.34	n.d.	n.d.	0.004	1.68	0.09
VTH08	24.77	6.01	8.75	0.70	57.34	n.d.	n.d.	0.72	0.21	n.d.	n.d.	0.003	3.06	0.15
VTH09	21.49	5.89	7.11	0.34	63.49	n.d.	n.d.	0.45	0.12	n.d.	n.d.	0.004	2.33	0.08
VTH10	22.74	5.45	8.10	0.44	58.05	0.75	n.d.	0.75	0.11	n.d.	n.d.	n.d.	3.48	0.11
AGS01	45.40	4.70	10.42	0.81	38.15	n.d.	n.d.	0.48	0.31	n.d.	0.23	0.018	0.24	0.02
AGS02	63.19	10.46	5.45	0.30	11.18	n.d.	9.74	0.66	n.d.	n.d.	0.29	n.d.	0.26	0.11
AGS03	35.55	8.13	9.70	0.53	41.72	n.d.	n.d.	0.39	0.70	0.10	0.22	n.d.	0.23	0.05
AGS04	31.44	8.38	12.11	0.59	35.02	n.d.	10.83	0.89	0.54	0.15	0.88	0.035	0.25	0.12
AGS05	34.31	8.37	14.06	0.60	39.32	n.d.	n.d.	0.40	0.72	0.23	0.47	0.031	0.26	0.07
AGS06	38.78	10.21	10.73	0.38	38.82	n.d.	n.d.	0.67	0.57	0.11	0.52	n.d.	0.22	0.10
AGS07	26.76	8.15	8.92	0.28	43.71	n.d.	9.76	0.40	0.77	0.17	0.93	0.049	0.20	0.09
AGS08	38.38	8.01	10.69	0.65	39.83	n.d.	n.d.	0.38	0.60	0.12	0.90	n.d.	0.32	0.08
AGS09	40.86	7.52	12.24	0.44	35.99	n.d.	n.d.	0.46	0.43	0.10	0.20	n.d.	0.28	0.04
AGS10	35.20	7.77	12.51	0.66	41.09	n.d.	n.d.	0.50	0.70	0.13	0.55	0.034	0.26	0.14

Sample no.	Rb	As	Sb	Sn	Cu	Zn	Mo (ppm)	Zr (ppm)	Bi (ppm)	Ni (ppm)	Cr (ppm)	V (ppm)	Ba (ppm)	Ag (ppm)	TOTAL
VTH01	0.002	n.d.	n.d.	n.d.	0.013	n.d.	58.34	5475.57	747.12	n.d.	681.67	5941.61	446.39	21.16	100.22
VTH02	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	44.77	5284.13	818.64	n.d.	387.62	6076.46	439.74	19.48	98.70
VTH03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	63.93	3214.29	343.46	n.d.	297.73	4109.01	n.d.	20.05	101.61
VTH04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	51.57	6835.16	679.92	n.d.	400.43	4909.66	344.19	n.d.	101.70
VTH05	n.d.	n.d.	n.d.	n.d.	0.011	n.d.	30.13	3640.04	360.05	n.d.	310.79	3505.03	n.d.	n.d.	100.12
VTH06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	33.39	3111.84	419.61	n.d.	316.47	4761.84	n.d.	n.d.	101.93
VTH07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	41.47	4207.47	473.16	n.d.	385.1	2658.73	182.74	n.d.	102.83
VTH08	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	58.79	5716.98	808.31	n.d.	369.57	4691.86	280.13	19.13	102.90
VTH09	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	38.49	5948.49	388.25	n.d.	210.43	4899.2	194.63	n.d.	102.48
VTH10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	45.78	4681.23	925.5	n.d.	311.75	4146.71	306.61	n.d.	101.02
AGS01	n.d.	n.d.	0.01	n.d.	0.009	0.092	56.26	32.63	n.d.	n.d.	88.61	103.86	n.d.	n.d.	100.89
AGS02	0.003	0.02	0.03	0.007	0.011	0.070	44.45	67.11	n.d.	n.d.	126.57	211.77	138.63	n.d.	101.81
AGS03	n.d.	n.d.	0.01	0.008	0.018	0.143	45.62	46.08	n.d.	139.63	85.48	128.61	n.d.	n.d.	97.52
AGS04	0.003	0.66	0.03	0.049	0.042	0.441	69.32	34.14	n.d.	n.d.	127.89	537.16	n.d.	n.d.	102.41
AGS05	0.002	0.19	0.01	0.020	0.015	0.238	39.26	41.23	n.d.	106.06	n.d.	268.54	n.d.	n.d.	99.30
AGS06	0.002	0.06	0.03	0.028	0.023	0.848	27.77	51.05	n.d.	141.72	n.d.	181.38	n.d.	n.d.	102.06
AGS07	0.002	0.09	0.09	0.067	0.022	0.622	75.05	30.85	n.d.	n.d.	n.d.	324.79	n.d.	n.d.	100.90
AGS08	0.002	0.07	0.06	0.038	0.025	0.232	73.44	46.49	n.d.	n.d.	n.d.	184.7	n.d.	n.d.	100.32
AGS09	n.d.	n.d.	0.01	0.008	0.007	0.163	19.17	20.16	n.d.	n.d.	86.34	136.6	n.d.	n.d.	98.77
AGS10	0.003	0.01	0.04	0.042	0.023	0.360	56.69	66.63	n.d.	n.d.	120.29	407.39	198.53	n.d.	99.99

Table 3. Precision and accuracy for GBW 01706 Converter Slag (Inst. of Wuhan Iron & Steel Co.)

GBW 01706		Si	Ca	Al	Ti	Fe	Mn	K	S
	Cert Oxide	18.63	49.38	4.81	0.45	16.01	3.63	0.04	0.19
	Anal 1	18.39	49.65	4.31	0.43	16.17	3.48	0.05	0.68
	Anal 2	19.05	49.23	5.27	0.50	15.28	3.38	0.05	0.48
	Anal 3	18.75	50.15	3.88	0.42	16.65	3.19	0.07	0.20
	Anal 4	19.01	49.92	4.52	0.47	16.30	3.86	0.05	0.16
	Anal 5	18.78	49.83	5.19	0.53	15.66	3.49	0.04	0.27
	Anal 6	18.36	49.24	5.02	0.46	15.62	3.58	0.05	0.67
	Anal7	18.80	49.85	4.70	0.44	15.71	3.79	0.04	0.30
	Anal 8	18.45	49.04	4.94	0.42	16.45	3.73	0.03	0.13
	Anal 9	18.84	49.30	4.99	0.48	16.40	3.29	0.01	0.44
	Anal 10	19.31	49.65	5.34	0.47	16.73	3.42	0.07	0.28
	Average	**18.77**	**49.59**	**4.82**	**0.46**	**16.10**	**3.52**	**0.05**	**0.36**
	precision (CV)	**1.64**	**0.73**	**9.64**	**7.76**	**3.07**	**6.17**	**38.01**	**54.97**
	Accuracy	**0.80**	**0.42**	**0.21**	**3.71**	**0.51**	**-2.95**	**21.98**	**88.49**

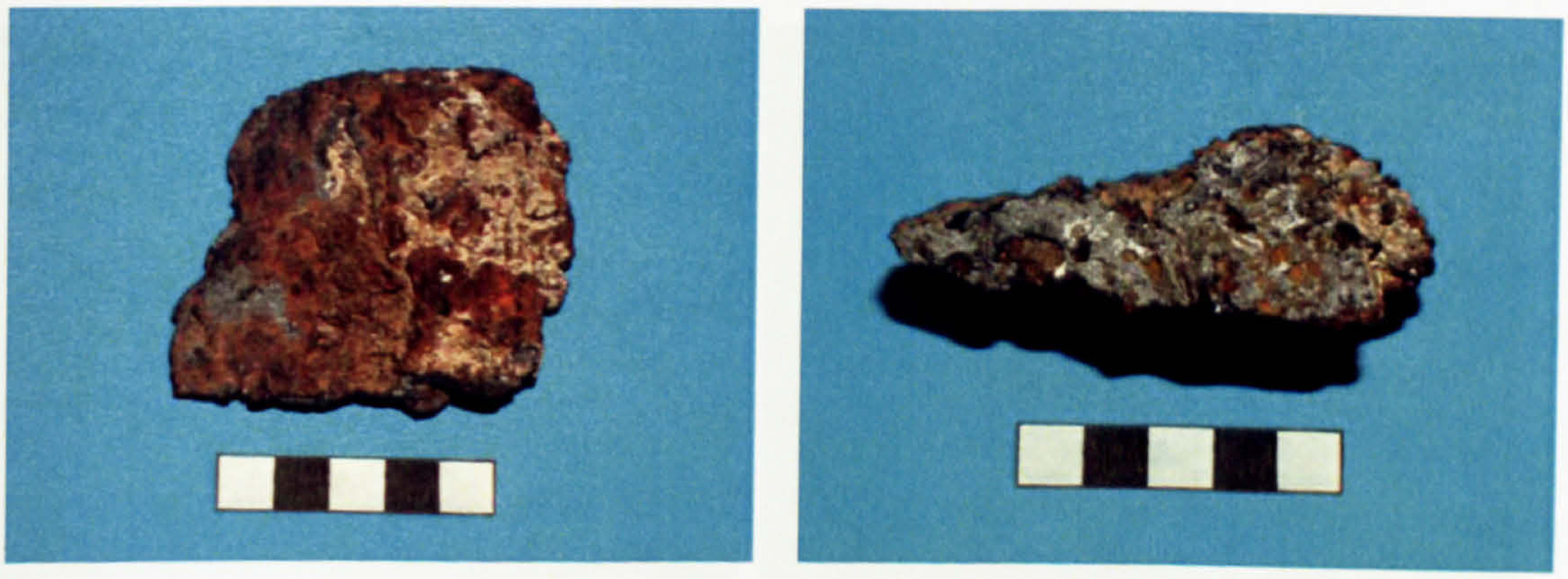
PAGE

NUMBERING

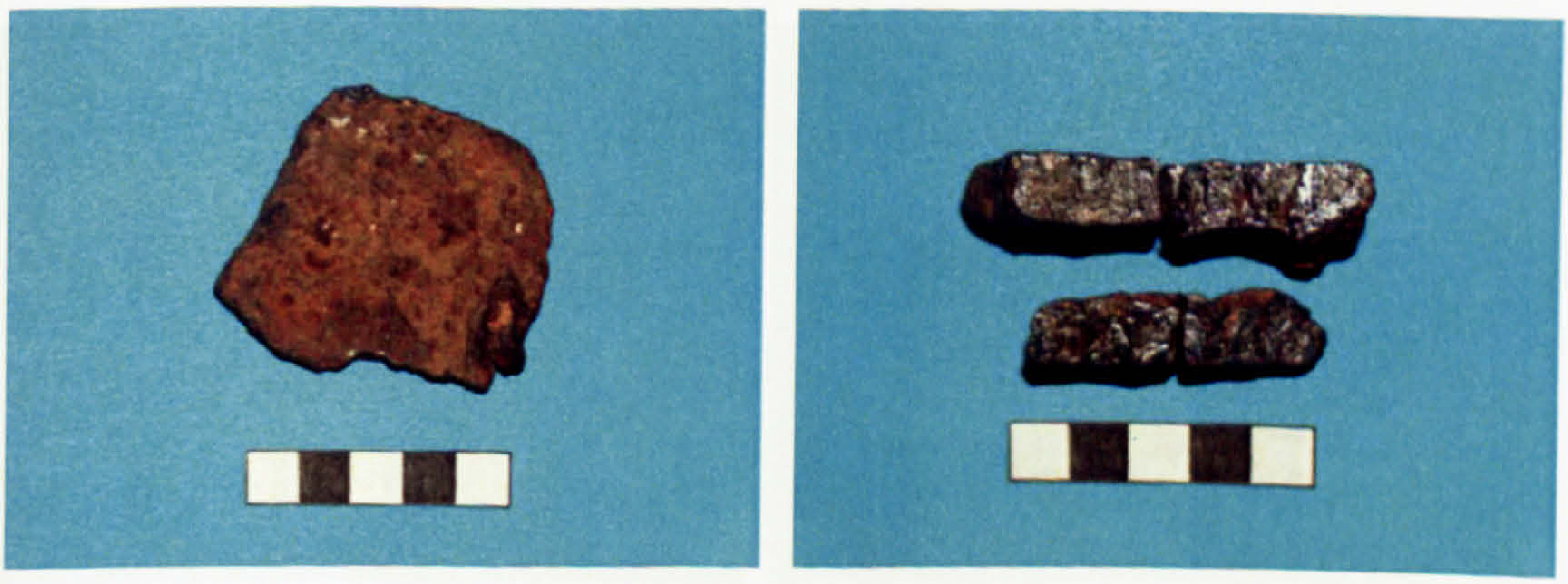
AS ORIGINAL

APPENDIX IV

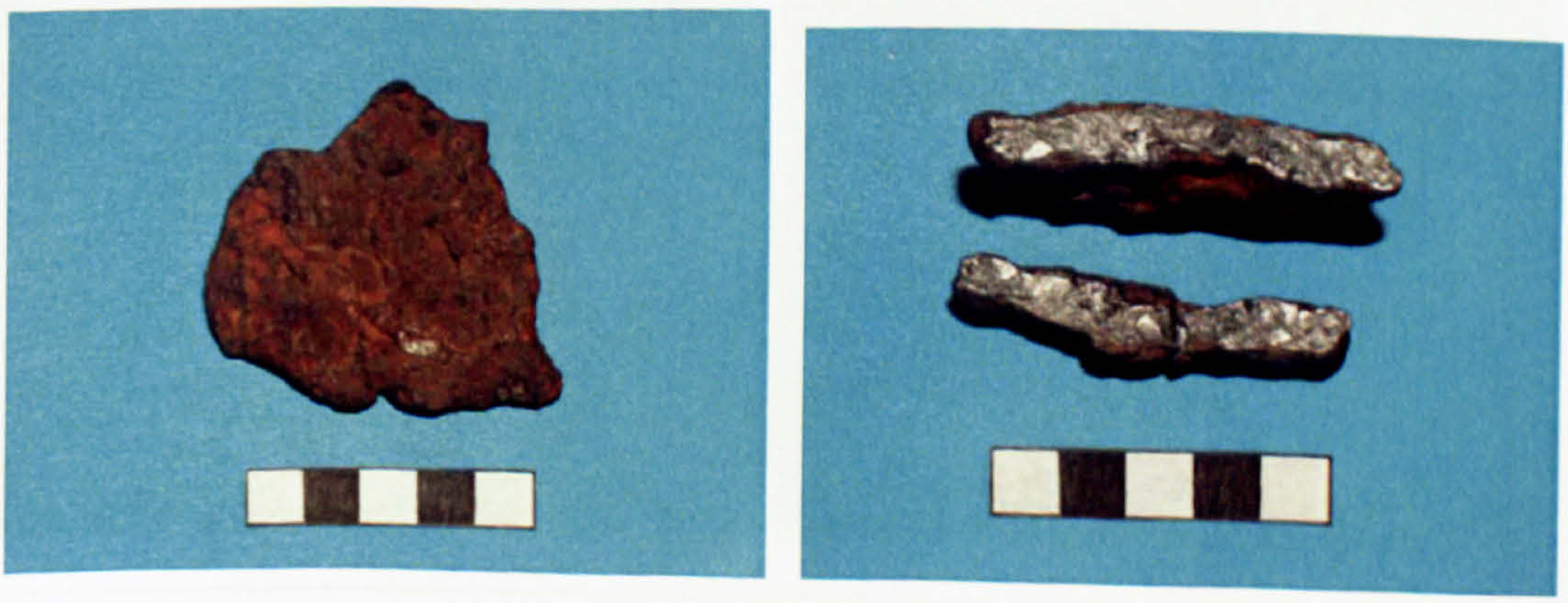
Sample No. AGS.SP01 speiss



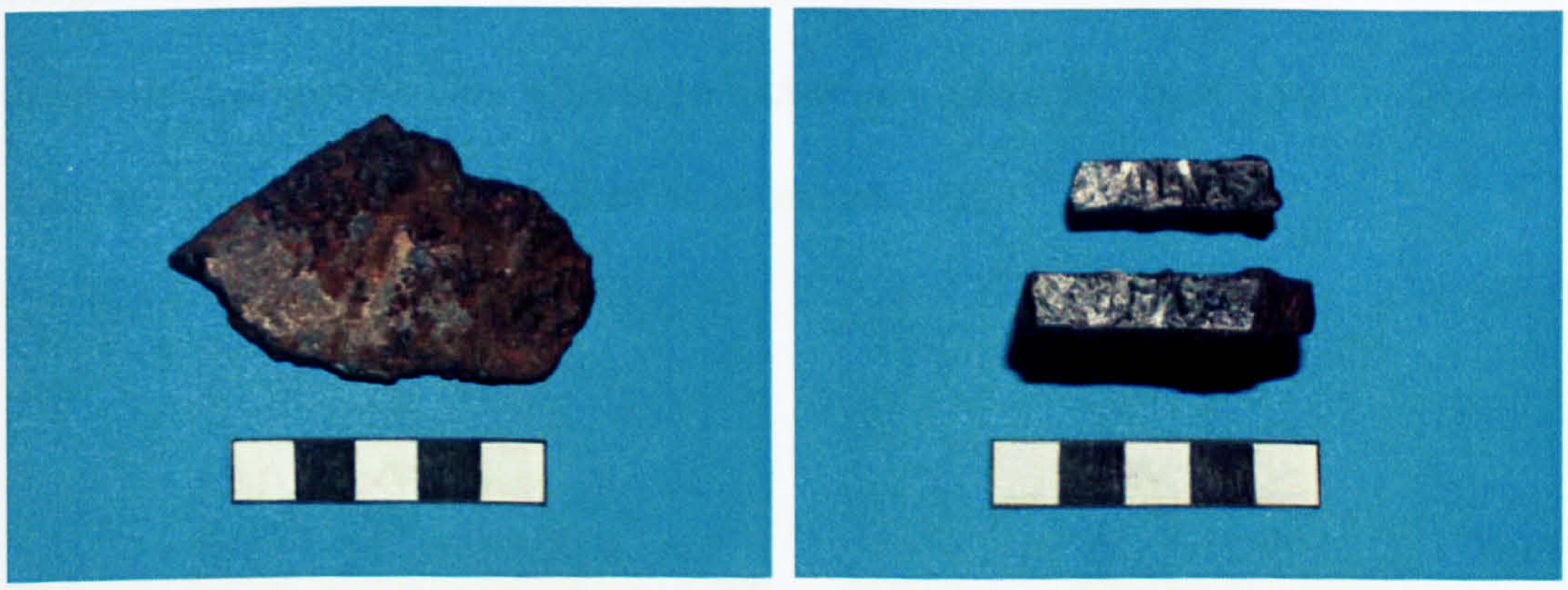
Sample No. MAK.SP03 speiss



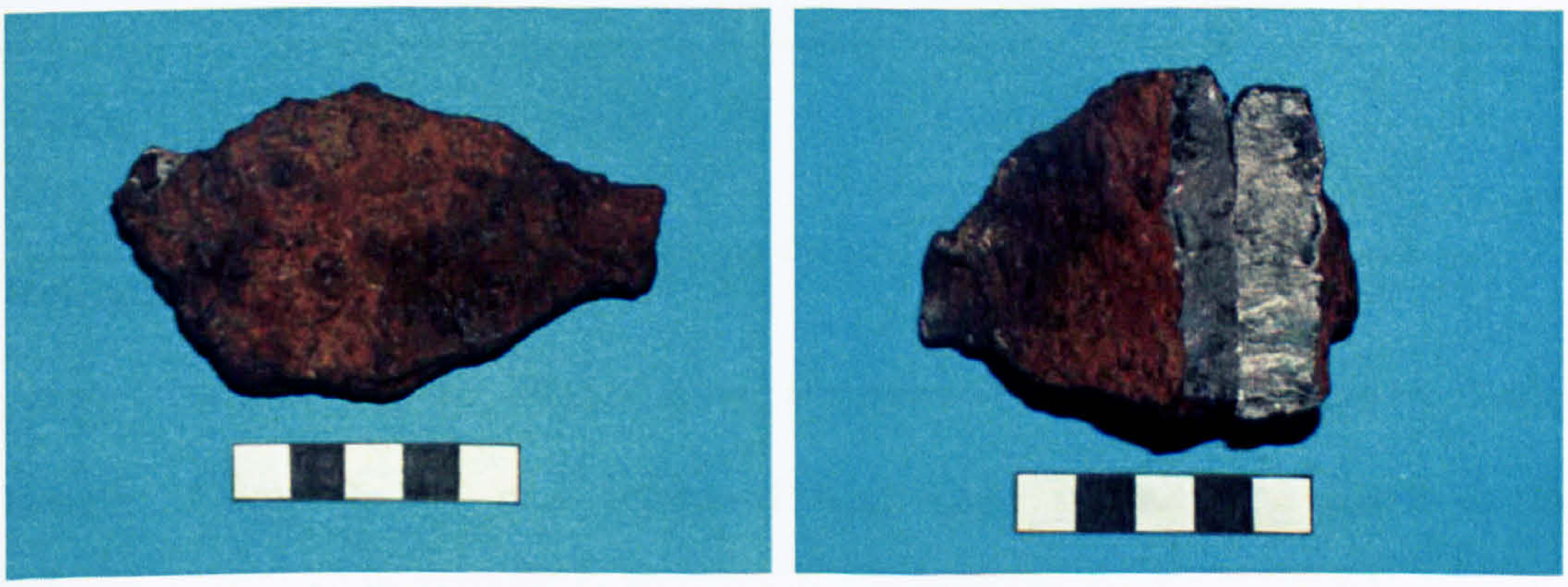
Sample No. MAK.SP08 speiss



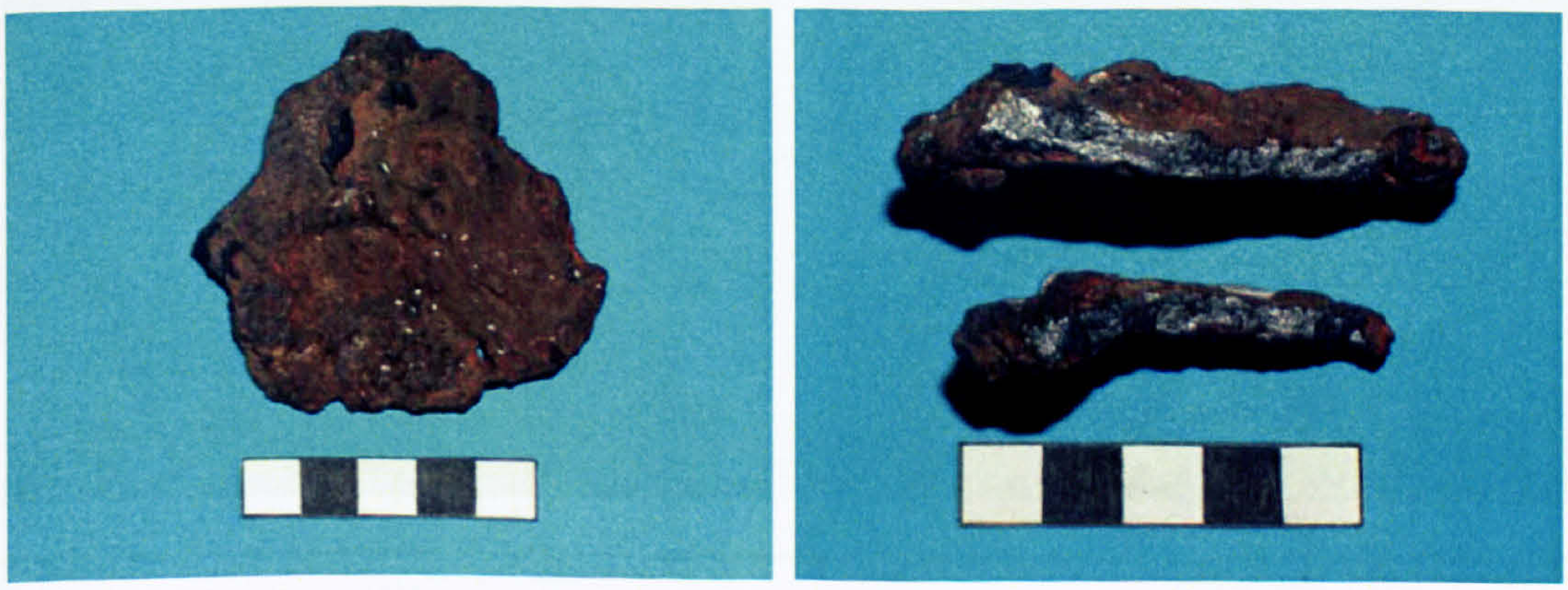
Sample No. MAK.SP10 speiss



Sample No. MAK.SP35 speiss



Sample No. MAK.SP36 speiss

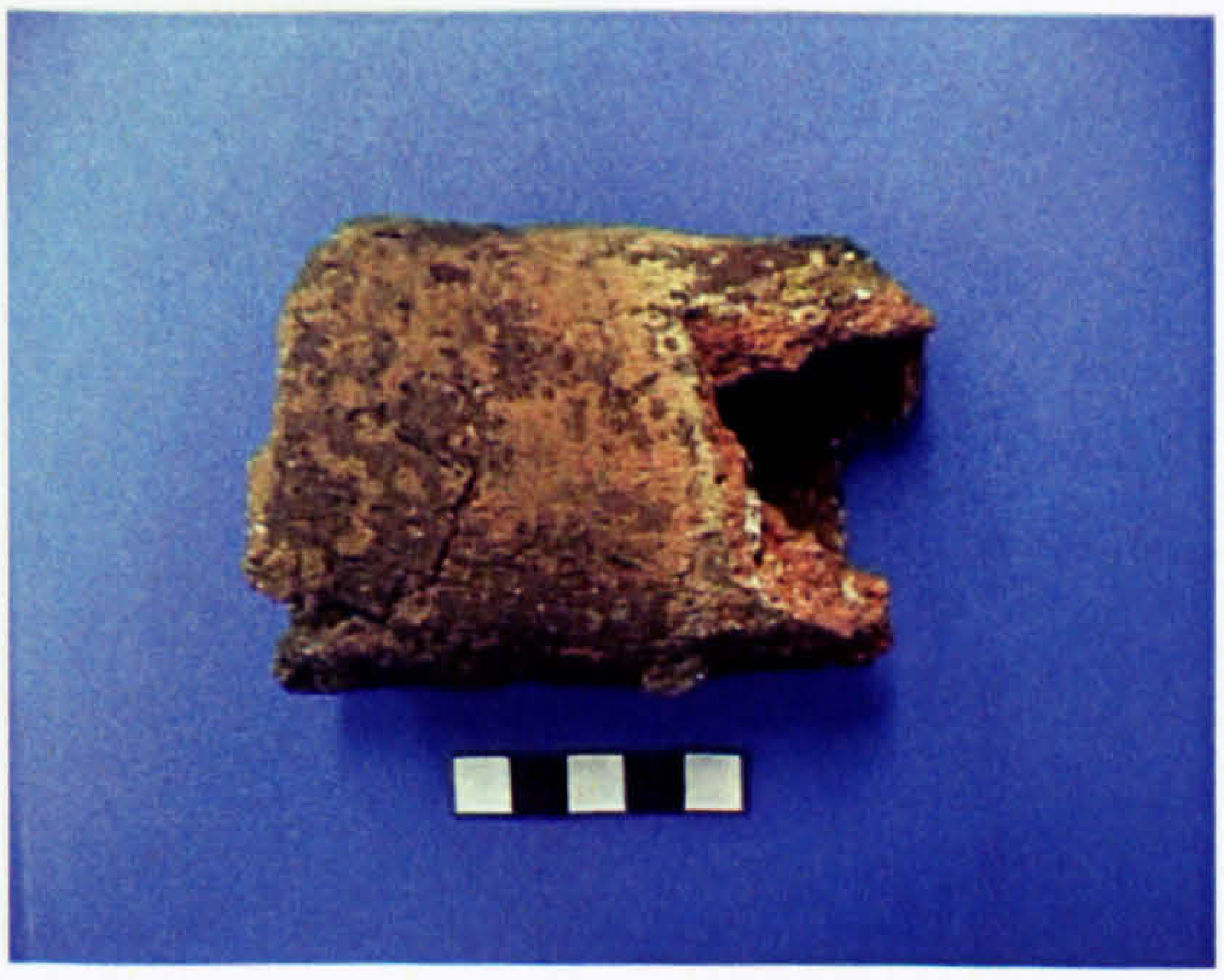


Refractory A.TU.01 (Angistro)

Fragmentary tuyère. Width: outer diameter 8.50cm, inner diameter 5.50cm. Length: 7cm. Reddish brown clay with large inclusions coated by thick layer of slag on the outer surface and partially blocked at the narrow rim.

Refractory K.TU.01 (Katafyto)

Almost complete tuyère. Width: outer diameter 8.30cm, inner diameter 5.40cm. Length: 12cm. Orange clay tempered with large inclusions exposed to high temperatures and adhering slag layer on inner surface.



Refractory K.TU.02 (Katafyto)

Tuyère fragment of cylindrical profile with signs of bloating. Length: 8cm. Reddish brown clay tempered with large inclusions.

Refractory K.TU.03 (Katafyto)

Tuyère fragment of cylindrical profile. Length: 6cm. Orange clay tempered with large quartz inclusions, bloated interior.

Refractory K.TU.04 (Katafyto)

Fragment of cylindrical profile belonging to a tuyère. Length: 5.5cm. Reddish brown clay tempered with large quartz inclusions, bloated interior.

Refractory K.TU.05 (Katafyto)

Tuyère fragment of cylindrical profile. Length: 7cm. Reddish brown clay tempered with large quartz inclusions, bloated interior.

Refractory K.TU.06 (Katafyto)

Tuyère fragment of cylindrical profile. Length: 6.5cm. Reddish brown clay tempered with large quartz inclusions, bloated interior.

Refractory K.TU.07 (Katafyto)

Fragment of cylindrical profile belonging to a tuyère. Length: 5cm. Reddish brown clay tempered with large inclusions.

Refractory V.TU.01 (Vathytopos)

Tuyère fragment of cylindrical profile. Length: 10cm. Brown clay, severely bloated interior.

K.CON.01: Furnace conglomerate with embedded tuyère (Katafyto)

K.CON.02: Furnace conglomerate (Katafyto)

K.CON.03: Furnace conglomerate bearing entrapped pieces of charcoal (Katafyto)

APPENDIX V

TABLE 6.1

XRF analyses on Palaea Kavala ores (Spathi *et al* 1982)

Major elements (%)

Sample no.	**Fe**	**Pb**	**As**	**Mn**	**Zn**	**Cu**	**Ba**
15002	41.1	0.24	5.66	0.07	0.72	0.049	0.029
15003	28.05	0.74	4.88	0.18	2	0.112	0.008
15004	53.5	0.1	0.15	2.15	0.15	0.01	0.046
15005	31.3	6	2.83	12.5	0.59	0.15	0.126
15007	16.7	0.65	18	0.113	0.015	0.097	0.011
15008	49.8	0.26	1.22	4.6	0.31	0.12	0.036
15009	31.5	0.4	0.43	18.18	1.92	0.04	0.65
15011	n.d.	57.5	9.33	0.32	0.39	0.08	0.032
15014	40.8	0.27	0.5	27.5	5.73	0.039	0.073
15015	27.3	2.3	1.35	20.8	4.95	0.04	0.182
15016	5.2	57	8.22	0.43	0.31	0.04	0.032
15017	26.6	3.4	7.37	17.3	1.65	0.09	0.5
15019	18.8	1.5	0.29	32.9	2.2	0.04	0.424
15020	28.7	5.2	0.29	21.8	2.52	0.03	n.d.
15021	18.7	0.75	1.29	31.8	4.1	0.04	0.189
15022a	21.9	2	0.46	27.1	4	0.04	0.04
15024	5.6	0.06	0.14	0.02	0.11	4	0.017
15024a	8	0.01	n.d.	n.d.	0.44	4.56	0.014
15027	16.6	0.001	0.1	0.03	0.025	0.011	0.023
15029	31.3	0.4	0.62	16.5	0.79	0.04	0.337
15030	54.2	0.018	10.8	0.02	0.11	0.015	0.021
15031	52	0.1	7.25	0.02	0.3	0.023	0.014
15032	17.5	0.254	0.78	10.17	1.48	0.026	0.022
15035	0.9	0.007	0.02	2.9	0.066	0.0011	0.015
15039	25.2	2.6	2.83	25.2	1.08	0.16	0.023
15044	40	0.1	0.35	0.31	0.1	1.61	0.04
15045	45	n.d.	0.35	0.016	0.002	0.24	0.012
15047	0.45	n.d.	0.66	1.737	0.175	0.71	0.021
15048	0.3	0.005	0.006	1.35	0.004	0.006	0.03
15051	27.6	6.2	0.53	16.18	3.9	0.08	0.273
15052	11.3	1.15	0.13	19.3	1.65	0.03	0.156
15053	7.7	1	0.51	15.2	0.91	0.04	0.03
15054	46	0.35	0.35	n.d.	0.15	0.01	0.044
15055	1.6	0.007	0.038	6.26	0.305	0.008	0.025
15811	46	0.02	5.49	7.4	0.043	0.045	0.019
15814	10.64	0.014	0.325	2.55	0.054	0.101	0.14
15815	50	0.018	3.09	0.02	0.0015	0.117	0.013
15817	46	0.798	5.49	0.044	0.093	0.115	0.085
15819	38.2	0.1	0.25	0.39	0.13	1.21	0.04
15822	30.2	0.4	3.03	15.4	2.15	0.15	0.04
15823	31	0.57	16.21	1.07	0.27	0.1	n.d.

XRF analyses on Palaea Kavala ores (Spathi *et al* 1982)

Minor elements (ppm)

Sample no.	Sb	Cd	Sr	Sn	Bi	Ag	Au
15002	1115	250	60	n.d.	n.d.	15	n.d.
15003	1438	140	80	n.d.	n.d.	25	n.d.
15004	65	n.d.	35	n.d.	n.d.	2	n.d.
15005	268	n.d.	40	n.d.	n.d.	83	1.0
15007	475	n.d.	50	n.d.	n.d.	10	n.d.
15008	240	n.d.	150	n.d.	n.d.	11	n.d.
15009	210	210	235	n.d.	n.d.	70	0.3
15011	1490	n.d.	n.d.	40	n.d.	420	0.5
15014	660	200	30	n.d.	n.d.	90	n.d.
15015	1060	280	150	n.d.	n.d.	98	0.1
15016	740	n.d.	n.d.	35	n.d.	275	0.2
15017	2490	237	140	5	n.d.	62	1.75
15019	240	250	130	n.d.	n.d.	88	0.1
15020	n.d.	n.d.	n.d.	n.d.	n.d.	27	0.16
15021	620	700	115	15	n.d.	216	0.18
15022a	780	90	5	n.d.	n.d.	110	0.18
15024	n.d.	60	n.d.	n.d.	50	70	1.32
15024a	n.d.	n.d.	n.d.	15	66	60	n.d.
15027	n.d.	75	5	n.d.	n.d.	3	n.d.
15029	400	200	110	n.d.	n.d.	18	0.08
15030	245	140	10	n.d.	n.d.	10	n.d.
15031	580	35	5	n.d.	n.d.	7	n.d.
15032	4160	420	140	n.d.	n.d.	10	n.d.
15035	n.d.	95	40	n.d.	n.d.	n.d.	n.d.
15039	1100	55	7	n.d.	n.d.	17	n.d.
15044	330	n.d.	n.d.	n.d.	1560	n.d.	22
15045	n.d.	40	n.d.	n.d.	1220	8	n.d.
15047	145	250	5	n.d.	n.d.	n.d.	n.d.
15048	n.d.	135	50	n.d.	n.d.	135	n.d.
15051	250	700	145	115	n.d.	98	0.08
15052	300	250	425	10	n.d.	59	n.d.
15053	4200	30	500	n.d.	n.d.	17	n.d.
15054	37	n.d.	5	n.d.	n.d.	3	4.3
15055	n.d.	140	75	n.d.	n.d.	n.d.	n.d.
15811	655	n.d.	40	n.d.	n.d.	35	n.d.
15814	120	n.d.	30	n.d.	n.d.	75	n.d.
15815	110	45	5	n.d.	n.d.	7	n.d.
15817	610	215	65	n.d.	n.d.	37	n.d.
15819	20	5	n.d.	5840	n.d.	15	4.05
15822	700	200	10	n.d.	n.d.	25	1.47
15823	n.d.	n.d.	n.d.	n.d.	n.d.	18	2.35

TABLE 6.2

AAS data on Pangaion Ores
site name: Asimotrypes (Papastamataki 1975)

%	vein	modern shaft 1	modern shaft 2	spoil	ancient shaft
FeO	31.4	39.0	33.0	42.4	37.8
SiO_2	19.8	14.5	15.8	11.0	5.0
CaO	0.57	0.49	0.45	0.5	0.93
Al_2O_3	0.5	0.3	0.3	0.15	1.1
MnO	trace	trace	trace	trace	trace
MgO	0.12	0.1	0.07	0.1	0.1
BaO	n.d.	n.d.	n.d.	n.d.	n.d.
Na_2O	0.05	0.05	0.05	0.04	0.04
K_2O	0.07	0.05	0.06	0.06	0.1
ZnO	0.04	0.04	0.04	0.04	0.05
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	0.16	0.05	0.05	0.02	0.5
Cu	n.d.	n.d.	n.d.	n.d.	n.d.
S	14.2	20.7	15	20.2	19.4
As	31	33	32.1	27.4	36.9
TiO_2	0.01	0.01	0.01	0.01	0.01
Cd	trace	trace	trace	trace	trace
Ni	0.01	n.d.	n.d.	0.01	0.01
Co	0.01	0.01	0.01	0.01	0.01
Sb*	340	320	300	372	468
Ag*	10	5	15	3	20
Au*	10	7	11	6	15

* in ppm

TABLE 6.3
AAS data: chemical composition of slag from Mt. Pangaeon sites (Papastamataki 1985)

	Livadia							Giannaki Vrysi		Avli		Kalias	
	284/83	1985/81	1986/81	659/82	661/82	670/82	676/82	1984/81	1987/81	660/82	662/82	663/82	672/82
FeO	46.6	42.6	49.8	61.7	62.4	45.5	38.6	47.8	42.8	1.12	70.8	68.2	35.4
SiO_2	27	26.7	24	14	4.5	24	25	25	27	39	16	4	2
CaO	8.8	9.35	8.7	0.6	1.6	8.4	8.4	9.6	8.75	14	6	0.84	28
Al_2O_3	5.3	6.1	4	1.7	0.9	5.9	5.8	4.7	6.1	11.3	4.7	3.2	0.6
MnO	1.7	0.7	1.5	0.03	0.1	0.8	8.7	1.8	0.86	7.6	2	0.15	0.02
MgO	1.3	1.7	0.9	0.25	0.3	1.8	1.9	1.08	1.8	2	0.7	0.6	0.45
BaO	0.17	n.d.	n.d.	n.d.	0.13	0.1	0.11	n.d.	n.d.	0.3	0.2	0.1	0.1
Na_2O	n.d.	0.6	0.3	0.06	0.1	0.5	0.06	0.4	0.6	0.6	0.6	0.06	0.05
K_2O	n.d.	1.7	1.2	0.5	0.3	1.7	1.78	1.5	1.9	1.4	1.25	0.05	0.05
ZnO	1	2.6	0.7	0.16	0.4	2.5	1.56	0.8	2.4	0.15	0.1	0.1	0.1
Cr_2O_3	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.04	0.01	0.01	0.01	0.01
Pb	2.6	2	2.5	0.07	0.6	2.2	1.6	2.3	1.2	0.1	0.1	0.09	0.06
Cu	0.04	0.2	0.18	0.02	1.22	0.08	0.07	0.04	0.2	0.05	0.01	0.02	0.02
S	0.57	0.73	1.18	10.5	0.65	0.7	0.65	0.57	1	0.12	0.09	0.15	0.11
As	0.26	2.6	0.2	0.03	32.8	1.1	1.4	0.05	4.2	n.d.	0.01	0.16	0.25
TiO_2	0.8	0.13	0.03	0.02	0.05	n.d.	n.d.	0.2	0.02	3.5	2.5	0.07	0.4
Cd	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	0.04	0.01	0.01	0.03	0.04	0.03	0.03	0.01	0.01	0.06	0.03	0.03	0.03
Co	0.04	0.02	0.01	0.05	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.04	0.02
Sb*	2788	338	1085	136	4080	4400	512	875	440	128	200	220	180
Ag*	5	15	4	3.6	30	9.5	10	5	13	2	2.5	1.6	3.2
Au*	n.d.	n.d.	n.d.	0.25	8	0.75	n.d.	n.d.	0.5	n.d.	n.d.	n.d.	n.d.

	Valtouda		**Lofos Sina**		**Gournes**		
	664/82	665/82	667/82	674/82	675/82	678/82	679/82
FeO	73.6	47.6	47.6	4.14	78.5	82.33	81.0
SiO_2	3.0	19.0	18.0	68.0	4.0	3.0	3.0
CaO	0.9	11.2	6.3	1.23	0.56	0.56	0.55
Al_2O_3	0.4	5.2	4.2	14.5	0.4	0.3	0.4
MnO	0.08	0.64	3.6	0.1	0.02	0.01	0.01
MgO	0.2	2.6	0.7	1.3	0.2	0.2	0.2
BaO	n.d.	0.13	0.09	0.09	0.09	n.d.	n.d.
Na_2O	0.1	0.5	0.4	1.5	0.08	0.09	0.09
K_2O	0.09	1.6	1.0	3.7	0.06	0.04	0.05
ZnO	0.14	0.72	0.5	0.6	0.16	0.09	0.09
Cr_2O_3	n.d.	0.01	n.d.	0.03	0.01	0.03	0.01
Pb	0.75	2.9	2.5	4.0	0.6	0.7	0.4
Cu	2.16	0.06	0.08	0.01	0.7	0.6	0.6
S	0.9	1.0	1.08	0.07	2.05	1.96	1.6
As	32.9	1.65	0.84	0.25	28.7	25.8	28.2
TiO_2	0.08	0.09	0.17	0.17	0.25	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	0.04	0.02	0.02	0.06	0.02	0.02	0.03
Co	0.03	0.02	0.02	0.03	0.03	0.01	0.02
Sb*	4200	244	3200	1000	2020	672	1640
Ag*	44	46	33	17	68	104	60
Au*	4.25	n.d.	0.9	n.d.	10	8.5	5.5

* in ppm