THE GEOCHEMISTRY AND MINERALOGY OF COAL AND COAL-BEARING STRATA FROM THE CANNOCK COALFIELD WITH SPECIAL REFERENCE TO CHLORINE

VOLUME 2

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VOLUME 2

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

APPENDIX 1 Total Chlorine in Coal Seam Profiles from the South Staffordshire (Cannock) Coalfield.

APPENDIX 2 Water-soluble Chlorine and Associated Major Cations from the Coals and Mudrocks of the Cannock and North Staffordshire Coalfields.

APPENDIX 3 The Distribution of Water-soluble Chlorine in coals using Stains and Acetate Peels.

LIST OF TABLES

TABLE 1.1 Proposed Classification of Mudrocks on Quartz percentage (after Spears 1980).

TABLE 1.2 Percentage Organic Matter, Ratio of Ferrous to Total Iron (Mole Fraction) and Munsell Colour in the Mudrocks.

TABLE 1.3 Coal Analyses.

TABLE 2.1 Classification of the Coal Measures (Hains and Horton, 1969).

TABLE 3.1 A Comparison of the Water-Soluble Experiments, Sheffield University, C.E.R.L. and N.C.B.

TABLE 3.2 Run-of-mine Lea Hall Shallow Seam Coal Water-Soluble Elements % (whole Rock).

TABLE 3.3 Percentage, Water-Soluble Cl^- and Major Cations with Time ('as received' 30-72 mesh B.S.S. Coal).

TABLE 3.4 Correlation Matrix for Water-Soluble and Exchangeable Elements, Total Chlorine, Water and Ash for Combined Coal and Mudrock Samples.

TABLE 3.5 Mean Sodium Values and Stratigraphic Depth.

TABLE 4.1 Total Cl^- (Average) with Depth.

TABLE 4.2 N.C.B. Ground Water Analyses.

TABLE 4.3 Coal Total Cl^- Values (Seam Averages).

TABLE 4.4 N.C.B. Ground Water Compositions and Water Centrifuged for Coal and Mudrock.

TABLE 4.5 Achieved and Calculated Water-Soluble Na^+ and Cl^- in the Yard Seam based on Water Centrifuged from Ydbl.

TABLE 4.6 Water-Soluble Na^+/ Total Cl^- Ratios.
TABLE 4.7 Water-Soluble Cl^- Contributed from Groundwaters (N.C.B.).
TABLE 5.1 Sample Colour (L.T.A.) and Percentage Ash.
TABLE 6.1 X.R.F. Totals.
TABLE 6.2 Mudrock XRF Analysis (Recalculated to 100%).
TABLE 6.3 Whole Rock Normative Mineralogy.
TABLE 6.4 Correlation Matrix of Major and Trace Elements in the Mudrock Samples.
TABLE 6.5 Relative % Clay Minerals, Tema Ground Whole Rock and <2μg Fraction on a Straight Area Basis.
TABLE 6.6 Relative % Illite plus M.L.C., Air Dried and 300°C.
TABLE 6.7 Calculation of Chlorite Composition from Relative Basal Peak Heights (modified after Collins, 1976).
TABLE 6.8 Illite Peak Positions, Glycolated and Air Dried.
TABLE 6.9 Kaolinite Percentage of Floor Measure Clay Minerals in Selected Seams and Marine Bands.
TABLE 6.10 Trace Elements in the Mudrock Samples (p.p.m.).
TABLE 6.11 Selected Trace Elements in Sulphides (p.p.m.)
TABLE 6.12 Average Trace Element Concentrations in Associated Environments.

TABLE 6.13 Table of Ionic Radii.
TABLE 6.14 N.C.B. Cone Indenter Number for Weak Rocks,
TABLE 6.15 Cone Indenter Number versus Quartz and Organic Matter.
TABLE 6.16 Correlation between Cone Indenter Number and Quartz Content for South Wales Coalfield Rocks.
TABLE 7.1 Cation Exchange Capacity versus Clay Type (%).
TABLE 7.2 Exchangeable Cations versus Clay Type (%).
TABLE 8.1 XRD Coal Ashes (Approximate Mineral Abundance).
TABLE 8.2 A Summary of the Probable Origins of the Coal Mineralogy.
TABLE 8.3 XRF Coal Ash Groupings.
TABLE 8.4 Coal Ash XRF Total (Recalculated to 100% including using Ignition loss and SO_3).
TABLE 8.5 Coal Ash (XRF as a % of Coal).
TABLE 8.6 XRD Mineral Abundance Based on Grouped L.T.A. Samples (for XRF back-up).
TABLE 8.7 Correlation Matrix of Coal Ash (L.T.A.).
TABLE 8.8 Water-Soluble Sodium and L.T.A. Sodium in the Coal Samples.
TABLE 9.1 Cleat Frequency (per cm).
TABLE 9.2 Coal Mineral Matter Analysis (XRD) of Cleat and L.T.A.
TABLE 9.3 Kaolinite Crystallinity.

TABLE 9.4 Clear Carbonate XRD Peak Position.

TABLE 9.5 Cleat Carbonate Analysis (Atomic Absorption),

TABLE 9.6 Carbonate Chemistry - Cleat Samples (% Carbonate).

LIST OF FIGURES

FIGURE 1.1 The Cannock and North Staffordshire Coalfields in relation to the 'Park' project.

FIGURE 1.2 Seam Profiles Lea Hall Colliery.
Seam Profiles Littleton Colliery.

FIGURE 1.3 Relationship between quartz content and TiO_2/Al_2O_3 ratio for the 'mudrock' samples (organic matter free).

FIGURE 1.4 Seam formation curves (not to scale).

FIGURE 2.1 A Generalised Geological Map of the South Staffordshire Coalfield.

FIGURE 2.2 The Geological Succession through the Staffordshire Coalfields (Haines and Horton, 1969).

FIGURE 2.3 The Coal Measures Succession at Lea Hall Colliery.

FIGURE 3.1 Hem Heath Winghay Seams (run-of-mine) water-soluble Na^+ from dull and bright coals (30-72 mesh B.S.S.).

FIGURE 3.2 Water-soluble elements leached from the Eight Feet Seam.

FIGURE 3.3 Water-soluble Na^+ versus Cl^- from the Eight Feet Seam (30 - 72 mesh B.S.S.).

FIGURE 3.4 Leaching ratios and coal types from the Eight Feet Seam.

FIGURE 3.5 Water-soluble Cl^- from different size fractions from the Eight Feet Seam.

FIGURE 3.6 Cl^- leaching rates from 'run-of-mine' Shallow Seam Coal (C.E.R.L. total Cl^- = 0.66%).

FIGURE 3.7 Percentage water-soluble elements leached related to time (30-72 mesh B.S.S.) 8S5 (Dull Coal).

FIGURE 3.8 Percentage water-soluble elements leached related to time (30-72 mesh B.S.S.) 8S6 (Dull Coal).

FIGURE 3.9 Percentage water-soluble elements leached related to time (30-72 mesh B.S.S.) 8S12 (Bright Coal).

FIGURE 3.10 Percentage water-soluble elements leached related to time (30-72 mesh B.S.S.) 8S13 (Bright Coal).

FIGURE 3.11 Calcite and Gypsum dissolution curves (1g/l, ambient temperature).

FIGURE 3.12 Water-soluble Na^+, Cl^-, total Cl^- and moisture profiles (tema ground).

FIGURE 3.13 Water-soluble Ca^{2+}, Mg^{2+} HCO_3^-, pH and $SO_4^=$ profiles (tema ground).

FIGURE 3.14 Water-soluble K^+ profiles (tema ground).

FIGURE 3.15 Water-soluble Ca^{2+} versus non-Na^+ equivalent Cl^-, Lea Hall Colliery.

FIGURE 3.16 Water-soluble Ca^{2+} and Mg^{2+} (Ca^{2+} equivalent basis) versus non-Na^+ equivalent Cl^-, Littleton Colliery.

FIGURE 4.1 Schematic model of coal structure.

FIGURE 4.2 Variation of N_2 and CO_2 surface areas of coals with carbon content (in Karr, 1978).

FIGURE 4.3 Organic matter versus Chlorine.

FIGURE 4.4 Total Cl^-% versus Moisture % (reduced major axis regression for coals only).

FIGURE 4.5 Total Cl^- percentage in the Park Seam section on a dry and dry mineral matter free basis.

FIGURE 4.6 Total Cl^- percentage in the Shallow Seam Section on a dry mineral matter free basis.

FIGURE 4.7 Lea Hall and Littleton Colliery 'Organic Chlorine' profiles.

FIGURE 5.1 Lea Hall Shallow Seam L.T.A. Profile (moisture free).

FIGURE 5.2 Lea Hall Yard Seam L.T.A. Profile (moisture free).

FIGURE 5.3 Littleton Park Seam L.T.A. Profile (moisture free).

FIGURE 5.4 Littleton Eight Feet Seam L.T.A. Profile (moisture free).

FIGURE 6.1 Quartz, $Ti0_2$, Zr (whole rock) and Quartz/$Ti0_2$ variations through the mudrock profiles.

FIGURE 6.2 Al_20_3/Combined Silica and K_20/Al_20_3 ratio variations through the mudrock profiles.

FIGURE 6.3 Fe0 and Mn (whole rock) variations through the mudrock profiles.

FIGURE 6.4 Normative siderite, Mn0 (whole rock) and Mn/Fe0 ratio through the mudrock profiles.

FIGURE 6.5 Fe_20_3, S and normative pyrite (whole rock) through the mudrock profiles.

FIGURE 6.6 Ca0, Mg0 and $C0_2$ (whole rock) through mudrock profiles.

FIGURE 6.7 $Mg0/Al_20_3$ ratio and normative dolomite and calcite (whole rock) through the mudrock profiles.

FIGURE 6.8 Carbonate Ca0 versus $C0_2$ showing different trends between Lea Hall and Littleton Colliery samples.

FIGURE 6.9 Na_20 and K_20 (whole rock) and Na_20/K_20 and Na_20/Al_20_3 ratios through the mudrock profiles.

FIGURE 6.10 P_2O_5 (whole rock) and P_2O_5/CaO ratios through the mudrock profiles.

FIGURE 6.11 Rationalised XRD diffraction trace of glycolated and air dried clay minerals (SSR2).

FIGURE 6.12 Relative Clay percentages.

FIGURE 6.13 Clay and quartz percentages (whole rock) and the illite/illite+ mixed-layer clay ratio through the mudrock profiles.

FIGURE 6.14 Illite Crystallinity (selected samples).

FIGURE 6.15 The relative intensity of the 002/001 illite peak ratios through the mudrock profiles.

FIGURE 6.16 Kaolinite Crystallinity and Ash Content (L.T.A.) through the seam profiles.

FIGURE 6.17 Ba, Mn, R, Sr and Zr through the mudrock profiles.

FIGURE 6.18 Co, Cr, Ni and V through the mudrock profiles.

FIGURE 6.19 Cu, Pb, Y and Zn through the mudrock profiles.

FIGURE 6.20 The ratios of K_2O to Ba, Rb and Sr through the mudrock profiles.

FIGURE 6.21 The ratios of K_2O to Cr, V and Y through the mudrock profiles.

FIGURE 6.22 The ratios of Total Clay/Co and Organic Matter/Cu through the mudrock profiles.

FIGURE 6.23 Standard versus Weak Cone Indenter Numbers on selected mudrock samples ($r = + 0.93$, 99.9% significance level).

FIGURE 7.1 Exchangeable cation profiles through the Shallow Seam.

FIGURE 7.2 Exchangeable cation profiles through the Yard Seam.

FIGURE 7.3 Exchangeable cation profiles through the Park Seam.

FIGURE 7.4 Exchangeable cation profiles through the Eight Feet Seam.

FIGURE 7.5 Exchangeable Mg/Ca and Na/K cation ratios through the mudrock profiles.

FIGURE 7.6 Cation exchange capacity and percentage clay minerals across the mudrock profiles (whole rock).

FIGURE 8.1 Mineral abundance in the coal ash (XRD peak height), carbonates and coal type, Lea Hall Colliery.

FIGURE 8.2 Mineral abundance in the coal ash (XRD peak height), carbonates and coal type, Littleton Colliery.

FIGURE 8.3 Mineral abundance in the coal ash (XRD peak height), chlorite, apatite and L.T.A. profiles, Lea Hall Colliery.

FIGURE 8.4 Mineral abundance in the coal ash (XRD peak height), chlorite, apatite and L.T.A. profiles, Littleton Colliery.

FIGURE 8.5 Mineral abundance in the coal ash (XRD peak height), illite, kaolinite and quartz, Lea Hall Colliery.

FIGURE 8.6 Mineral abundance in the coal ash (XRD peak height), illite, kaolinite and quartz, Littleton Colliery.

FIGURE 8.7 Mineral abundance in the coal ash (XRD peak height), marcasite, purite and gypsum, Lea Hall Colliery.

FIGURE 8.8 Mineral abundance in the coal ash (XRD peak height) marcasite, sphalerite, pyrite and gypsum, Littleton Colliery.

FIGURE 8.9 Al_2O_3, SiO_2 and K_2O profiles through the grouped coal samples.

FIGURE 8.10 Na_2O, TiO_2 and 'calculated quartz' profiles through the grouped coal samples.

FIGURE 8.11 SiO_2/Al_2O_3, K_2O/Al_2O_3, TiO_2/Al_2O_3 and MgO/CaO ratios through the grouped coal samples.

FIGURE 8.12 CaO, MaO, MgO and total Fe_2O_3 profiles through the grouped coal samples.

FIGURE 8.13 SO_3, CO_2 and FeO (selected) profiles through the grouped coal samples.

FIGURE 8.14 Losses and L.T.A. profiles through the grouped coal samples.

FIGURE 8.15 P_2O_5 profile through the grouped coal samples.

FIGURE 9.1 Cleat carbonates from selected samples.

FIGURE 9.2 Carbonate Classification (Watt, 1968).

FIGURE 9.3 Average compositions of carbonate minerals in British Coals (from Pringle and Bradburn, 1958).

FIGURE 9.4 Classification scheme of coal cleat (Fellows, 1979 Ph.D).

LIST OF PLATES

PLATE 5.1 Lead Bismuth Fusion Sphere produced by L.T.A.

PLATE 5.2 The Effect of L.T.A. on Dull and Bright Coal.

PLATE 8.1 A Pyrite Framboid.

PLATE 8.2 An Irregular Pyrite Framboid.

PLATE 8.3 Close-up of Pyrite Crystals in 8.1.

PLATE 8.4 Close-up of Pyrite Crystals in 8.2.

PLATE 8.5 Kaolinite in Coal after L.T.A.

PLATE 8.6 Irregular Quartz Grain.

PLATE 8.7 Sub-rounded Quartz Grain.

PLATE 8.8 C.P.L. and Reflected Light Section through a Stigmaria.

PLATE 8.9 Cuspate Diagenetic Quartz in Stigmaria, surrounded by a Pyrite Ground-mass.

PLATE 8.10 Kaolinite in the Stigmaria Core.

PLATE 9.1 Pyrite surrounded by Kaolinite in Shallow Seam Cleat (x 700).

PLATE 9.2 Pyrite Ornamentation (x 3500).

PLATE 9.3 Subhedral Pyrite in Y7 Cleat (x 350).

PLATE 9.4 Surface Relief of Pyrite (9.3) showing a Prefered Orientation (x 3500).

PLATE 9.5 Surface Relief of Pyrite (x 3500)

PLATE 9.6 Shallow Seam Cleat Kaolinite (x 3600).

PLATE 9.7 Shallow Seam Cleat Kaolinite (x 3800).

PLATE 9.8 Shallow Seam Clear Kaolinite showing a high degree of Porosity between and within Kaolinite Books (x 3600).

PLATE 9.9 Pyrite and Carbonate in Y7 Cleat showing Differences in Pyrite Surface Form (x 15).
PLATE 9.10 Pyrite and Carbonate Close-up of 9.9 (x 25).
PLATE 9.11 Concentric Pattern in Pyrite Cleat (x 25).
PLATE 9.12 T.E.M. Photomicrographs of Well Crystallised Cleat Kaolinite (x 20000).
PLATE 9.13 T.E.M. Photomicrograph of Floor Measure (8F1) Clays (x 20000).
PLATE 9.14 Dilational Cleat in 8R2.
PLATE 9.15 Calcite after Ankerite in 8R2 Cleat.
PLATE 9.16 Calcite Clear Cross-Cutting Ankerite in 8R2.
PLATE 9.17 Thin Vitrain Band in 8R2 showing small Carbonate Cleat.
PLATE 9.18 Cleat Displacement by Non-Coally Material.
PLATE 9.19 Thin Cleat in 8R2 showing Minor Lateral Movement.
PLATE 9.20 The Relationship between Early Diagenetic Siderite Nodules and Late Carbonate Cleat (2.6).
PLATE 9.21 Siderite with a Minor Pyrite Core.
PLATE 9.22 Pyrite Cleat (Y7) showing Rafted Coal and later Carbonate Infilling.
PLATE 9.23 Pyrite Clear (Y7) showing Angular Fracturing.
PLATE 9.24 Coarse Crystalline Ankerite in a Pyrite Cleat (Y7).

PLATE 9.25 Rafted Coal Fragments showing Multiple Activation during the Sulphide Phase.

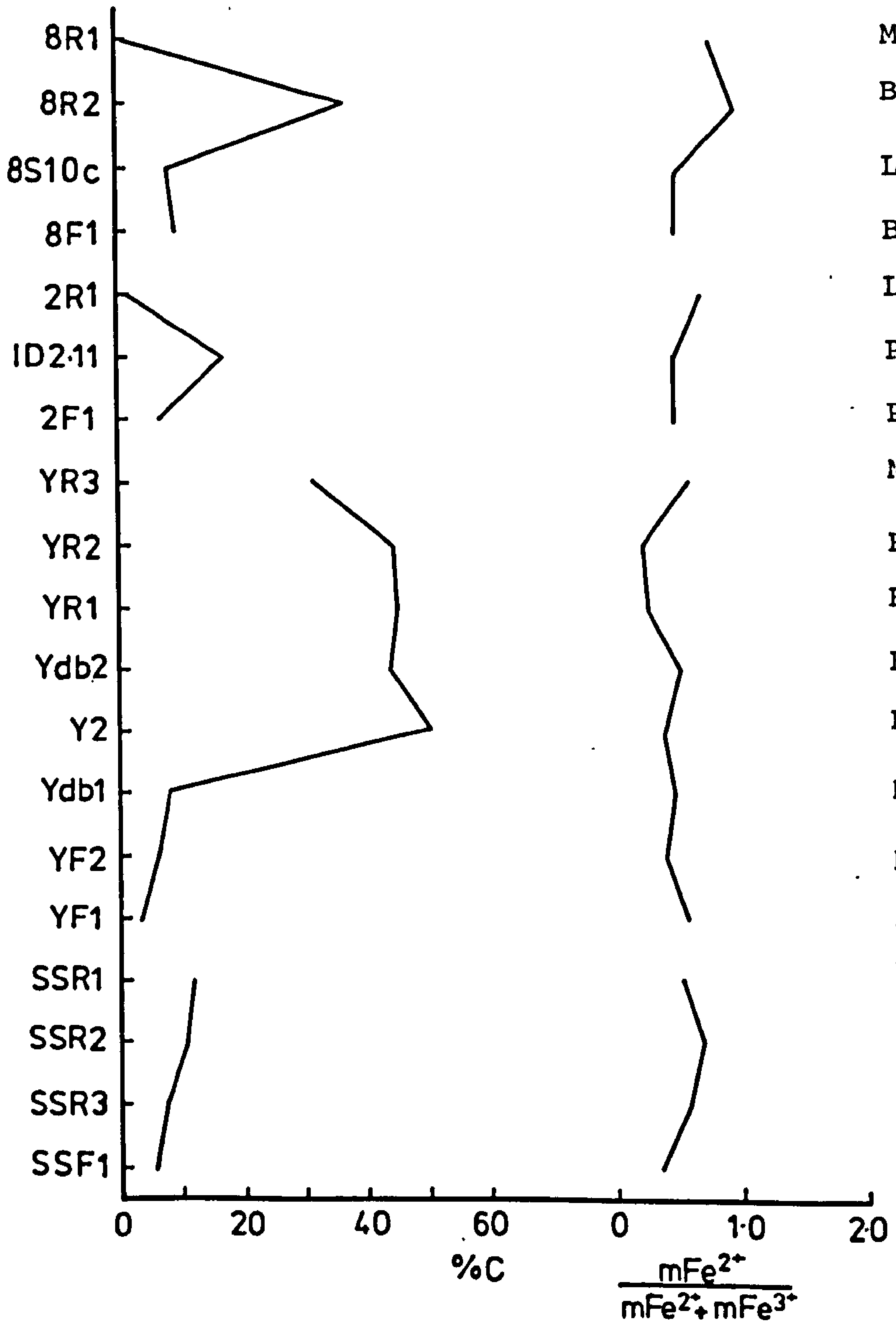
PLATE 9.26 A Pyrite Cleat showing Multiple Rafting of Coal Fragments.

PLATE 9.27 Close-up of Fractured and Rafted Coal.

TABLE 1.1: Proposed Classification of Mudrocks on Quartz Percentage (After Spears, 1980)

	Mudrocks	
	Fissile	Non-Fissile
>40% quartz	flaggy siltstone	massive siltstone
30-40% quartz	very coarse shale	very coarse mudstone
20-30% quartz	coarse shale	coarse mudstone
10-20% quartz	fine shale	fine mudstone
<10% quartz	very fine shale	very fine mudstone

TABLE 1.2 Percentage Organic Matter, Ratio of Ferrous to Total Iron (Mole Fraction) and Munsell Colour in the Mudrocks.



Munsell Colour (streak)	
Medium light grey	N6
Black	N1
Light brownish grey	5YR 6/1
Brownish black	5YR 2/1
Light brownish grey	5YR 6/1
Pale brown	5YR 5/2
Pinkish grey	5YR 8/1
Medium light grey	N6
Black	N1
Brownish black	5YR 2/1
Brownish black	5YR 2/1
Brownish black	5YR 2/1
Medium light grey	N6
Medium light grey	N6
Medium light grey	N6
Brownish Grey	5YR 4/1
Brownish Grey	5YR 4/1
Brownish Grey	5YR 4/1
Light brownish grey	5YR 6/1

TABLE 1.3: Coal Analyses

Seam	Ultimate Analysis (dry analysis)						Proximate Analysis (dry analysis)					
											d.a.f.	
	% Cw/w	% Hw/w	% N+Ow/w	Ash	S(total)	(Cl)	V.M.	F.C.	Moisture	Ash	V.M.	F.C.
Eight Feet	75.58	5.42	6.82	8.60	3.58	0.62	35.5	55.9	-	8.6	38.8	61.3
Park	76.67	5.43	10.13	6.70	1.07	0.94	36.2	57.1	-	6.7	38.8	61.2
Yard	75.78	5.38	11.47	5.00	2.57	0.74	38.9	56.1	-	5.0	40.9	59.1
Shallow	76.40	5.24	12.66	4.60	1.10	0.93	35.5	59.9	-	4.6	37.2	62.8
		d.a.f (should be m.m.f.)										
Eight Feet	82.69	5.93	7.46		3.92							
Park	82.18	5.82	10.75		1.15							
Yard	79.56	5.66	12.67		2.71							
Shallow	80.08	5.49	13.27		1.15							

TABLE 2.1

Classification of the Coal Measures

MAJOR DIVISIONS	PLANT CLASSIFICATIONS		NON-MARINE LAMELLIBRANCH ZONES	IMPORTANT MARINE BANDS
Stubblefield and Trotter 1957	Heerlen Congress 1927	Kidston and Crookall		
UPPER COAL MEASURES	Westphalian D	Radstock Group of Radstockian - - - - - - - - Farrington Group of Radstockian	*Anthraconaia prolifera* and *Anthraconauta tenuis*	
	- - - - - -	- - - - - - - -	- - - - - - - - - -	
		Staffordian	*Anthraconauta phillipsii*	*Anthracoceras cambriense* (Bay)
—M——M—	Westphalian C	—M——M—	—M——M—	
MIDDLE COAL MEASURES			Upper *Anthracosia similis* and *Anthraconaia pulchra*	*Anthracoceras hindi* or *A. aegiranum* (Gin Mine=Charles=Chance Pennystone=Eymore Farm=Nuneaton=Overseal)
	—M——M—		—M——M—	
	Westphalian B	Yorkian	Lower *A. similis* and *A. pulchra*	
			- - - - - - - - - -	
			Upper *Anthraconaia modiolaris*	*Anthracoceras vanderbeckei* (7-Ft Banbury=Stinking=Pennystone=Seven Feet=Molyneux=Bagworth)
—M——M—	—M——M—		—M——M—	
LOWER COAL MEASURES	Westphalian A		Lower *A. modiolaris*	
			- - - - - - - - - -	
		- - - - - - - -	*Carbonicola communis*	
			- - - - - - - - - -	
		Lanarkian (=Pre-Yorkian) down to 'plant-break' of Scotland	*Anthraconaia lenisulcata*	
—M——M—	—M——M—		—M——M—	*Gastrioceras subcrenatum*
MILLSTONE GRIT SERIES	Namurian			

(Hains & Horton, 1969)

TABLE 3.1: A Comparison of the Water-Soluble Chlorine Experiments, Sheffield University, C.E.R.L. and N.C.B.

Total Cl^-				Water-Soluble Cations		
C.E.R.L.	N.C.B.	Sheffield		C.E.R.L.	N.C.B.	Sheffield
Run-of-Mine Shallow Seam Coal (Lea Hall) (Supplied by C.E.R.L.)						
0.66%	0.61%	-	Na^+		1185 μg/g	1330 μg/g
Water-soluble Cl^- (24 hours)			K^+		70	70
38.9%	37.4%	38.0% (based on CERL Total Cl^-)	Ca^{2+}		285	290
			Mg^{2+}		40	50

Run-of-Mine Winghay Seam Coal (Hem Heath)
(Supplied by C.E.R.L.)

24 hours leaching	Water-soluble Na^+
Dull Coal	2100 μg/g
Bright Coal	835 μg/g

TABLE 3.2: Run-of-Mine Lea Hall Shallow Seam Coal
Water-Soluble Elements % (Whole Rock)

Sample Number	Sample Time	Coarse	Sample Time	Fine
		Cations Na^+		
1	1 minute	0.05	1 minute	0.07
2	10 minutes	0.08	10 minutes	0.10
3	50 minutes	0.10	50 minutes	0.12
4	112 minutes	0.12	100 minutes	0.13
5	340 minutes	0.13	340 minutes	0.13
6	1400 minutes	0.15	1400 minutes	0.14
		Ca%		
1			1 minute	0.03
2			10 minutes	0.04
3			50 minutes	0.06
4			100 minutes	0.07
5			340 minutes	0.08
6			1400 minutes	0.09
		Mg%		
1	1 minute	0.003	1 minute	0.001
2	10 minutes	0.005	10 minutes	0.005
3	50 minutes	0.006	50 minutes	0.005
4	112 minutes	0.006	100 minutes	0.005
5	340 minutes	0.006	340 minutes	0.007
6	1400 minutes	0.007	1400 minutes	0.007
		K%		
1	1 minute	0.002	1 minute	0.002
2	10 minutes	0.006	10 minutes	0.003
3	50 minutes	0.003	50 minutes	0.002
4	112 minutes	0.008	100 minutes	0.004
5	340 minutes	0.004	340 minutes	0.004
6	1400 minutes	0.003	1400 minutes	0.004

If Total Chlorine = 0.66% (C.E.R.L.), therefore % Water-Soluble Chlorine =

Sample Number	Sample Time	Coarse	Sample Time	Fine
1	1 minute	7.8%	1 minute	18.5%
2	10 minutes	14.8%	10 minutes	26.7%
3	50 minutes	22.2%	50 minutes	28.4%
4	112 minutes	21.6%	100 minutes	33.5%
5	340 minutes	36.1%	340 minutes	35.5%
6	1400 minutes	36.6%	1400 minutes	38.6%
C.E.R.L.		38.9%		

TABLE 3.3: % Water-Soluble Cl^- and Major Cations with Time
('as received' 30-72 mesh B.S.S. Coal)

		Cl^-	%	Na^+	%	Ca^{2+}	%	Mg^{2+}	%	Leaching Extraction Time Mins.
8S5	1	813	14.5	413	31.8	78	9.8	23	15.3	3
	2	1163	20.7	644	49.5	121	15.1	36	24.0	10
	3	1290	23.0	757	58.2	140	17.5	41	27.3	50
	4	1350	24.0	842	64.8	155	19.4	44	29.3	100
	5	1550	27.6	942	72.5	174	21.8	49	32.7	350
	6	1735	30.9	1110	85.4	223	27.9	62	41.3	1500
		5622		1300		800		150		
8S6	1	513	10.1	283	28.2	45	8.9	12	11.4	3
	2	745	14.6	430	42.8	79	15.6	20	19.1	10
	3	988	19.4	643	64.0	108	21.4	28	26.7	50
	4	1140	22.4	758	75.4	122	24.2	33	31.4	100
	5	1200	23.5	805	80.1	150	29.7	36	34.3	350
	6	1343	26.3	874	87.0	168	33.3	41	39.1	1500
		5098		1005		505		105		
8S12	1	144	2.2	68	11.0	16	1.1	13	3.4	3
	2	380	5.9	137	22.1	35	2.5	34	9.0	30
	3	605	9.3	239	38.6	71	5.0	72	19.0	100
	4	847	13.0	320	51.6	137	9.7	141	37.1	350
	5	975	15.0	356	57.4	215	15.3	235	61.8	1500
		6495		620		1410		380		
8S13	1	185	2.8	95	13.1	16	5.8	14	18.4	3
	2	350	5.4	190	26.2	28	10.2	27	35.5	30
	3	750	11.5	340	46.9	43	15.6	47	61.8	100
	4	960	14.7	488	67.3	63	22.9	65	85.5	350
	5	1020	15.6	605	83.5	71	25.8	72	94.7	1500
		6524		725		275		76		

TABLE 3.4: Correlation Matrix for Water-Soluble and Exchangeable Elements, Total Chlorine, Water and Ash for Combined Coal and Mudrock Samples

	XNa	XK	XCa	XMg	Na	K	Ca	Mg	pH	HCO_3	SO_4	WSCL	TCl	H_2O	Ash
XNa															
XK	0.60														
XCa	0.76	0.74													
XMg	0.65	0.96	0.83												
Na	-0.29	-0.30	-0.29	-0.28											
K	0.67	0.39	0.52	0.45											
Ca	-0.36		-0.32	-0.45		-0.38									
Mg		-0.36	-0.35	-0.37			0.53								
pH															
HCO_3			0.43				0.36								
SO_4															
WSCl	-0.55	-0.59	-0.59	-0.61	0.70		0.77	0.42							
TCl	-0.68	-0.75	-0.82	-0.80	0.55	-0.49	0.60	0.32				0.84			
H_2O	-0.51	-0.69	-0.68	-0.73	0.43	-0.35	0.65	0.27				0.79	0.85		
Ash	0.71	0.79	0.87	0.85		0.59	-0.54	-0.38				-0.67	-0.88	-0.83	

Significance Level 95% 0.25
99% 0.33
99.9% 0.41

TABLE 3.5: Mean Sodium Values and Stratigraphic Depth

Seam	µg/g Mudrock	µg/ml in moisture
	Water-Soluble Na^+ in Mudrocks	
Eight Feet	730	40420
Park	800	41665
Yard	1215	39700
Shallow	730	44090
	Water-Soluble Na^+ in Coals	
Eight Feet	880	13295
Park	1200	23255
Yard	1745	25790
Shallow	2275	28180

TABLE 4.1: Total Cl^- (Average) with Depth

Seam	Littleton Colliery	Lea Hall Colliery
Eight Feet	0.64	
Park	0.82	
Yard	-	0.75
Shallow	0.39*	0.92
Deep	-	1.01*

*Calculated by Dr. I.F. Holmes

TABLE 4.2: N.C.B. Groundwater Analyses

Location	Yard Ragman	Benches	Eight Feet	Yard*	Shallow	Deep*[1]	Deep*[2]	Deep*[3]	Sea Water (Blatt, Middleton and Murray, 1972)
(Seam)	105s	222s	317s	B40s	1014s	1103s	1131s	1130s	
pH	5.5	6.8	6.2	4.6	7.2	7.2	7.8	6.6	
Total Dissolved Solids	247800	90100	62600	91600	27100	40860	28000	39720	
Total Hardness	58300	17600	11000	18700	3390	5240	4400	5600	
Calcium Hardness	41200	11200	66000	11200	2260	3530	3030	3800	
Magnesium Hardness	171100	6400	4400	7500	1130	1710	1370	1800	
Alkalinity	30	140	170	15	150	80	290	290	
Chloride	138100	52000	34000	52500	15370	24850	17570	21200	18980
Sulphate	-	-	-	2300	-	20	316	480	2649
Iron	24	3	6	15	-	0.6	1.0		
Nitrates	-	-	-	-	-	-	-	-	
Ca^{2+}	-	-	-	-	905	1410	1210	-	400
Mg^{2+}	-	-	-	-	275	410	333	-	1272
Na^{+}	-	-	-	-	8480	13760	9737	-	10556
K^{+}	-	-	-	-	-	-	123	-	380
Date	3.4.80	25.6.79	29.8.79	21.12.77	26.8.69	6.8.69	26.3.73	1.10.75	

*The presence of sulphate in the groundwaters is indicative of contamination from old mine workings. This is particularly noticeable in the Yard Seam sample where iron is also found along with a low pH. Oxidation of pyritic matter would produce such results. Apart from this contamination, the analyses are all reported by the N.C.B. to be 'typical of waters originating from productive Coal Measures' normally encountered from each of the seams.

TABLE 4.3: Coal Total Chlorine Values
(Seam Averages)

Seam	C.E.G.B.	Present Study
Eight Feet	0.62	0.64
Park	0.84	0.82
Yard	0.74	0.75 (Y1, Y3-Y7)
Shallow	0.93	0.92

TABLE 4.4: N.C.B. Groundwater Compositions and Water Centrifuged from Coal and Mudrock

μg/ml	Yard-Ragman*	1131's Deep*	1103's Deep*	1014's Shallow*	Shallow (coal)^{o}	Ydbl^{o}
Cl	138100	17570	24850	15370	2300	23000
Ca		1210	1410	905	330	1610
Mg		333	410	275	50	330
Na		9737	13760	8480	1305	14375
K		123	-	-	20	340
Relative % of Cations						
Ca		10.6	9.1	9.4	19.4	9.7
Mg		2.9	2.6	2.8	3.0	2.0
Na		85.4	88.3	87.8	76.4	83.3
K		1.1	-	-	1.2	2.0
Na(Cl eq.)		15017	21220	13078	2010	22170
Na(Cl eq.)/Cl		0.85	0.85	0.85	0.87	0.96

Ydbl moisture = 5.80% = 0.13% Cl
Total Cl = 0.14% Cl

* - Groundwater

o - Centrifuged Water

TABLE 4.5: Achieved and Calculated Water-Soluble Na^+ and Cl^- in the Yard Seam Based on Water Centrifuged from Ydb1

	W.S. Na^+	Calculated Na^+	$Cl^- \equiv$ W.S. Na^+	Calculated Cl^-
Y7	1894	915	2920	1460
Y6	1970	1030	3035	1645
Y5	1960	1130	3020	1810
Y4	1890	1050	2910	1680
Y3	1540	1100	2370	1760
Ydb2	1545	315	2380	505
Y2	1570	585	2420	935
Ydb1	1030	835	1585	1335
Y1	1200	605	1850	970
YF2	1310	250	2015	400
YF1	615	215	945	345

TABLE 4.6: Water-Soluble Na^+/Total Cl^- Ratios

Hem Heath Colliery		Littleton Colliery		Lea Hall Colliery	
*Yard Ragman Seam	0.13	Eight Feet Seam	0.14	Yard Seam	0.24
		Park Seam	0.15	Shallow Seam	0.25
		*Shallow Seam	0.15	*Deep Seam	0.20

*Sampled by Dr. I.F. Holmes (W.S. Na^+ on 72 mesh B.S.S.)

TABLE 4.7: Water-Soluble Cl^- Contributed from Groundwaters (N.C.B.)

	Eight Feet	Park	Yard	Shallow	*Yard Ragman
Moisture %	6.62		6.37	8.09	2.67
Cl^- p.p.m.	34000	No value available	52500	13080	138100
Calculated Cl^-% in Coal	0.23		0.33	0.12	0.37
W.S. Cl^- (Based on Cl^- equivalent to W.S. Na^+)	0.21		0.28	0.36	0.40

*N.C.B. Sources

TABLE 5.1: Sample Colour (L.T.A.) and Percentage Ash

	Sample Colour						LTA%		Sample Colour						LTA%
	Eight Feet Seam								Yard Seam						
8S1				✓			13.0	Y9			✓				36.9
8S2				✓			6.3	Y8				✓			5.6
8S3					✓		3.0	Y7	✓						26.6
8S4						✓	2.8	Y6						✓	8.9
8S5				✓			2.2	Y5			✓				6.0
8S6				✓			2.2	Y4			✓				4.0
8S7						✓	4.3	Y3						✓	8.4
8S8				✓			4.0	Y2				✓			55.7
8S9				✓			14.1	Y1		✓					55.8
8S10				✓			14.3								
8S11			✓				9.1								
8S12			✓				7.0								
8S13		✓					7.4								
	Park Seam								Shallow Seam						
2.1				✓			14.8	SS1		✓					10.5
2.2					✓		9.3	SS2				✓			8.5
2.3				✓			10.1	SS3					✓		13.4
2.4					✓		8.9	SS4					✓		4.1
2.5		✓					6.3	SS5				✓			6.0
2.6						✓	9.6	SS6				✓			6.1
2.7		✓					21.1	SS7				✓			5.7
2.8			✓				4.6	SS8				✓			5.5
2.9				✓			3.0	SS9				✓			11.6
2.10			✓				19.9	SS10				✓			9.8
2.12		✓					15.2	SS11				✓			12.8
	Black	Dark Grey	Grey	Light Grey	White	Brown			Black	Dark Grey	Grey	Light Grey	White	Brown	
	← Increasing Pyrite								← Increasing Pyrite						

TABLE 6.1: XRF Totals

	XRF Total^1	XRF Total^2	Organic C	L.T.A. Loss	100-XRF^1 (Discrepancy)
8R1	101.35	100.95	0.92	0.66	-
8R2	87.85	98.49	16.84	33.97	12.15
8S10c	98.70	103.14	6.34	7.34	1.30
8F1	98.16	100.01	8.04	8.20	1.84
2R1	100.53	100.14	1.99	1.05	-
ID.2.11	97.64	100.11	14.82	15.78	2.36
2F1	96.22	100.73	5.68	2.90	3.78
YR3	99.17	99.48	4.18	3.69	0.83
YR2	92.47	97.33	31.18	39.35	7.53
YR1	88.37	101.22	25.60	22.48	11.63
Ydb3	84.26	100.03	32.00	34.34	15.74
Y2	88.55	101.63	38.39	44.35	11.45
Ydb1	94.46	99.00	3.30	3.20	5.56
YF2	95.46	99.11	2.86	1.69	4.54
YF1	97.29	99.46	0.97	0.11	2.71
SSR1	95.18	99.74	6.13	6.00	4.82
SSR2	94.23	99.89	8.27	4.79	5.77
SSR3	97.20	99.70	6.10	4.75	2.80
SSF1	98.25	99.56	4.67	4.66	1.75

1 - XRF including wet chemical analysis

2 - XRF using ignition loss

L.T.A. loss vs. discrepancy $r = +0.81$ (99.9% significance)

TABLE 6.2: Mudrock XRF Analysis
(Recalculated to 100%)

	SiO_2	Al_2O_3	TiO_2	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	S	CO_2	H_2O^-	H_2O^+	(Quartz)
8R1	52.85	22.57	0.79	4.64	2.71	1.73	0.30	0.41	4.22	0.13	0.15	0.12	2.37	1.09	5.92	20.62
8R2	19.00	8.55	0.39	33.13	3.47	1.38	1.62	0.27	1.12	0.99	0.58	0.35	25.62	0.68	2.85	6.66
8S1Oc	54.02	27.46	1.07	0.97	1.97	1.42	0.28	0.50	4.67	0.03	0.15	0.26	-	1.20	6.01	15.48
8F1	59.51	22.22	1.19	0.87	2.09	1.33	0.18	0.49	3.42	-	0.12	0.52	-	1.47	6.60	30.94
2R1	54.36	24.88	0.75	1.78	1.90	1.70	0.17	0.61	4.37	-	0.10	0.06	0.21	1.72	7.39	17.48
ID.2.11	47.37	31.85	1.25	0.73	1.80	1.35	0.19	0.63	5.64	-	0.09	0.35	-	1.96	6.79	-
2F1	56.60	25.82	0.94	0.70	1.54	1.10	0.17	0.59	4.35	0.01	0.08	0.21	0.15	1.64	6.10	19.39
YR3	57.83	23.21	0.96	1.37	2.02	1.38	0.20	0.64	4.08	0.02	0.10	0.33	-	1.29	6.58	27.84
YR2	50.36	23.08	0.72	0.78	5.71	1.17	0.23	0.61	3.51	0.04	0.06	3.43	-	2.27	8.04	20.16
YR1	52.67	23.83	0.78	0.60	3.43	1.34	0.22	1.25	4.01	-	0.06	1.18	0.82	1.66	8.18	20.86
Ydb2	58.16	28.23	1.76	0.58	1.15	0.72	0.28	0.81	2.51	0.01	0.05	0.55	0.55	1.26	3.40	23.65
Y2	54.42	30.08	1.54	0.53	1.68	0.72	0.33	0.78	2.34	0.01	0.05	0.66	0.33	1.73	4.81	19.54
Ydb1	52.80	29.54	1.29	0.55	1.30	1.00	0.17	0.64	3.89	-	0.07	0.13	0.18	1.15	7.31	16.08
YF2	59.20	25.11	1.03	0.79	2.55	1.00	0.15	0.52	3.97	0.03	0.05	0.96	0.66	0.85	3.12	22.47
YF1'	68.21	20.42	1.21	0.62	1.01	0.89	0.10	0.37	3.13	-	0.04	0.14	0.49	0.70	2.67	43.50
SSR1	58.84	24.88	1.00	1.02	1.64	1.30	0.18	0.50	3.47	0.01	0.13	0.21	-	1.11	5.71	24.93
SSR2	55.71	25.85	1.07	1.87	2.07	1.11	0.20	0.61	3.24	0.06	0.12	0.21	0.64	0.98	6.28	20.55
SSR3	55.82	27.10	1.03	0.84	1.65	1.19	0.21	0.51	3.31	-	0.12	0.41	0.02	1.18	6.60	20.87
SSF1	75.20	14.43	1.40	0.37	1.43	0.50	0.12	0.31	1.76	-	0.05	0.68	-	0.58	3.19	50.06

TABLE 6.3: Whole Rock Normative Mineralogy

	Quartz	Chlorite	Illite	M.L.C.	Kaolinite	Calcite	Dolomite	Siderite	Fe Sulphide	Apatite	Fe_2O_3	H_2O	TiO_2	Organic C	Excess	
															CaO	CO_2
8R1	20.34	6.87	30.88	19.74	9.60			6.05	0.32	0.34	2.40		0.78	1.38		
8R2	4.21		2.69	3.89	9.13			36.61	0.61	0.87	1.64	1.05	0.25	36.80		3.37
8S10c	14.16	2.57	23.94	24.93	20.86				0.66	0.31	1.21	1.54	0.98	8.54	0.09	
8F1	27.94	4.18	19.02	20.60	12.15				1.28	0.24	0.73	2.65	1.07	9.70	0.03	
2R1	17.30	6.36	30.54	20.35	12.60			0.50	0.17	0.23	1.73	4.31	0.74	1.50		
ID.2.11			28.60	30.40	18.12				0.80	0.18	0.76	2.66	1.03	17.77	0.06	
2F1	18.12	1.76	27.94	23.80	16.06	0.20	0.10		0.54	0.16	0.95	2.79	0.88	6.57		
YR3	26.59	3.65	24.10	20.53	14.27				0.86	0.22	1.15	2.82	0.92	4.49	0.07	
YR2	11.31	1.88	13.64	12.60	7.99				4.17	0.07		2.95	0.40	43.91	0.16	
YR1	14.29	1.41	16.49	16.49	10.81			0.97	2.21	0.09	0.35	4.07	0.53	31.50		0.23
Ydb2	13.16		4.13	12.38	24.72	0.30	0.02	0.65	0.76	0.07			0.98	44.36		
Y2	9.63	1.57	2.37	12.45	22.67	0.10	0.25		0.89	0.06	0.01		0.76	50.72		
Ybd1	14.70		13.65	20.48	38.20	0.02	0.09	0.26	0.32	0.16	0.90	1.34	1.18	9.43		
YF2	21.09		23.27	16.17	29.26			1.54	2.47	0.10	0.15		0.97	6.15		0.01
YF1	42.27		16.10	11.66	24.19			1.10	0.38	0.10	0.64		1.18	2.82		0.05
SSR1	22.03	3.80	18.48	14.51	25.71				0.50	0.27			0.88	11.64	0.02	
SSR2	18.44	2.94	13.40	15.86	34.29	0.30	0.30	1.54	0.56	0.27		0.99	0.96	10.28		
SSR3	19.32	1.50	13.92	15.70	39.23	0.50			1.05	0.28	0.57		0.95	7.42	0.01	
SSF1	47.40		10.89	12.27	18.86				1.59	0.29	0.23		1.33	5.32	0.06	

TABLE 6.4: Correlation Matrix of Major and Trace Elements in the Mudrock Samples

	Qtz.	SiO_2	Al_2O_3	TiO_2	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	S	Org.C	CO_2	H_2O^-	H_2O^+	Ni	Co	Mn	V	Cr	Zn	Cu	Rb	Sr	Y	Zr
Qtz.																												
SiO_2																												
Al_2O_3		0.96																										
TiO_2	0.60	0.53	0.55																									
FeO		-0.52	-0.57	-0.60																								
Fe_2O_3				-0.59																								
MgO		0.62	0.58																									
CaO		-0.50	-0.65	-0.61	0.99																							
Na_2O		0.49	0.65		-0.50			-0.49																				
K_2O		0.91	0.88				0.80		0.54																			
MnO		-0.55	-0.60	-0.61	1.00			0.99	-0.62																			
P_2O_5				-0.48	0.92			0.93			0.90																	
S						0.59																						
Org.C	-0.55	-0.75	-0.69	-0.57			-0.68			-0.74																		
CO_2		-0.57	-0.62	-0.60	0.99			0.98	-0.50	-0.45	0.99	0.88																
H_2O^-		0.62	0.59				0.57		0.56	0.72																		
H_2O^+		0.69	0.71				0.74		0.63	0.78				-0.56		0.79												
Ni						0.61																						
Co		-0.57	-0.61	-0.68	0.88	0.51		0.86			0.88	0.81			0.97			0.61										
Mn		-0.51	-0.66	-0.59	0.99			0.98	-0.49		0.99	0.92			0.98				0.87									
V		0.65	0.70		-0.49			-0.46		0.55	-0.51				-0.53	0.71	0.54		-0.48									
Cr		0.87	0.90	0.57	-0.59		0.54	-0.57		0.84	-0.62			-0.60	-0.64	0.69	0.66		-0.59	-0.58	0.82							
Zn							0.79							-0.52			0.63	0.58										
Cu	-0.47													0.52														
Rb		0.93	0.90				0.77		0.55	0.99				-0.75		0.71	0.77				0.57	0.84	0.53					
Sr		0.69	0.75				0.50			0.60				-0.55			0.67				0.65	0.66	0.66		0.65			
Y	0.50		0.63	0.72			0.48			0.63				-0.85			0.47					0.65			0.64	0.53		
Zr	0.82			0.84										-0.50													0.65	
Pb													0.52					0.73										
Ba		0.85	0.85				0.73			0.80				-0.82			0.71					0.72			0.82	0.83	0.74	

Significance Level: 95% 0.46
99% 0.58
99.9% 0.69

TABLE 6.5: Relative % Clay Minerals, Tema Ground Whole Rock and <2 µg Fraction on a Straight Area Basis

	Chlorite (14Å)		Illite + M.L.C.		Kaolinite + Chlorite (7Å)	
	1	2	1	2	1	2
8R1	6.90	4.49	53.90	60.88	39.10	34.63
8F1	5.60	3.13	53.30	62.67	41.10	34.21
ID.2.11	0	4.17	76.40	67.30	23.60	28.52
2F1	2.20	2.50	65.50	66.06	32.20	31.44
YF1	2.10	1.00	48.90	53.14	50.00	45.84
SSR1	4.80	3.61	42.80	46.84	49.55	49.55
SSF1	0	3.16	55.12	50.60	44.88	46.24

1 - Tema ground whole rock

2 - <2 µg fraction separated in an end-over-end shaker

TABLE 6.6: Relative % Illite plus M.L.C., Air Dried and 300°C

	1	2
8R1	53.90	46.04
8S10c	59.30	44.02
8F1	53.50	48.40
2R1	51.50	44.86
2F1	65.50	59.80
YR3	55.70	49.56
Ydb2	36.70	29.58
YF1	48.50	38.38
SSR3	38.80	39.89

1 - Air Dried

2 - 300°C

TABLE 6.7: Calculation of Chlorite Composition from Relative Basal Peak Heights (Modified after Collins, 1976)

	I001 c/s	I003	I004	Modified		Calculated			$\frac{F003}{F001}$	Excess Fe	Theoretical			10^3xC	y	F002	cF002	I002	$\frac{I002}{I001}$
				001	004	cF001	cF003	cF004			F001	F003	F004						
SSR1	150	100	240	206	138	0.56	1.18	1.88	2.11	+2.10	56.5	-118	207	9.91	5	160	1.46	203	1.35
SSR2	75	100	250	103	144	0.39	1.18	1.92	3.08	+2.95	44.5	-130	219	8.76	6	174	1.52	220	2.93
SSR3	70	70	300	90	173	0.38	0.99	2.11	2.61	+2.50	50.0	-125	278	7.60	11.5	240	1.82	315	4.50
YR3	120	100	345	164	199	0.50	1.18	2.26	2.36	+2.35	52.0	-124	235	9.62	7.5	190	1.83	319	2.66
YR1	40	50	190	55	110	0.29	0.83	1.68	2.86	+2.80	46.9	-129	300	5.59	12	262	1.46	203	5.08
YF2	50	50	305	69	176	0.32	0.83	2.12	2.59	+2.52	52.6	-123	379	6.08	12	355	2.16	444	8.88
YF1	90	70	410	123	237	0.43	0.99	2.47	2.30	+2.34	52.0	-124	299	8.27	12	263	2.18	452	5.02
2R1	100	80	300	137	173	0.45	1.05	2.11	2.33	+2.36	52.0	-124	244	8.65	8.5	226	1.95	362	3.62
8R1	100	75	255	137	147	0.45	1.02	1.94	2.27	+2.25	53.5	-121	231	8.41	7.3	187	1.57	235	2.35
8S10c	70	70	245	96	141	0.38	0.99	1.90	2.61	+2.56	49.0	-126	245	7.76	8.5	203	1.58	238	3.40
8F1	45	50	170	62	98	0.31	0.83	1.59	2.68	+2.62	48.5	-127	249	6.36	9.0	207	1.32	166	3.69

Average $\frac{I002}{I001} = 3.95$

Average for Collins (1976) = 3.96

I Intensity (peak height in counts per second)

Modified Peak height modified to allow for anatase contribution to 004

y Fe per unit cell

TABLE 6.8: Illite Peak Positions Glycolated and Air Dried (two-thirds peak height)

	$d\mathring{A}^1$	$d\mathring{A}^2$	Brindley and Brown (1980) p.290	
			Illite	$d\mathring{A}^1$
8R1	10.050	10.026	100%	10.16Å
8R2	Not determined	10.103	90%	10.00Å
8S10c	10.071	10.014	80%	9.83Å
8F1	10.038	10.050		
2R1	10.003	10.026		
ID.2.11	10.106	10.342		
2F1	10.049	10.105		
YR2	9.995	10.049		
YR2	10.104	10.049		
YR1	10.104	10.105		
Ydb2	10.071	10.003		
Y2	10.164	10.003		
Ydb1	9.981	10.049		
YF2	10.026	9.981		
YF1	9.990	9.990		
SSR1	10.991	9.990		
SSR2	10.014	9.990		
SSR3	9.971	9.990		
SSR1	9.990	9.947		

1 - Glycolated

2 - Air Dried

TABLE 6.9: Kaolinite Percentage of Floor Measure Clay Minerals in Selected Seams and Marine Bands

	South Wales Coalfield				Cannock Coalfield		Yorkshire/Nottinghamshire Coalfield	
	West			East				
			Cefn Coed M.B.		Charles M.B.		Mansfield M.B.	64.8%
Westphalian B			Four Feet Seam	35.5%				
			Six Feet Seam	40.0%	Eight Feet Seam	21.7%	Barnsley/Top Hard Seam	21.1%
	20.0%	Upper	Nine Feet Seam	30.8%	Park Seam	21.1%		
	32.6; 24%	Lower						
			Amman M.B.		Stinking M.B.		Clay Cross M.B.	
Westphalian A			Seven Feet Seam	60.0%	Yard Seam	45.5%		
	31.2%		Gellideg Seam	60.6%	Shallow Seam	44.9%		
			Garw Seam	82.0%				
					Fair Oak M.B.		Alton M.B.	70%
			Gastrioceras subcreantum M.B.				Pot Clay M.B.	66.43%

TABLE 6.10: Trace Elements in the Mudrock Samples (p.p.m.)

	Ni	Co	Mn	V	Cr	Zn	Cu	Rb	Sr	Y	Zr	Pb	Ba
8R1	51	50	1291	145	130	55	45	189	141	45	132	30	629
8R2	75	135	4919	70	33	35	35	29	51	29	73	46	199
8S10c	28	12	196	134	131	42	49	203	137	45	158	29	624
8F1	82	55	112	175	146	43	27	150	155	49	215	43	474
2R1	48	25	253	179	129	62	37	209	127	50	147	31	581
1D.2.11	41	9	45	217	163	27	48	219	172	56	172	35	535
2F1	90	34	63	200	149	48	27	193	162	44	151	69	496
YR3	56	34	203	137	126	46	32	192	157	52	157	33	508
YR2	88	57	50	116	74	29	43	98	95	28	84	69	259
YR1	47	36	57	128	86	28	33	130	123	31	95	31	342
Ydb2	13	16	20	153	94	12	56	68	79	34	160	22	248
Y2	17	8	16	163	100	13	77	51	66	25	125	27	197
Ydb1	15	21	46	145	125	24	17	169	167	43	201	30	525
YF2	51	30	82	132	115	31	32	189	144	43	173	68	509
YF1	24	19	98	118	112	20	15	139	100	48	276	35	445
SSR1	68	39	171	174	120	70	50	151	244	45	169	40	608
SSR2	60	32	879	174	121	58	55	149	211	49	163	50	575
SSR3	62	31	115	188	126	40	52	158	225	51	164	55	755
SSF1	22	20	33	87	83	17	30	80	79	57	392	35	386
SSF1 Rep.	21	15	37	87	85	17	26	79	78	56	393	32	403
SSR1 Rep.	66	34	165	174	119	68	49	151	244	44	166	42	621

TABLE 6.11: Selected Trace Elements in Sulphides (p.p.m.)

		Co	Cu	Ni	Pb	Zn
Y7 Cleat		10	685	485	425	-
8S7 Cleat		90	1815	325	665	80
8S10a Nodule	(Centre)	5	150	20	25	-
8S10a	(Edge)	5	35	25	30	-
Mansfield M.B. Nodule	(Edge)	15	25	30	10	25
Mansfield M.B.	(Total)	5	5	15	5	305
Heavy Separate M.M.B.	(Brackish)	15	165	65	-	-
Heavy Separate M.M.B.	(Marine)	15	160	65	30	280
				(Whole Rock)		

TABLE 6.12: Average Trace Element Concentrations in Associated Environments

	1	2	3	4	5	6	7	8	9
Ni	49	47	64	1	66	42	21	68	75
Co	35	14	33	n.d.	23			19	25
Mn	455*	315		10	929			850	950
V	149	137	162	1	258	134	53	130	135
Cr	114	114	130	10	110	72	31	90	100
Zn	37	50		50				95	70
Cu	40	32	33	20	69	33	15	45	55
Rb	146	129	143					140	90
Sr	139	127	74	n.d.	123			300	375
Y	43	36						26	33
Zr	169	212	258	n.d.				160	165
Pb	41	49	6	40	42	24	12	20	13
Ba	468	476	492	n.d.	794			580	425

n.d. - not detected

1. Present study
2. South Wales Mudrocks (Al-Jalili, 1982, Ph.D.)
3. Besham Rocks (Nicholls and Loring, 1962)
4. Ruhr Coal (Stach et al., 1975)
5. Mansfield Marine Band (Curtis, 1969)
6. Marine Argillaceous Sediments
7. Freshwater Argillaceous Sediments
8. Average Shale
9. Average Crustal Abundance

6-7 Potter et al., 1963
8-9 Turekian and Wedepohl, 1961

*143 excluding 8R1, 8R2
n.d. not detected

TABLE 6.13: Table of Ionic Radii Å

1	Ni^{2+}	0.69 Å
1	Co^{3+}/Co^{4+}	0.73/0.63
1	Mn^{4+}	0.60
2	$V^{3+}/V^{4+}/V^{5+}$	0.72/0.67/0.62
1	Cr^{3+}	0.63
1	Zn^{2+}	0.74
1	Cu^{+}	0.96
1	Rb^{+}	1.47
1	Sr^{2+}	1.12
2	Y^{3+}	0.98
2	Zr^{4+}	0.80
1	Pb^{2+}	1.20
1	Ba^{2+}	1.34

1. Rutley's Elements of Mineralogy (Read, 1970)

2. Krauskopf, (1979)

TABLE 6.14: N.C.B. Cone Indenter Number for Weak Rocks

	C.I. No. (Weak Rocks)	Standard Deviation	Uniaxial Compressive Strength[1]
8R1	0.82	0.025	13.5
8R2	1.12	0.020	20.0
8S10c	0.66	0.067	10.9
8F1	0.66	0.085	10.9
2R1	0.88	0.035	14.5
ID.2.11	0.52	0.116	8.6
YR3	0.74	0.046	12.2
YR2	0.61	0.079	10.1
YR1	0.72	0.067	11.9
SSR1	0.82	0.041	13.5
SSR2	2.09/0.74	0.026/0.052	12.2
SSR3	0.79	0.050	13.0
SSF1	1.05	0.057	17.3

C.I. No. vs. Standard Deviation = $r = -0.61$ (95% significance)

[1] Uniaxial Compressive Strength in MPa

fc = 16.5 Iw MPa

fc - uniaxial compressive strength in MPa

Iw - cone indenter No. for weak rocks

TABLE 6.15: Cone Indenter No. vs. Quartz and Organic Matter

	C.I. No.	Quartz %	Organic Matter%
8R1	0.82	20.34	1.38
(8R2	1.21	4.21	36.80)
8S10c	0.66	14.16	8.54
8F1	0.66	27.94	9.70
2R1	0.88	17.30	1.05
ID.2.11	0.52	n.d.	17.77
YR3	0.74	26.59	4.49
YR2	0.61	11.31	43.91
YR1	0.72	14.29	31.50
SSR1	0.82	22.03	11.64
SSR2	0.74	20.32	10.28
SSR2	0.79	19.32	7.42
SSF1	1.05	47.40	5.32

n.d. - not detected

C.I. No. vs.Quartz $r = +0.80$
(99% significance)

C.I. No. vs. Organic Matter $r = -0.52$
(90% significance)

TABLE 6.16: Correlation between Cone Indenter Number and Quartz Content for South Wales Coalfield Rocks.

	Cone Indenter No.		Quartz %
	Al-Jalili	Caswell	
2F	1.44	1.14	28.11
3F	0.95	0.93	18.10
11F	0.95	0.77	-
12F	0.55	0.81	29.51
13F	1.00	0.73	-
14F	1.53	0.69	25.27
3R	1.00	0.96	20.51
4R	1.17	1.36	31.93
6R	0.71	3.12/0.86	30.10
8R	0.96	1.35	30.96
11R	1.12	1.21	28.57
12R	7.70	4.85	80.36
14R	1.43	0.90	12.00
15R	6.00	4.47	76.67
17R	6.00	3.77	30.00

cc. Al-Jalili vs. Caswell = + 0.98
(99.9% significance)

Cone Indenter No. (Caswell) vs. Quartz = 0.62
(99% significance)

TABLE 7.1: Cation Exchange Capacity versus Clay Type (%)

			Correlation Coefficient	Significance Level
C.E.C.	vs.	Total Clay(%)	+0.62	99%
C.E.C.	vs.	Illite	+0.46	95%
C.E.C.	vs.	M.L.C.	+0.48	95%
C.E.C.	vs.	Kaolinite		Not significant (95%)
C.E.C.	vs.	Chlorite		Not significant (95%)

TABLE 7.2: Exchangeable Cations versus Clay Type (%)

	Exchangeable Cation				Significance Level	
Clay Type	XNA	XK	XCa	XMg	95%	= +0.46
Illite		+0.52		+0.46	99%	= +0.58
M.L.C.	+0.61	+0.54		+0.48	99.9%	= +0.69
Kaolinite	+0.51		+0.53			
Chlorite				+0.46		

TABLE 8.1:. XRD Coal Ashes
(Approximate Abundance)

	Gypsum	Kaolinite	Chlorite	Illite + M.L.C.	Apatite including Goyazite	Quartz	Sphalerite	Marcasite	Pyrite	Siderite	Calcite	Ankerite	Anatase
Y9	H	M	T	L		H			L				
Y8	H	H						T	L				
Y7	L	M							H		M	L	
Y6	H	H				T			L		H	M	
Y5	H	H				L			L			H	
Y4	H	H				T							
Y3	H	H	T	L		L			T				
Y2		M		M		H							
Y1		H		M		H			M				
SS1	H	M				L			H	T	H		
SS2	H	H				T			M	T	H		
SS3	M	H			T	M		T	T				T
SS4	H	H				L			L				
SS5	M	M							T		H	M	
SS6	M	H							L		H	M	
SS7	M	H							M		M	M	
SS8	M	H				T			L		M	M	
SS9	M	M				T		T			H	H	
SS10	M	M									H	H	
SS11	M	M									H	M	

H - High
M - Medium
L - Low
T - Trace

TABLE 8.1: XRD Coal Ashes
(Approximate Abundance)

	Gypsum	Kaolinite	Chlorite	Illite + M.L.C.	Apatite including Goyazite	Quartz	Sphalerite	Marcasite	Pyrite	Siderite	Calcite	Ankarite	Anatase	Chalybitic Calcite
8S1	H	M	T	T	T	M			T			H		
8S2	H	H				M		T	T			M		
8S3	H	H			T	M			L			L		
8S4	H	H			T	M			T			H		
8S5	H	M			L	H			T			M		
8S6	H	H			T	H						M		
8S7	M	H			M	L			T			H		
8S8	H	H			T	L		T	L					
8S9	L	M		T	L				L				T	
8S10	M	H		M	L			T	L				T	
8S11	H	H			T	T	T	L	L		T	H		
8S12	H	H				M		L	M			M		
8S13	H	H		T		M		M	M					
2.1	H	H		L		M	L		L			H		
2.2	H	H			M							M		
2.3	M	H				L	H				L	H		H
2.4	M	M				T						H		
2.5	M	M			M		T		L			H		
2.6	L	L							L	H		M		
2.7	H	H			T	T	T		L			-		
	H	M			-	-	L		M			M		
2.8	M	M					T	T	T					
2.9	H	H		T	T		T	T	T					
2.10		H	T	M			T		L					
2.12	M	H	T	M		M		T	M		L			

TABLE 8.2: A Summary of the Probable Origins of the Coal Mineralogy

		Detrital	Diagenetic	
			Early	Late
Clay Group	Kaolinite	✓	?	✓
	Illite + M.L.C.	✓		
	Chlorite	✓		
Sulphide Group	Pyrite		✓	✓
	Marcasite		?	✓
	Sphalerite		?	✓
	Galena		?	✓
Carbonate Group	Ankerite		?	✓
	Calcite		?	✓
	Siderite		✓	
'Others'	Quartz	✓	?	✓
	Apatite incl. goyazite		✓	✓
	Anatase	?		
	Gypsum	Product of L.T.A. or seam oxidation		

✓ Confirmed

? Literature evidence, but not confirmed in the present study although indirect evidence may point to this origin.

TABLE 8.3: XRF Coal Ash Groupings

Shallow Seam		Yard Seam		Park Seam		Eight Feet Seam	
1	SS1	5	Y9	8	2.1	12	8S1
	SS2		Y8		2.2		8S2
2	SS3	6	Y7		2.3		8S3
	SS4		Y6		2.4		8S4
3	SS5		Y5		2.5		8S5
	SS6		Y4	9	2.6		8S6
	SS7	7	Y3	10	2.7	13	8S7
	SS8		Y2		2.8		8S8
4	SS9		Y1		2.9	14	8S9
	SS10			11	2.10		8S10c
	SS11				2.12	15	8S11
							8S12
							8S13

TABLE 8.4: Coal Ash XRF Totals
(Recalculated to 100% including using ignition loss and SO_3)

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	SO_3	Losses	Calc. Qtz.
1	22.69	7.10	0.38	22.97	1.15	20.78	3.85	0.55	0.05	0.10	15.73	4.65	14.33
2	43.15	28.41	1.08	1.22	0.63	4.50	3.06	0.27	-	3.93	4.44	9.31	9.67
3	24.89	9.78	0.13	10.29	2.88	19.12	5.60	0.28	0.05	0.08	12.25	14.65	13.36
4	5.29	3.11	0.11	7.59	5.41	37.28	1.43	0.10	0.20	0.08	4.93	34.46	1.62
5	41.50	19.36	0.62	12.13	1.26	2.93	3.77	2.81	-	0.09	6.91	8.62	18.98
6	14.07	9.78	0.17	37.09	0.99	5.38	1.28	0.77	0.01	0.10	6.11	24.25	2.54
7	44.85	24.84	1.08	5.29	0.90	0.38	0.83	2.72	-	0.05	0.42	18.64	17.14
8	31.79	15.48	0.93	10.24	3.75	10.62	2.31	0.48	0.06	0.18	6.51	17.65	13.54
9	3.59	1.33	0.02	47.18	3.72	8.60	1.29	0.10	0.49	0.87	4.13	28.64	2.03
10	22.96	16.16	0.48	15.96	2.15	7.88	4.83	0.56	-	1.41	14.22	13.39	3.91
11	36.16	25.05	0.66	8.49	1.05	0.93	1.17	3.02	-	0.20	2.79	20.48	7.19
12	18.57	11.00	0.38	11.78	5.46	17.69	0.41	0.52	0.21	0.59	6.35	27.04	5.60
13	22.29	13.08	0.15	13.74	3.05	7.95	0.58	0.68	-	0.38	7.33	30.78	6.87
14	34.32	27.91	0.77	8.64	1.08	2.71	0.91	3.27	-	3.74	7.30	9.35	1.65
15	22.18	16.82	0.22	13.69	2.24	7.44	2.79	0.45	-	0.99	4.42	28.77	2.35
Average	25.89	15.28	0.48	15.09	2.38	10.28	2.27	1.11	0.07	0.85	6.92	19.38	(Ash 12.37%)

TABLE 8.5: Coal Ash
(XRF as a % of coal)

		SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	SO_3	Losses	Ash	Calc. Qtz.
Shallow	1	2.15	0.67	0.04	2.18	0.11	1.97	0.36	0.05	-	0.01	1.49	0.44	9.47	1.36
	2	3.78	2.48	0.09	0.11	0.06	0.39	0.27	0.02	-	0.34	0.39	0.81	8.74	0.85
	3	1.45	0.57	0.01	0.60	0.17	1.11	0.33	0.02	-	-	0.71	0.85	5.83	0.78
	4	0.60	0.35	0.01	0.86	0.62	4.25	0.16	0.01	0.02	0.01	0.56	3.92	11.37	0.18
Average		2.00	1.02	0.04	0.94	0.24	1.93	0.28	0.03	0.01	0.09	0.79	1.51	8.88	
Yard	5	8.83	4.12	0.13	2.58	0.27	0.62	0.80	0.60	-	0.02	1.47	1.83	21.28	4.04
	6	1.64	1.14	0.02	4.31	0.12	0.63	0.15	0.09	-	0.01	0.71	2.82	11.62	0.30
	7	17.77	9.84	0.43	2.10	0.36	0.15	0.33	1.08	-	0.02	0.17	7.39	39.62	6.79
Average		9.41	5.03	0.19	3.00	0.25	0.47	0.43	0.59	-	0.02	0.78	4.01	24.17	
Park	8	3.14	1.53	0.09	1.01	0.37	1.05	0.23	0.05	0.01	0.02	0.64	1.74	9.88	1.34
	9	0.34	0.13	-	4.52	0.36	0.82	0.12	0.01	0.05	0.08	0.40	2.75	9.59	0.19
	10	2.19	1.55	0.05	1.53	0.21	0.75	0.46	0.05	-	0.13	1.36	1.28	9.57	0.37
	11	6.33	4.39	0.12	1.49	0.18	0.16	0.20	0.53	-	0.04	0.49	3.59	17.51	1.26
Average		3.00	1.90	0.07	2.14	0.28	0.70	0.25	0.16	0.02	0.07	0.72	2.34	11.64	
Eight Feet	12	0.92	0.54	0.02	0.58	0.27	0.87	0.02	0.03	0.01	0.03	0.31	1.34	4.94	0.28
	13	0.92	0.54	0.01	0.57	0.13	0.33	0.02	0.03	-	0.02	0.30	1.27	4.14	0.28
	14	4.87	3.96	0.11	1.23	0.15	0.38	0.13	0.46	-	0.53	1.04	1.33	14.18	0.23
	15	1.73	1.32	0.02	1.07	0.18	0.58	0.22	0.04	-	0.08	0.35	2.25	7.82	0.18
Average		2.11	1.59	0.04	0.86	0.18	0.54	0.10	0.14	-	0.17	0.50	1.55	7.77	

TABLE 8.6: XRD Mineral Abundance Based on Grouped L.T.A. Samples (for XRF back-up)

	Gypsum	Kaolinite	Chlorite	Illite + MLC	Apatite + Goyazite	Quartz	Sphalerite	Marcasite	Pyrite	Siderite	Calcite	Ankerite	Anatase	Chalybitic Calcite
1	M	M							M	L	H			
2	M	M			T			L	L				T	
3	M	H							L		M	M		
4	L	L						T	T		H	M		
5	M	M		M		H		T	L					
6	H	H				T			M		H	M		
7	M	M		L		L			L		L			
8	M	M				L	L		L		T	H		
9	L	L							L	H		H		
10	H	M			T		T	T	L		L			
11	L	H	L	M			T		L					
12	H	H			T	M		T	T			M		
13	H	H			T	T		T	T			H		
14	M	H		M	T		T		T				T	
15	M	H		T	T	L		T	L		T	M		

Relative Mineral Abundance Based on XRD Peak Height (c.p.s.)

H = high

M = medium

L = low

T = trace

TABLE 8.7: Correlation Matrix of Coal Ash (L.T.A.)

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	SO_3	Loss	Ash
SiO_2													
Al_2O_3	0.98												
TiO_2													
Fe_2O_3													
MgO													
CaO					0.65								
Na_2O													
K_2O	0.96	0.96											
MnO					0.57								
P_2O_5													
SO_3							0.68						
Loss	0.70	0.70			0.53			0.70					
Ash	0.96	0.94						0.95				0.82	

Significance Level 95% - 0.51
99% - 0.64
99.9%- 0.76

TABLE 8.8: Water-Soluble Sodium and L.T.A. Sodium in the Coal Samples

	Na_2O (Water-Soluble)	Na_2O (Whole Coal)	Excess in Coal
1	0.29	0.36	0.07
2	0.28	0.27	-
3	0.31	0.33	0.02
4	0.33	0.16	-
5	0.62	0.33	0.14
6	0.26	0.15	-
7	0.19	0.80	0.22
8	0.16	0.23	0.07
9	0.15	0.12	-
10	0.16	0.46	0.30
11	0.17	0.20	0.03
12	0.14	0.02	-
13	0.10	0.02	-
14	0.09	0.13	0.04
15	0.09	0.22	0.13

TABLE 9.1: Cleat Frequency (per cm)

Shallow Seam				Yard Seam		Park Seam		Eight Feet Seam			
SS1	2.50	0.17	(dull)	Y9	0.50	2.1	3.33	8S1	3.60		
SS2	3.13	0.77	(dull)	Y8	2.86	2.2	0.11	8S2	3.18		
SS3	0.09			Y7	2.05	2.3	0.08	8S3	0.13		
SS4	2.50			Y6	3.34	2.4	2.38	8S4	1.25	0.90	(dull)
SS5	2.07			Y5	2.86	2.5	2.19	8S5	0.12		
SS6	1.78			Y4	3.10	2.6		8S6	0.32		
SS7	2.50			Y3	2.00	2.7	2.63	8S7	2.89		
SS8	4.71			Y2		2.8	2.63	8S8	1.70		
SS9	2.63			Y1	1.00	2.9	6.00	8S9	4.07		
SS10	2.43					2.10	2.31	8S10			
SS11	2.07					2.12	2.31	8S11	4.17		
								8S12	2.22		
								8S13	3.47		

TABLE 9.2: Coal Mineral Matter Analysis (XRD)

	Gypsum	Kaolinite	Chlorite	Illite	Anatase	Quartz	Galena	Sphalerite	Marcasite	Pyrite	Siderite	Fe Dolomite	Calcite	Chalybitic Calcite	Apatite
Eight Feet Seam															
8S1	O	√	+	+		+				√		√			+
8S3	O	√				+				√		√			+
8S4	O	√				+				√		√			+
8S8	O	√				+				√					+
8S9	O	√		+	+					√					+
8S10	O	√		+	+					√					
8S11	O	√				+		√	√	√		√	√		+
8S12	O	√				+			√	√		√			
8S13	O	√		+		+			√	√					
Park Seam															
2.1	O	√		+		+	√	√		√		√			
2.2	O	√										√			
2.3	O	√				+		√				√	√	√	
2.4	O	√				+						√			
2.7	O	√				+		√		√		√			+
2.9	O	√		+				√	√	√					+
2.10		√	+	+				√		√					
2.12	O	√	+	+		+	√		√	√			√		
Yard Seam															
Y9	O	√	+	+		√				√					
Y8	O	√				√				√					
Y7	O	√								√		√	√		
Y1		√		+		+				√					
Shallow Seam															
SS1	O	√	+	+		+				√			√		
SS4	O	√				+				√					
SS5	O	√								√		√	√		
SS9	O	√				+						√	√		

Mineral Source:

O - L.T.A. by-product
\+ - Detrital or early diagenetic
√ - Cleat

TABLE 9.3: Kaolinite Crystallinity

	Cleat	L.T.A.		Cleat	L.T.A.
8R1		1.85	YR3		1.66
8R2		1.45	YR2		1.60
8S1		1.18	YR1		1.63
8S2		1.09	Y9	1.19	1.53
8S3		1.11	Y8	1.07, 1.13	1.08
8S4		1.11	Y7	1.17, 1.24	1.05
8S5		1.15	Y6		1.12
8S6		1.12	Y5		1.12
8S7		1.12	Y4		1.10
8S8		1.20	Y3		1.27
8S9	1.14	1.28	Ydb2		1.72
8S10		1.32	Y2		1.91
8S10c	1.15, 1.07	2.04	Ydb1		2.20
8S11	1.20	1.16	Y1		1.96
8S12	1.07, 1.15	1.15	YF2		2.07
8S13	1.18	1.19	YF1		2.09
8F1		1.75			
			SSR1		2.01
2R1		2.05	SSR2		2.21
2.1	1.13, 1.16	1.31	SSR3		2.24
2.2		1.21	SS1	1.11	1.12
2.3		1.09	SS2		1.08
2.4	1.27	1.13	SS3		1.19
2.5		1.06	SS4	1.14	1.12
2.6			SS5	1.12	1.14
2.7	1.13	1.29	SS6		1.19
2.8		1.25	SS7		1.12
2.9		1.23	SS8		1.13
2.10	1.26	1.48	SS9		1.09
1D2.11		2.24	SS10		1.13
2.12	1.13, 1.14	1.43	SS11		1.12
2F1		1.71	SSF1		1.77

TABLE 9.4: Cleat Carbonate XRD Peak Position

	Calcite	Ankerite
Cleat - Selected from Coal		
Mean ($\bar{X}$)	29.47	30.80
No. of Samples	12	14
S.D.	0.04	0.06
Cleat - in L.T.A.		
Mean ($\bar{X}$)	29.46	30.78
No. of Samples	15	27
S.D.	0.01	0.04
Cleat - Yorkshire/Nottinghamshire Coalfield (Fellows, 1979 - Ph.D. Thesis)		
Mean ($\bar{X}$)	24.49	30.78
No. of Samples	28	18
S.D.	0.03	0.03

TABLE 9.5: Cleat Carbonate Analysis (Atomic Absorption)

	Ca%	Mg%	Fe%	Mn%
8S1	58.23	19.18	21.65	0.94
8S6	55.73	20.04	23.06	1.17
8S12	57.58	19.74	21.50	1.18
8S13	56.94	20.24	21.63	1.19
2.1	54.99	21.07	22.97	0.98
2.4	61.98	7.67	29.81	0.55
2.5	55.49	19.70	23.86	1.12
2.6	55.31	20.39	23.24	1.06
2.7	84.84	5.95	8.67	0.54
2.8	63.18	15.06	20.91	0.86
2.9	95.69	3.87	-	0.44
Y7	97.87	0.32	1.47	0.34
Y6	55.54	18.91	24.60	0.95
Y5	55.36	20.21	23.40	1.03
Y4	95.77	1.33	2.70	0.20
Y1	59.63	5.40	34.97	-
SS2	98.66	0.22	0.61	0.51
SS4	97.29	0.18	1.81	0.73
SS5	71.25	15.22	12.52	1.01
SS6	86.60	5.88	6.87	0.64
SS7	71.92	13.75	13.47	0.86
SS8	64.55	16.42	18.07	0.96
SS9	96.62	1.21	1.67	0.50
SS10	73.47	13.42	12.39	0.72
SS11	72.74	15.89	10.41	0.96

TABLE 9.6: Carbonate Chemistry - Cleat Samples
(% Carbonate)

	Ca%	Mg%	Fe%	Mn%
		Calcite		
Shallow Seam	98.66	0.22	0.61	0.51
Fellows (1979 - Ph.D. Thesis)	98.17	0.27	1.03	0.54
		Ankerite		
Eight Foot Seam	57.12	19.80	21.96	1.12
S.D. (4 samples)	1.07	0.46	0.74	0.12
Fellows (1979 - Ph.D. Thesis)	56.79	19.69	21.77	1.75

FIGURE 1.1 The Cannock and North Staffordshire Coalfields in relation to the 'Park' project.

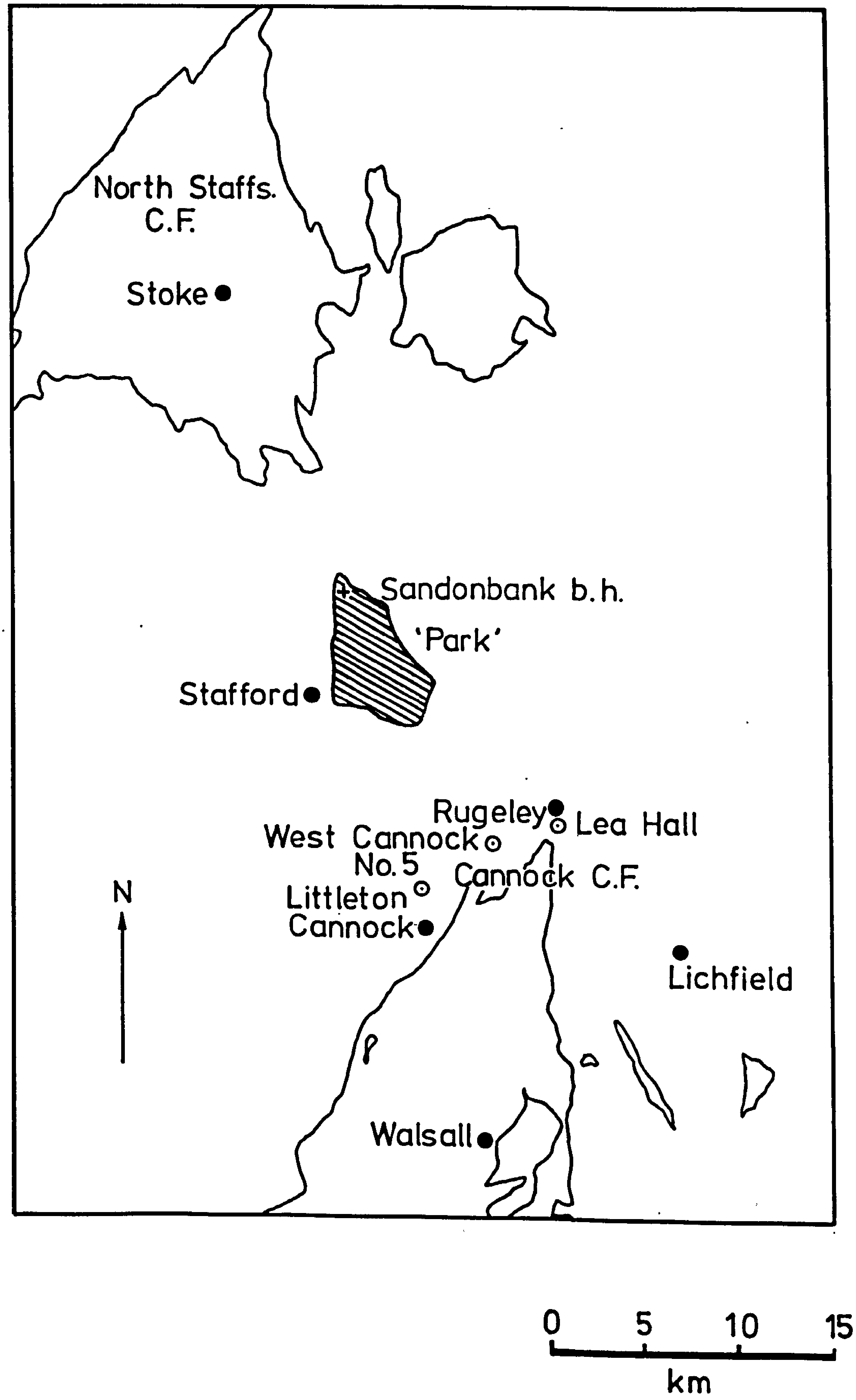


FIGURE 1.2 Seam Profiles Lea Hall Colliery.

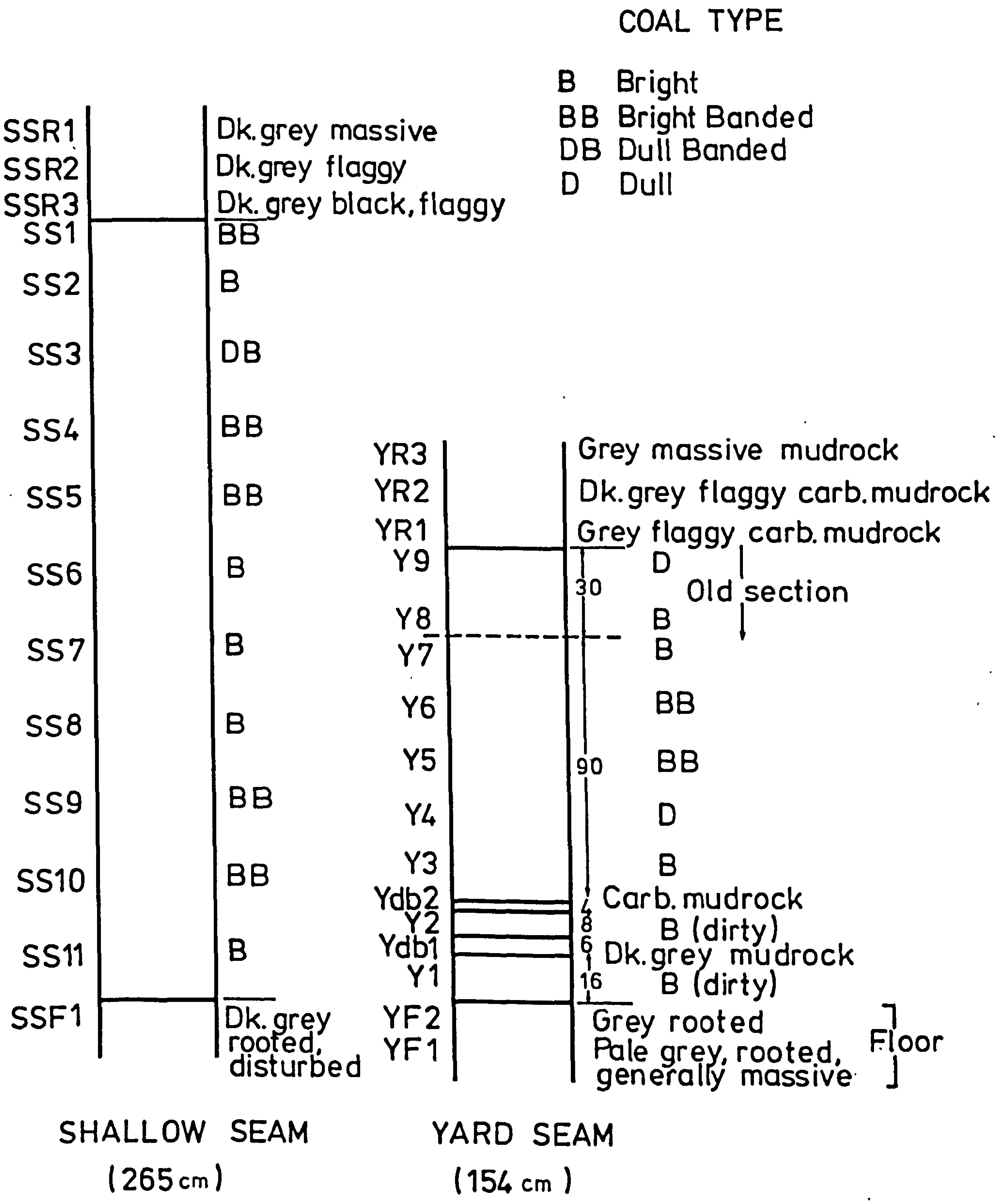


FIGURE 1.24 Seam Profiles Littleton Colliery.

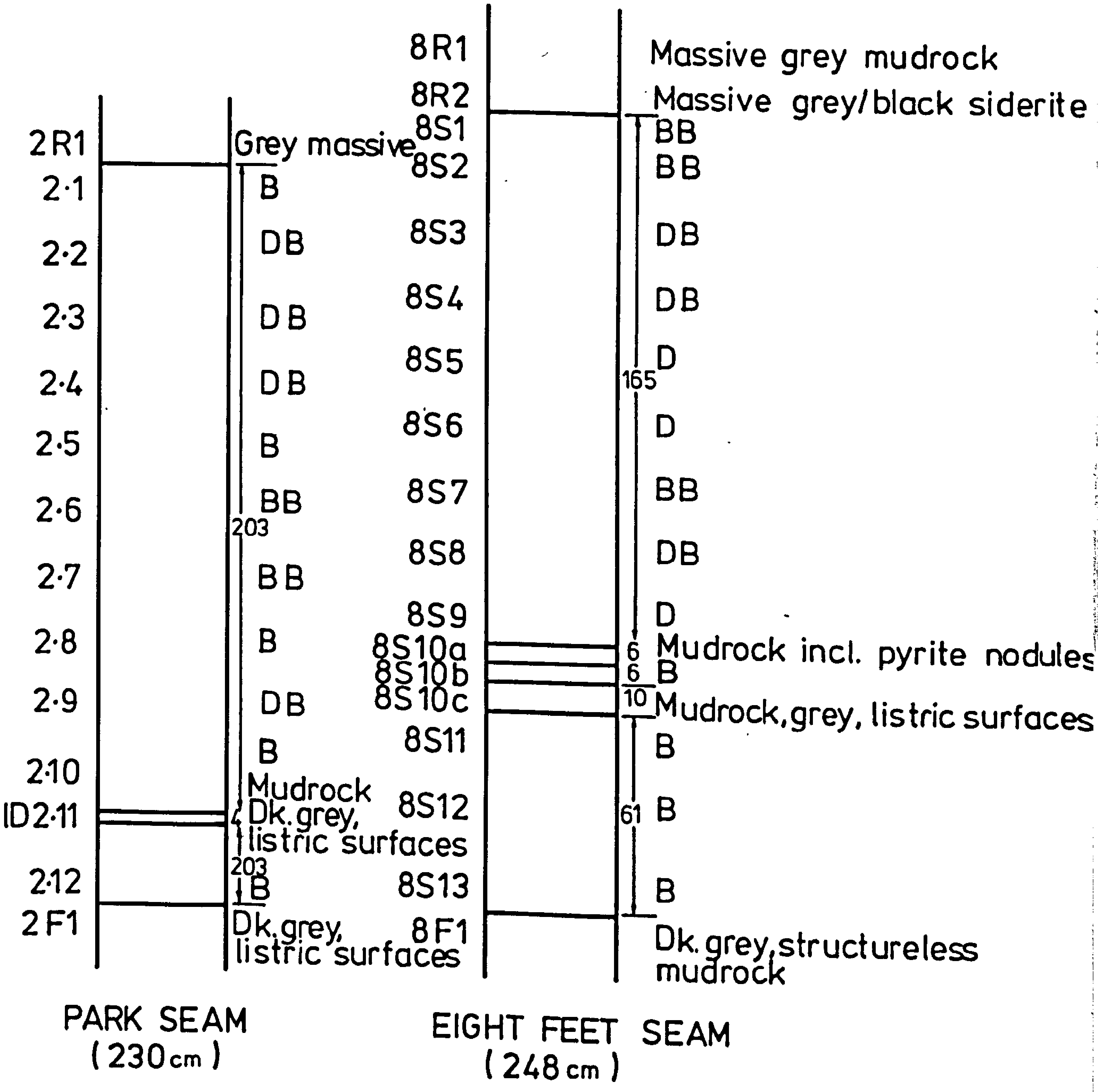


FIGURE 1.3 Relationship between quartz content and TiO_2/Al_2O_3 ratio for the 'mudrock' samples (organic matter free).

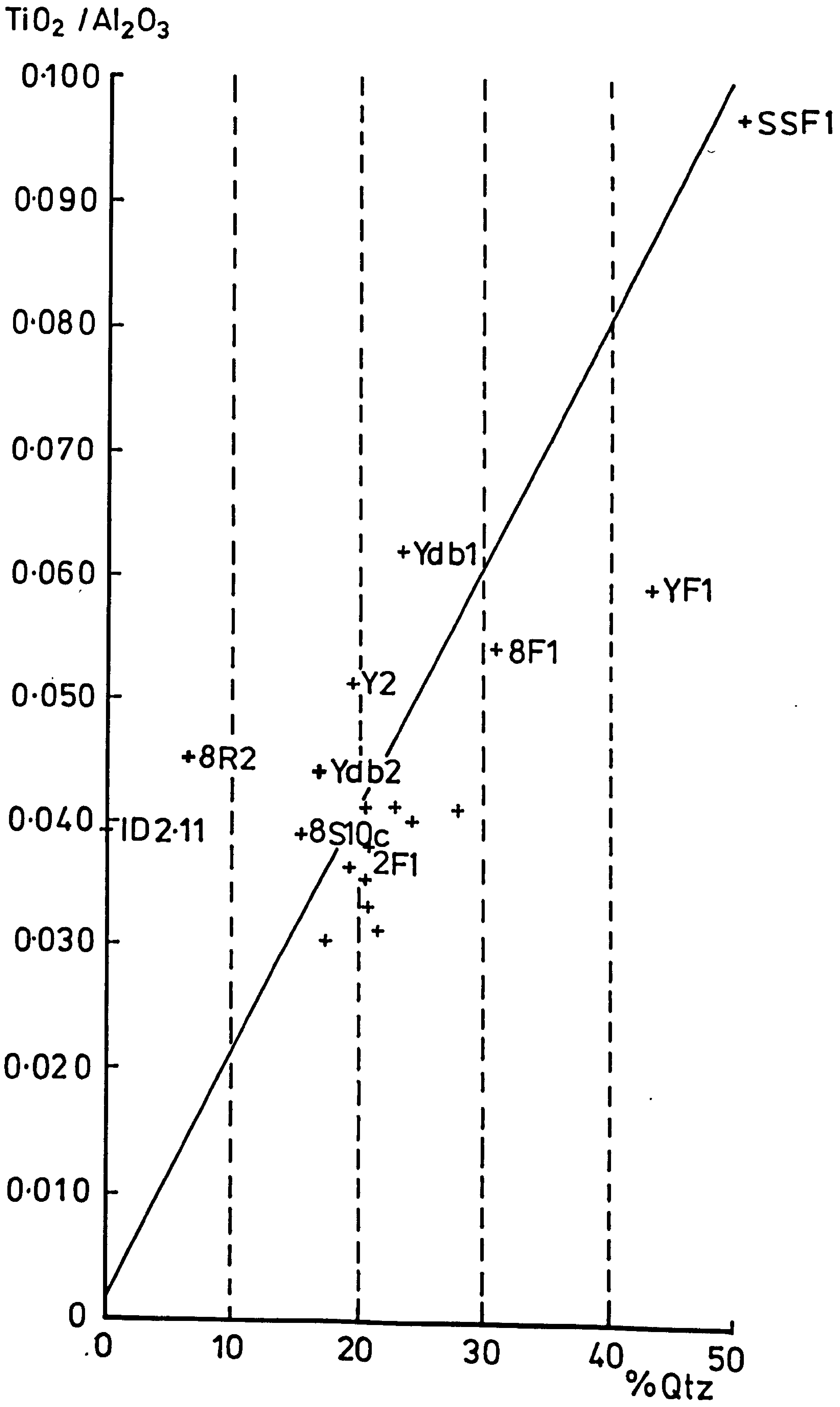


FIGURE 1.4 Seam formation curves (not to scale).

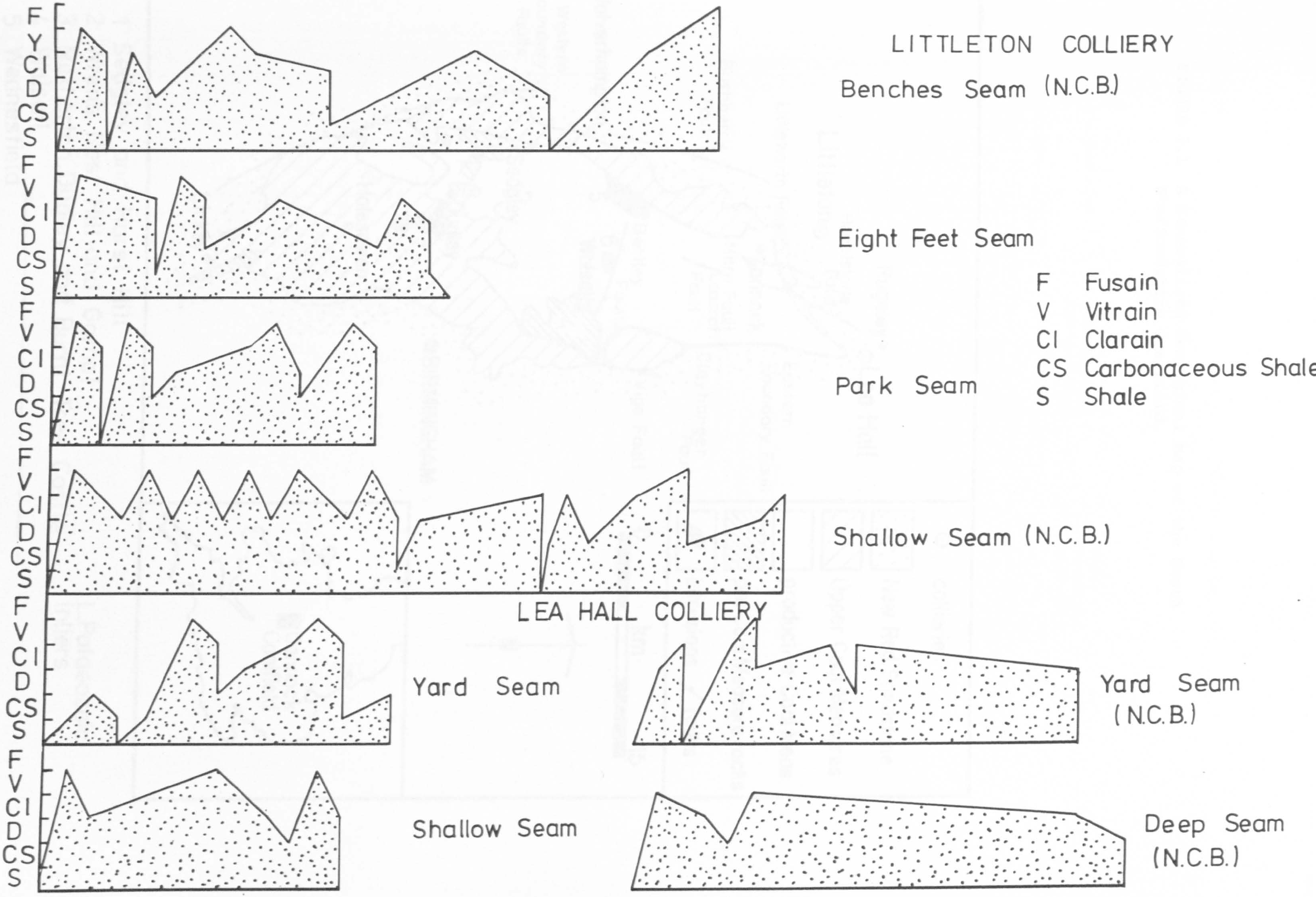
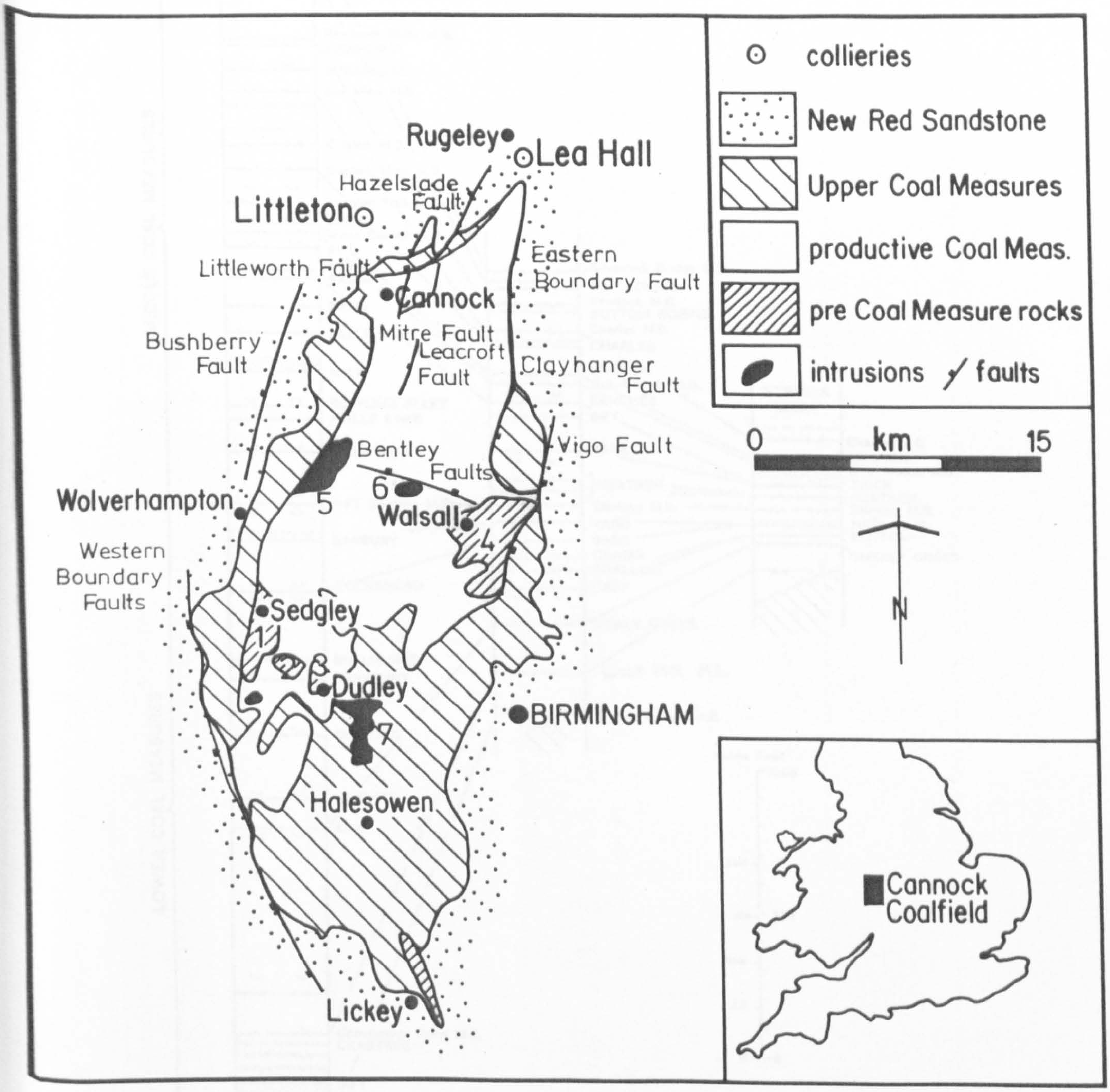


FIGURE 2.1 A Generalised Geological Map of the South Staffordshire Coalfield.



1 Sedgley and Hurst Hill
2 Wren's Nest Hill and Gornal
3 Netherton, Dudley and Burnt Tree Castle
4 Walsall

L.Palaeozoic inliers

5 Wednesfield
6 Pouk Hill
7 Rowley Regis

Intrusions

after Mitchell (1954)

FIGURE 2.2 The Geological Succession through the Staffordshire Coalfields (Hains and Horton, 1969).

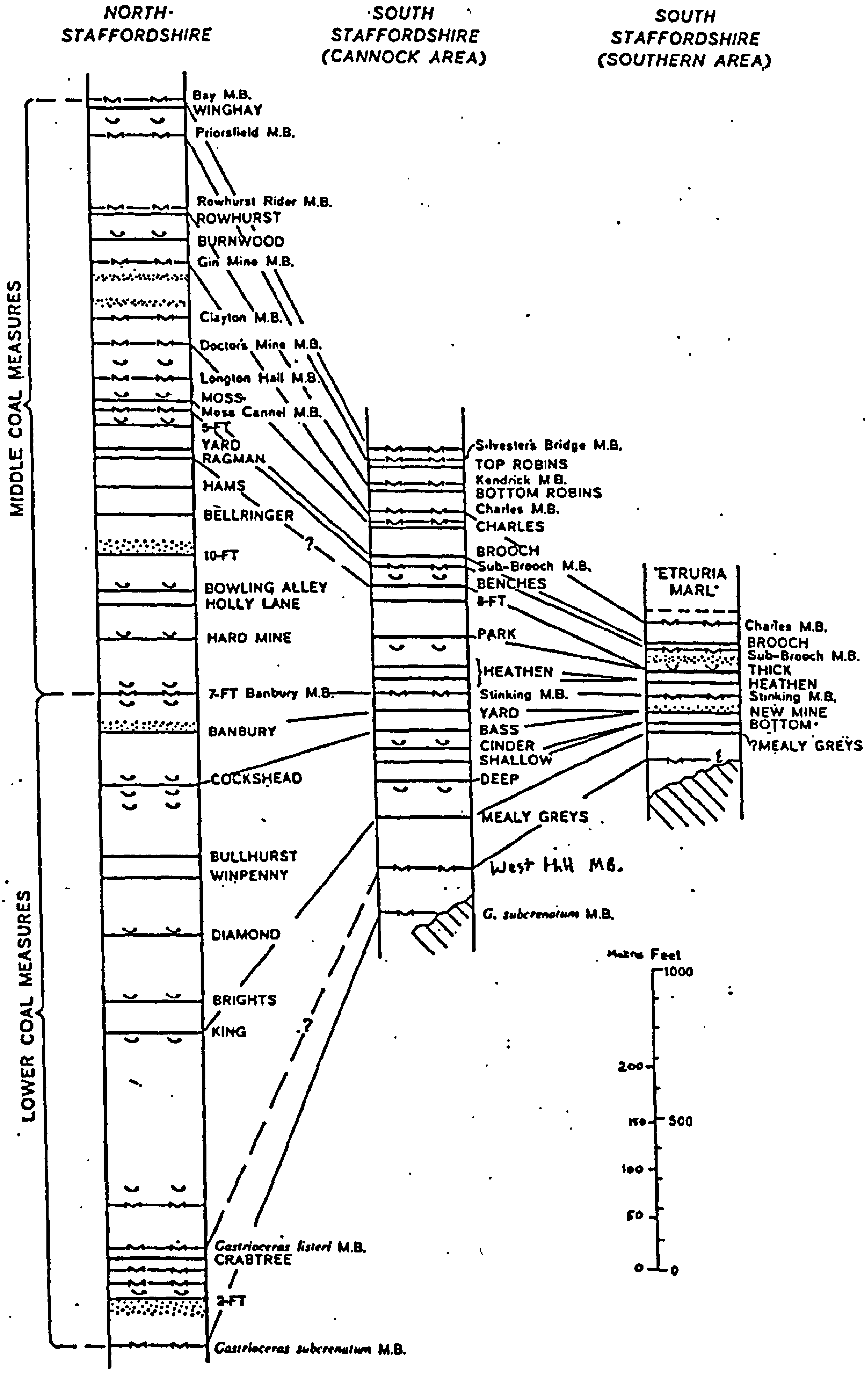


FIGURE 2.3 The Coal Measures Succession at Lea Hall Colliery.

FIGURE 3.1 Hem Heath Winghay Seams (run-of-mine) water-soluble Na$^+$ from dull and bright coals (30 - 72 mesh B.S.S.).

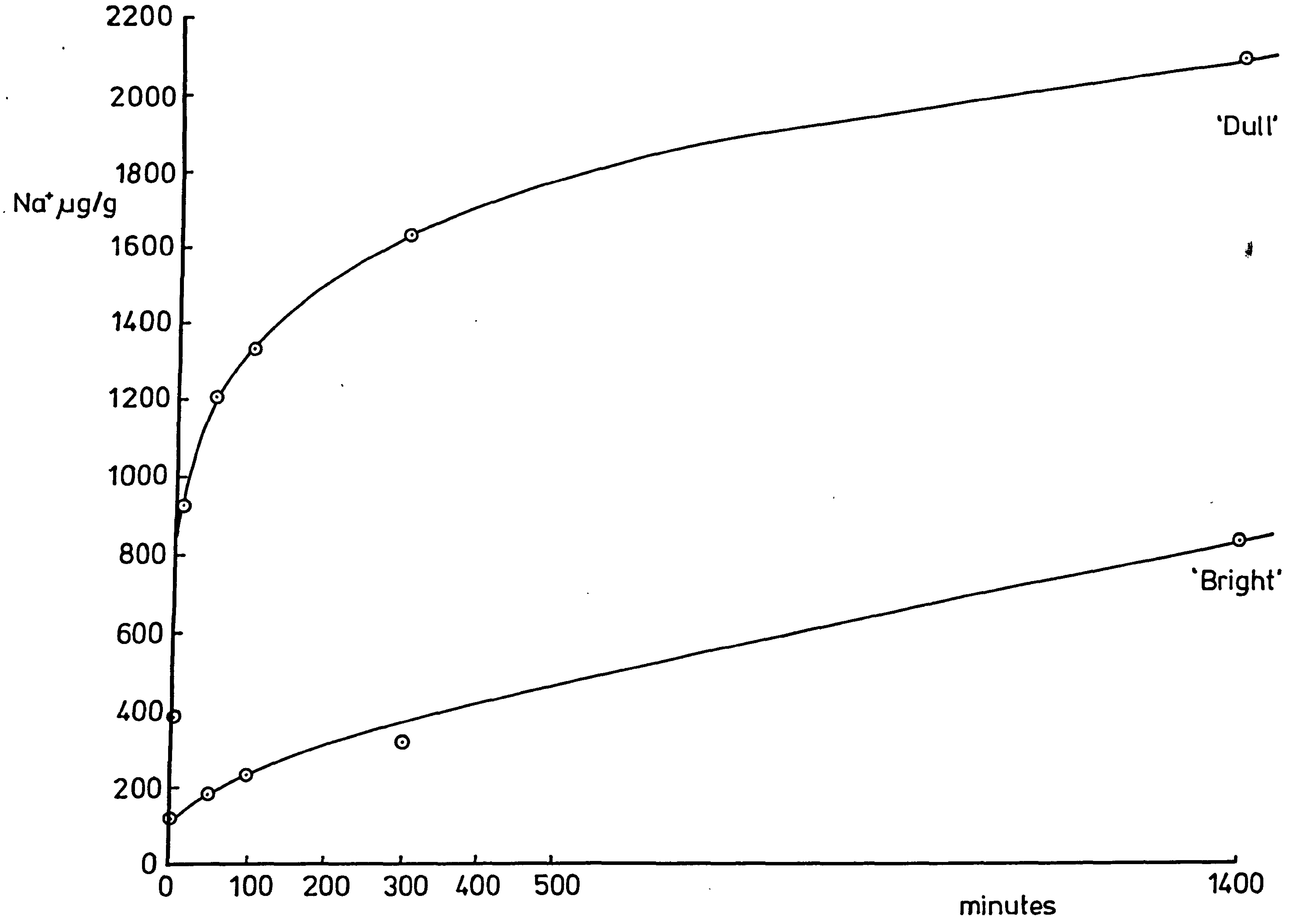


FIGURE 3.2 Water-soluble elements leached from the Eight Feet Seam.

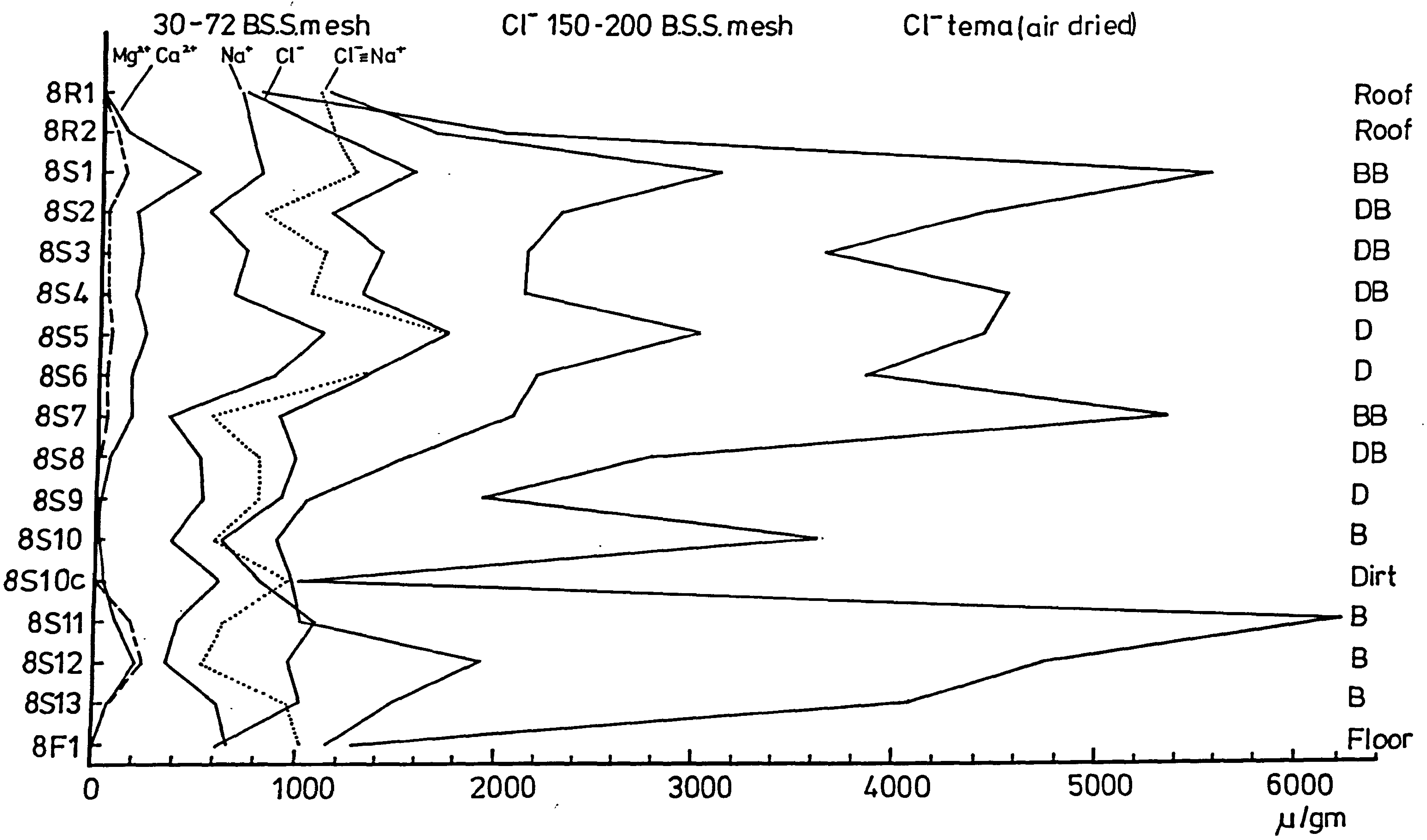


FIGURE 3.3 Water-soluble Na^+ versus Cl^- from the Eight Feet Seam (30-72) mesh B.S.S.).

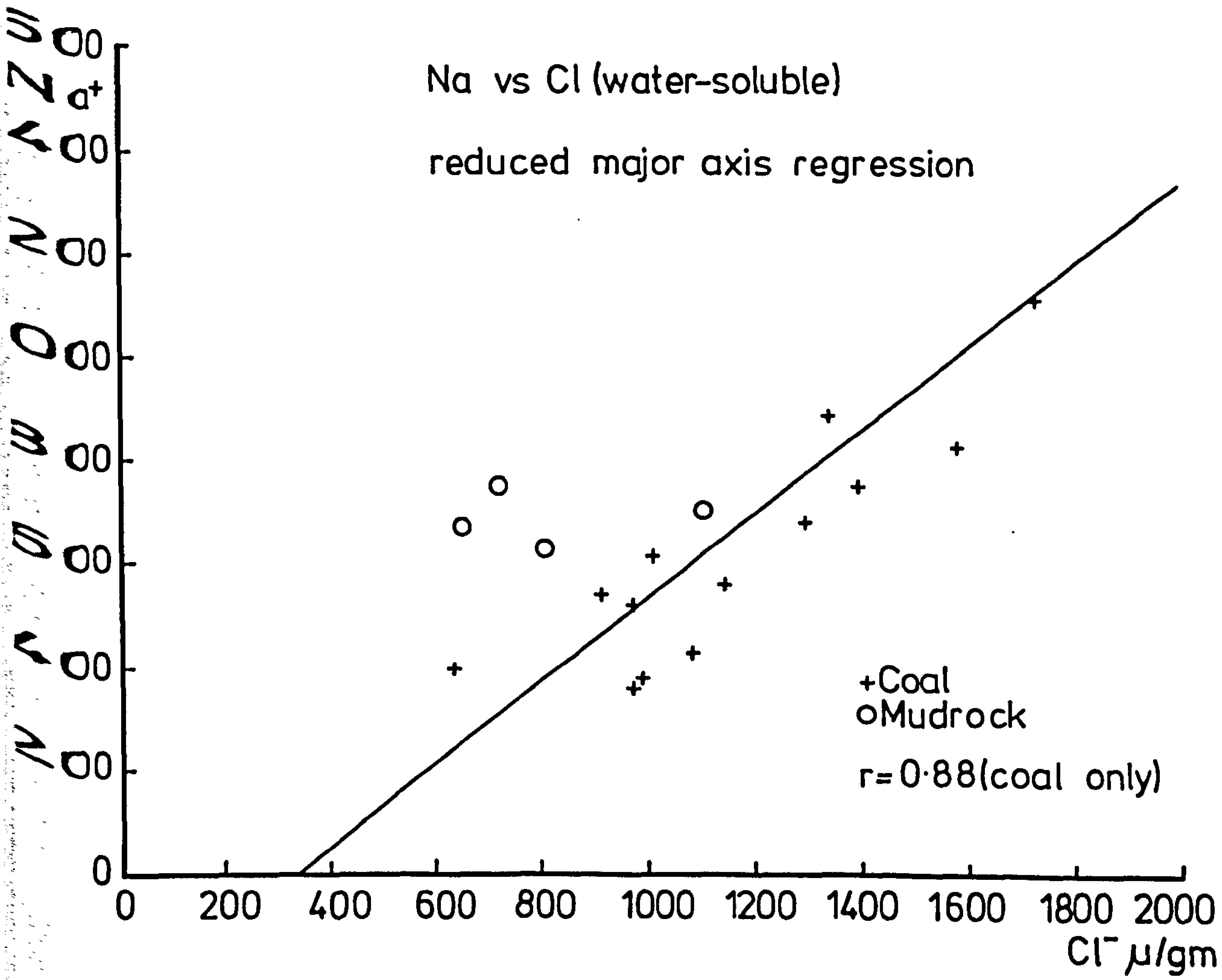


FIGURE 3.4 Leaching ratios and coal types from the Eight Feet Seam.

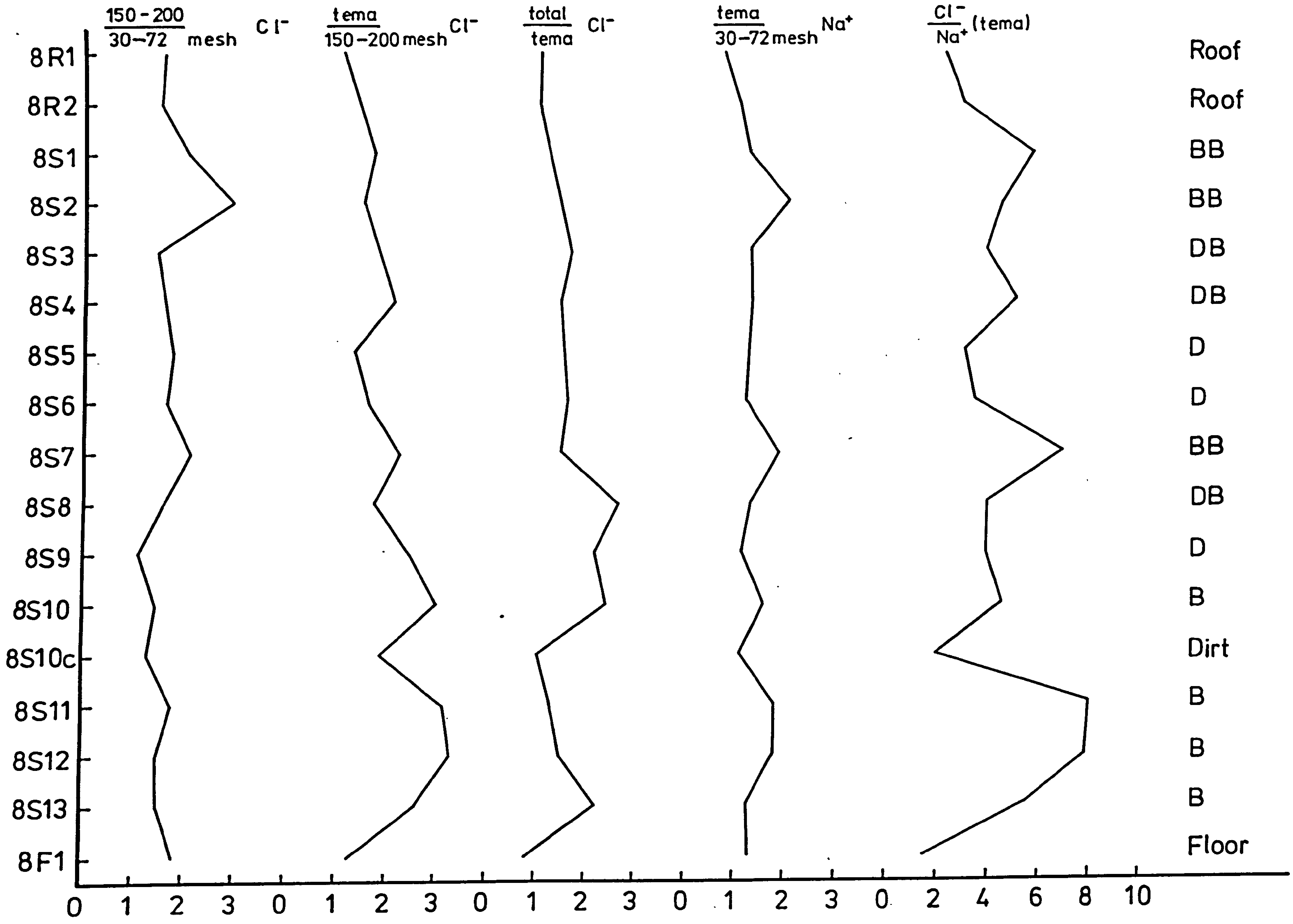


FIGURE 3.5 Water-soluble Cl$^-$ from different size fractions from the Eight Feet Seam.

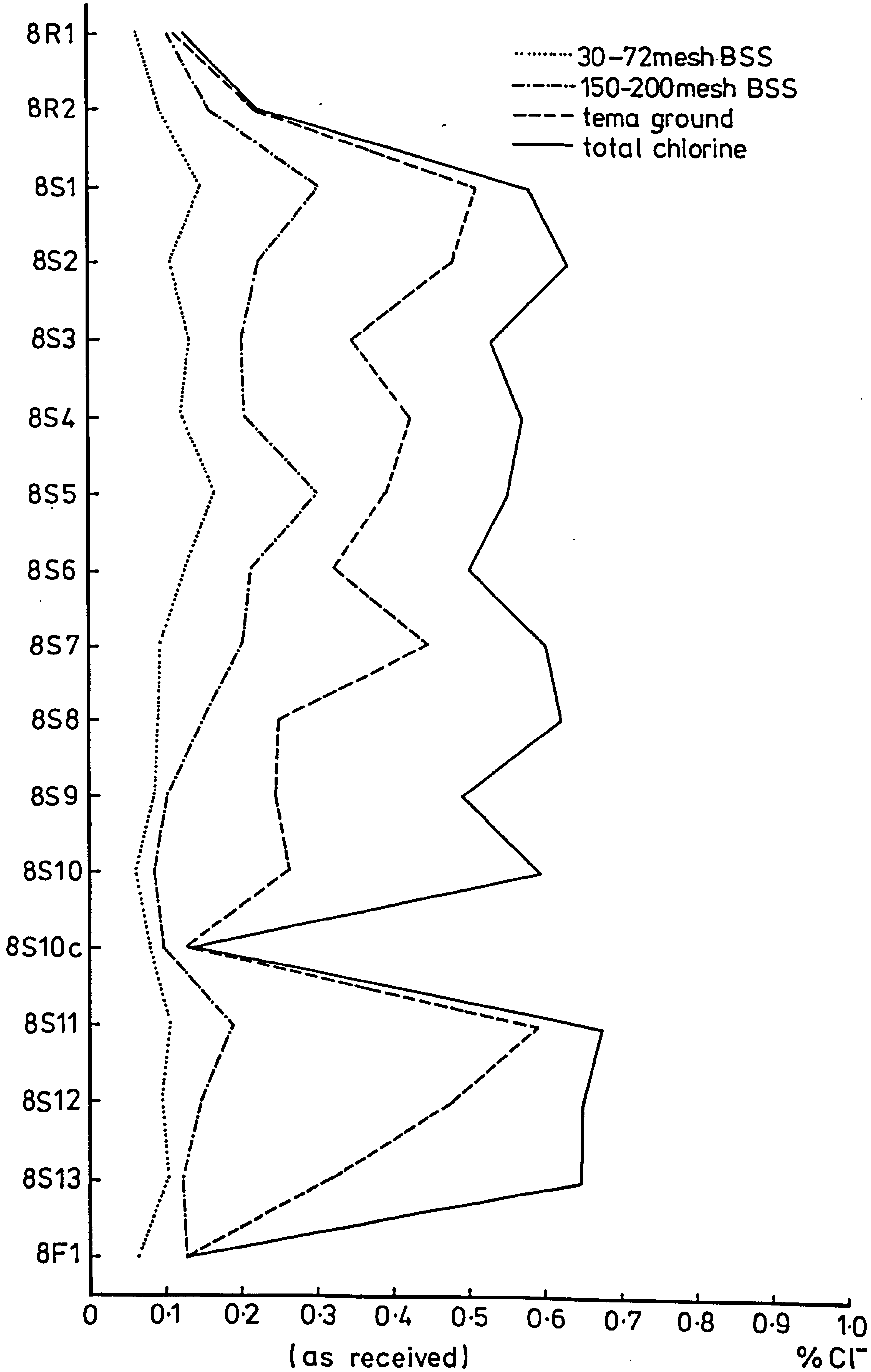


FIGURE 3.6 Cl^- leaching rates from 'run-of-mine' Shallow Seam Coal (C.E.R.L. total Cl^- = 0.66%).

FIGURE 3.7 Percentage water-soluble elements leached related to time (30-72 mesh B.S.S.) 8S5 (Dull Coal).

FIGURE 3.8 Percentage water-soluble elements leached related to time (30-72 mesh B.S.S.) 8S6 (Dull Coal).

FIGURE 3.9 Percentage water-soluble elements leached related to time (30-72 mesh B.S.S.) 8S12 (Bright Coal).

FIGURE 3.10 Percentage water-soluble elements leached related to time (30 - 72 mesh B.S.S.) 8S13 (Bright Coal).

FIGURE 3.11 Calcite and Gypsum dissolution curves (lg/l, ambient temperature).

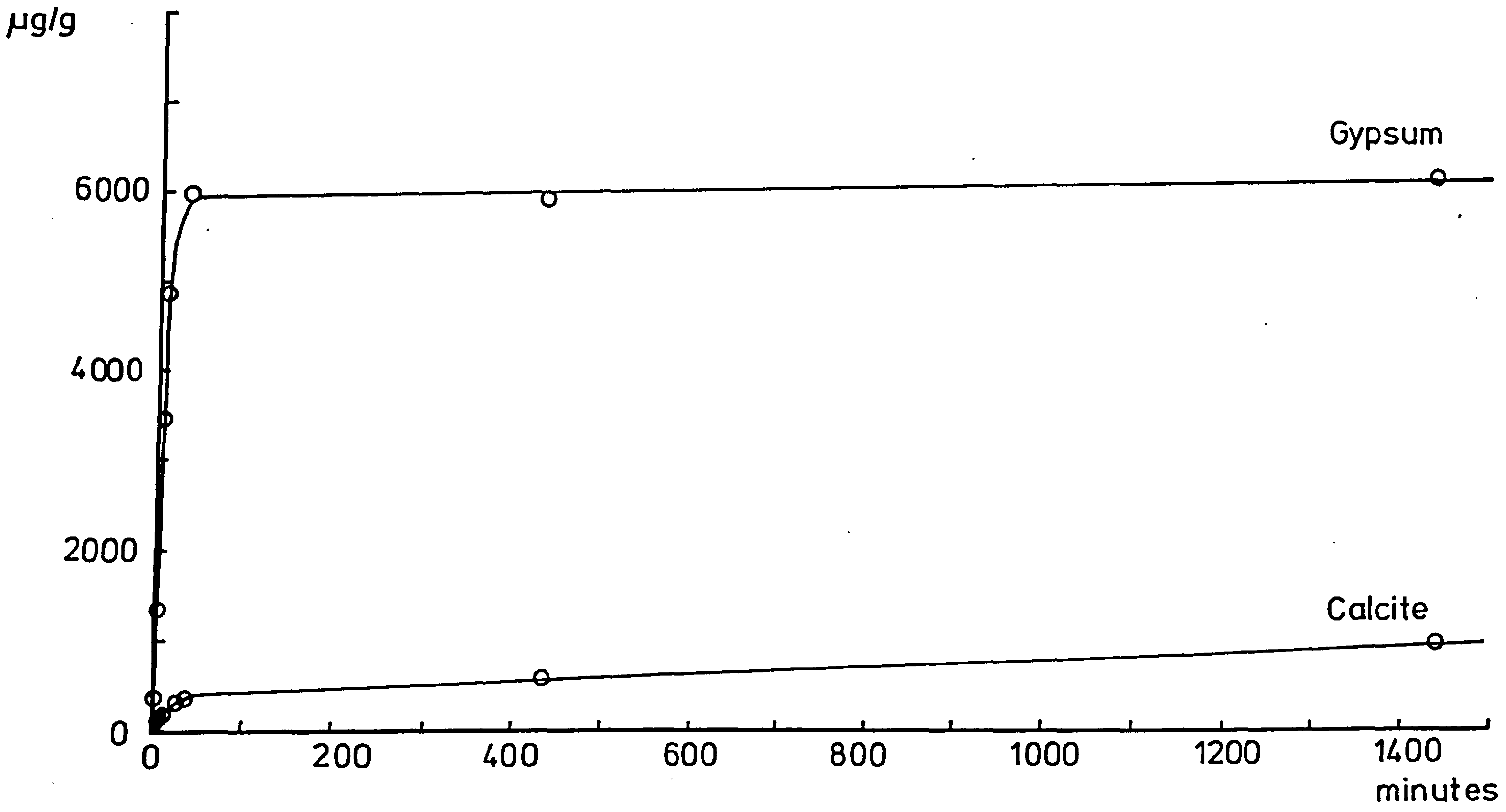


FIGURE 3.12 Water-soluble Na$^+$, Cl$^-$, total Cl$^-$ and moisture profiles (tema ground).

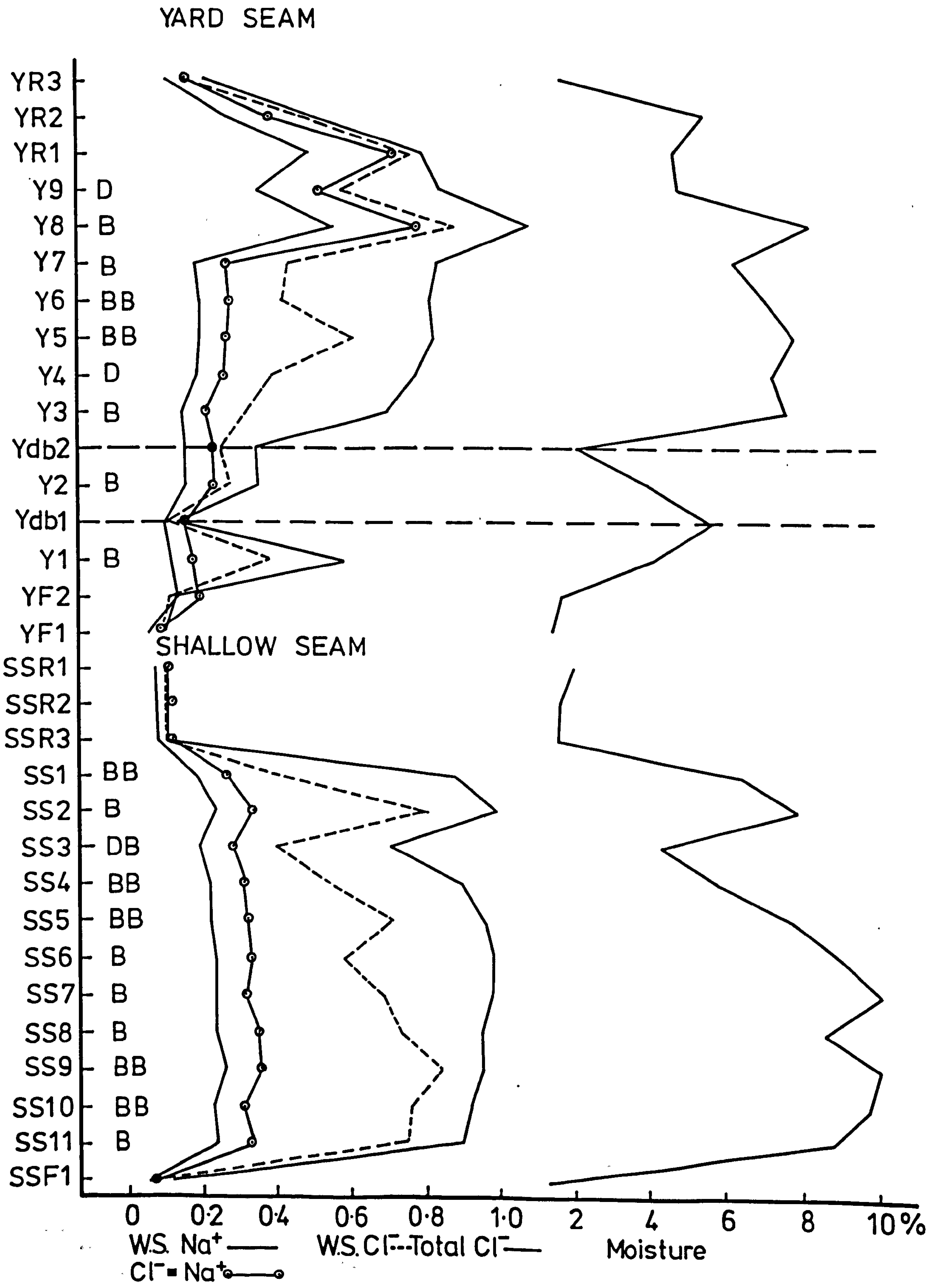


FIGURE 3.12A Water-soluble Na$^+$, Cl$^-$, total Cl$^-$ and moisture profiles (tema ground).

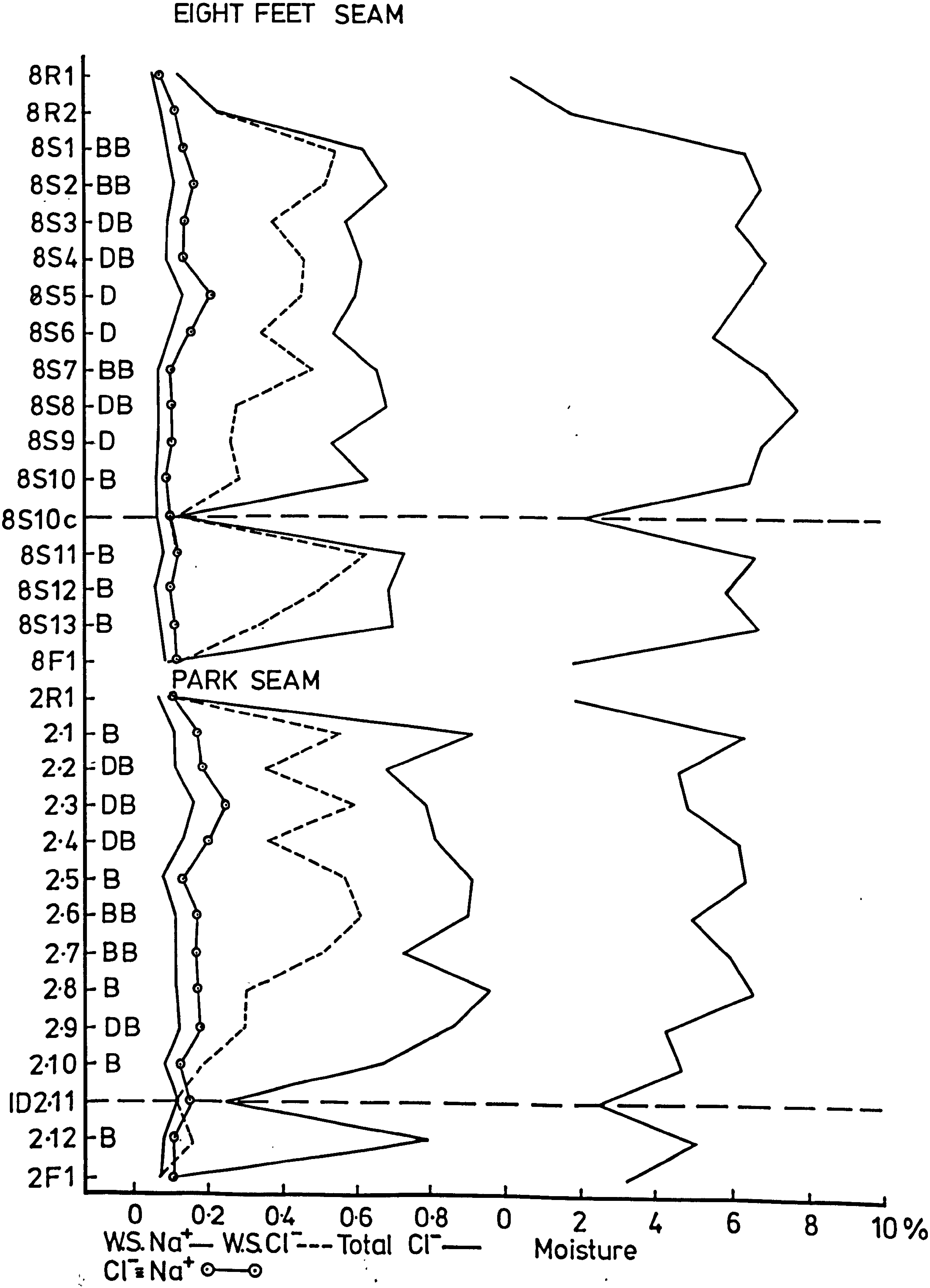


FIGURE 3.13 Water-soluble Ca^{2+}, Mg^{2+}, HCO_3^-, pH and $SO_4^=$ profiles (tema ground).

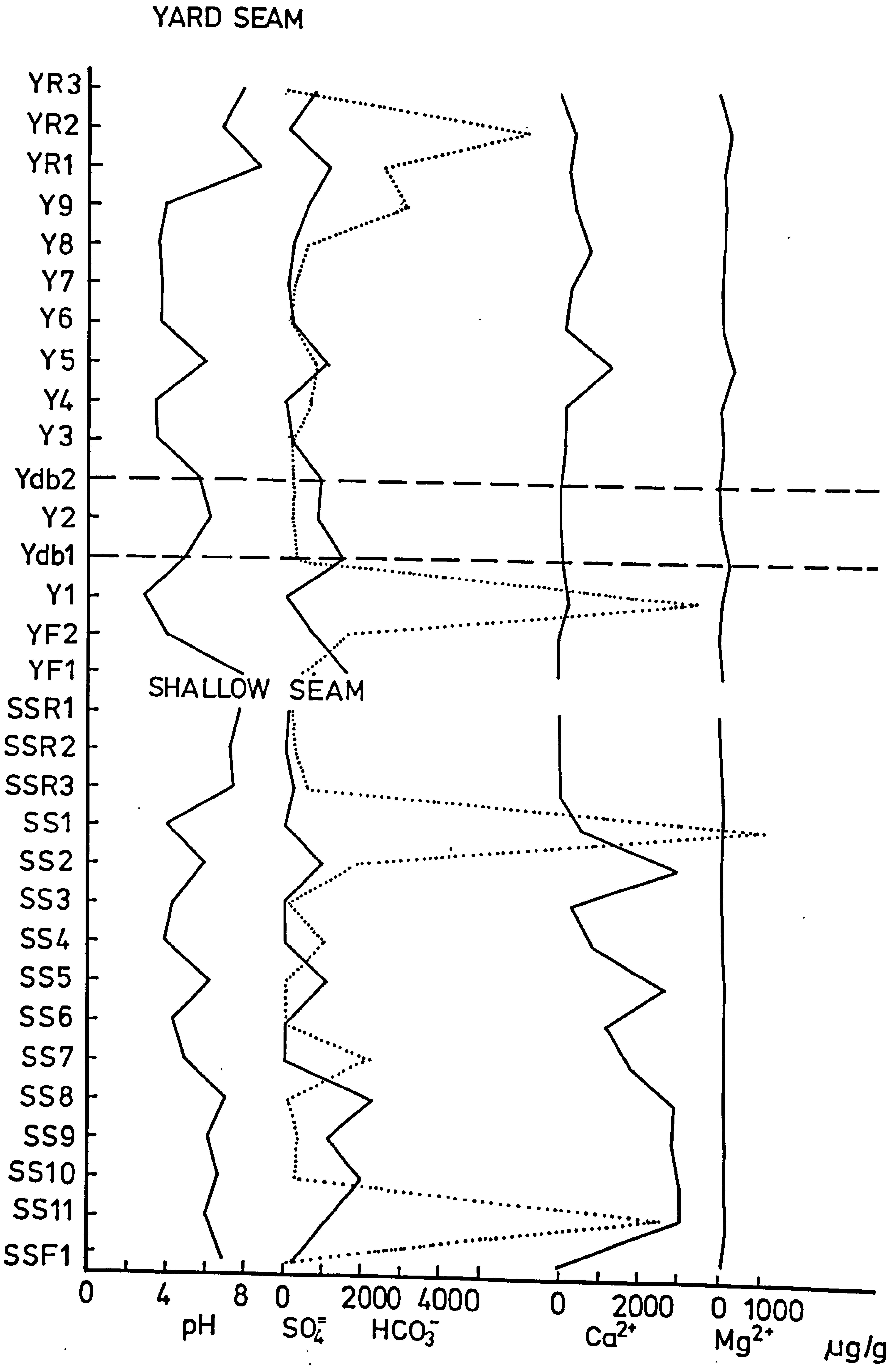


FIGURE 3.13A Water-soluble Ca^{2+}, Mg^{2+}, HCO_3^-, pH and $SO_4^=$ profiles (tema ground).

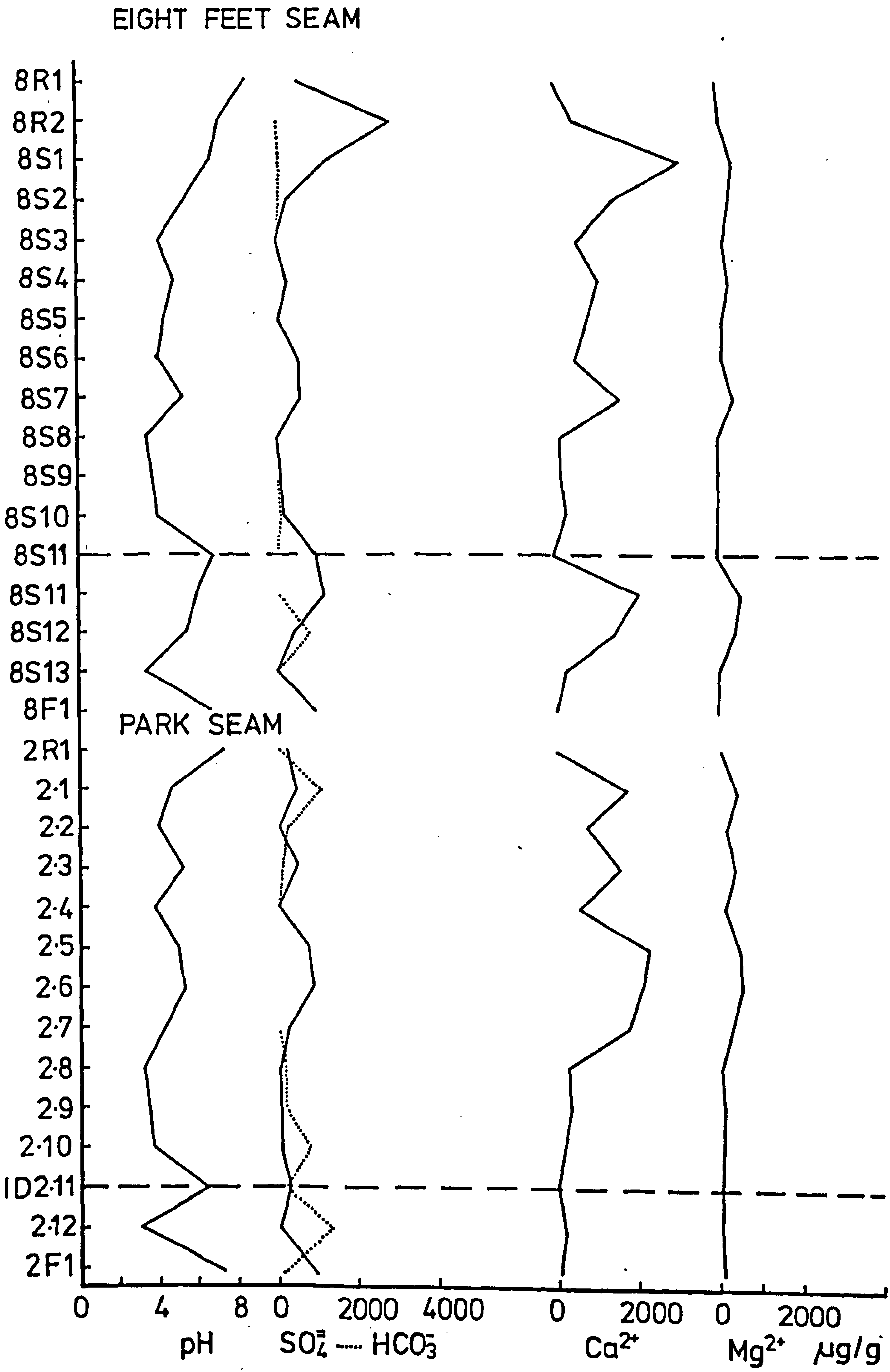


FIGURE 3.14 Water-soluble K^+ profiles (tema ground).

FIGURE 3.144 Water-soluble K^+ profiles (tema ground).

FIGURE 3.15 Water-soluble Ca^{2+} versus non-Na^{+} equivalent Cl^{-}, Lea Hall Colliery.

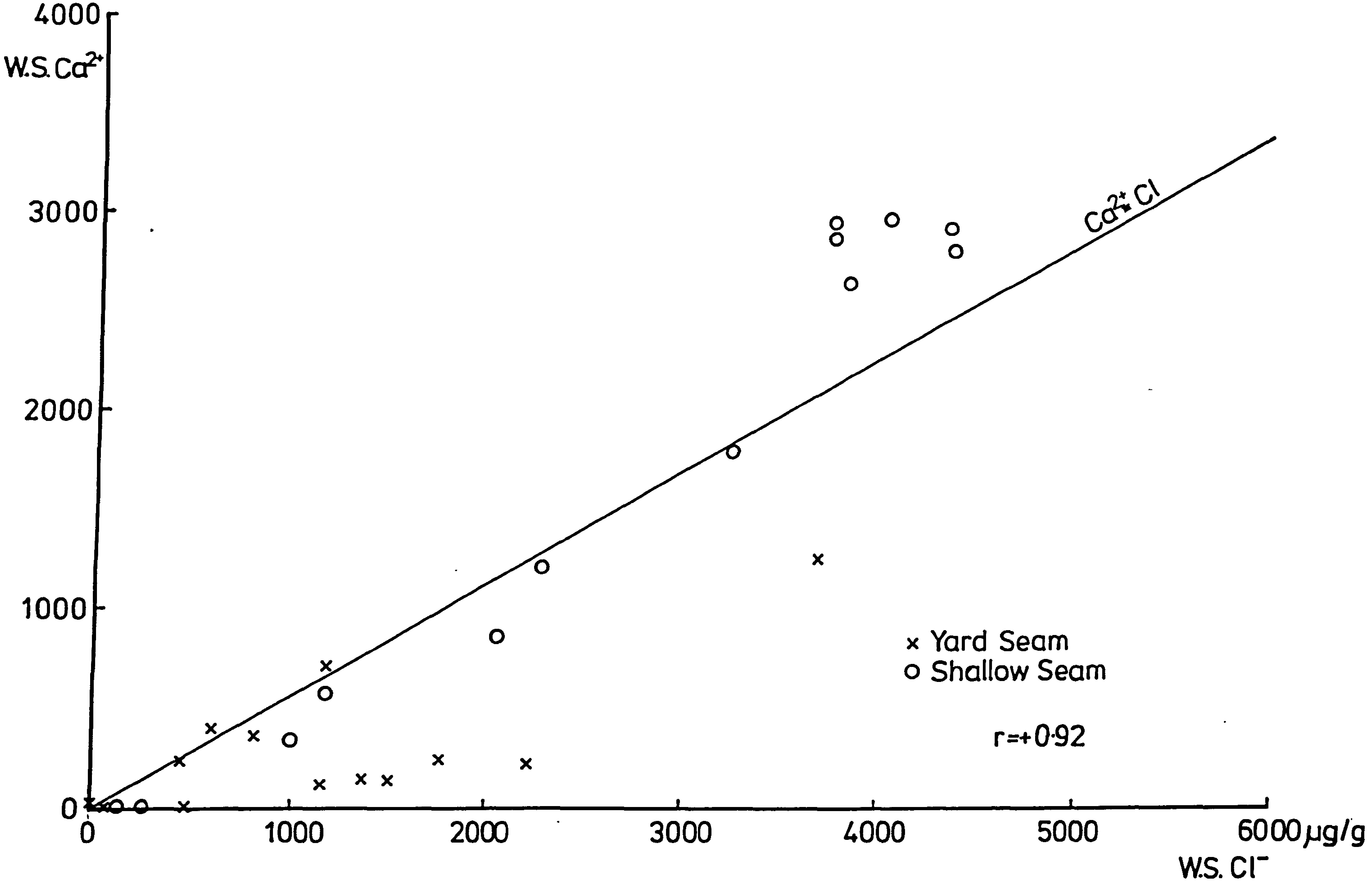


FIGURE 3.16 Water-soluble Ca^{2+} and Mg^{2+} (Ca^{2+} equivalent basis) versus non-Na^+ equivalent Cl^-, Littleton Colliery.

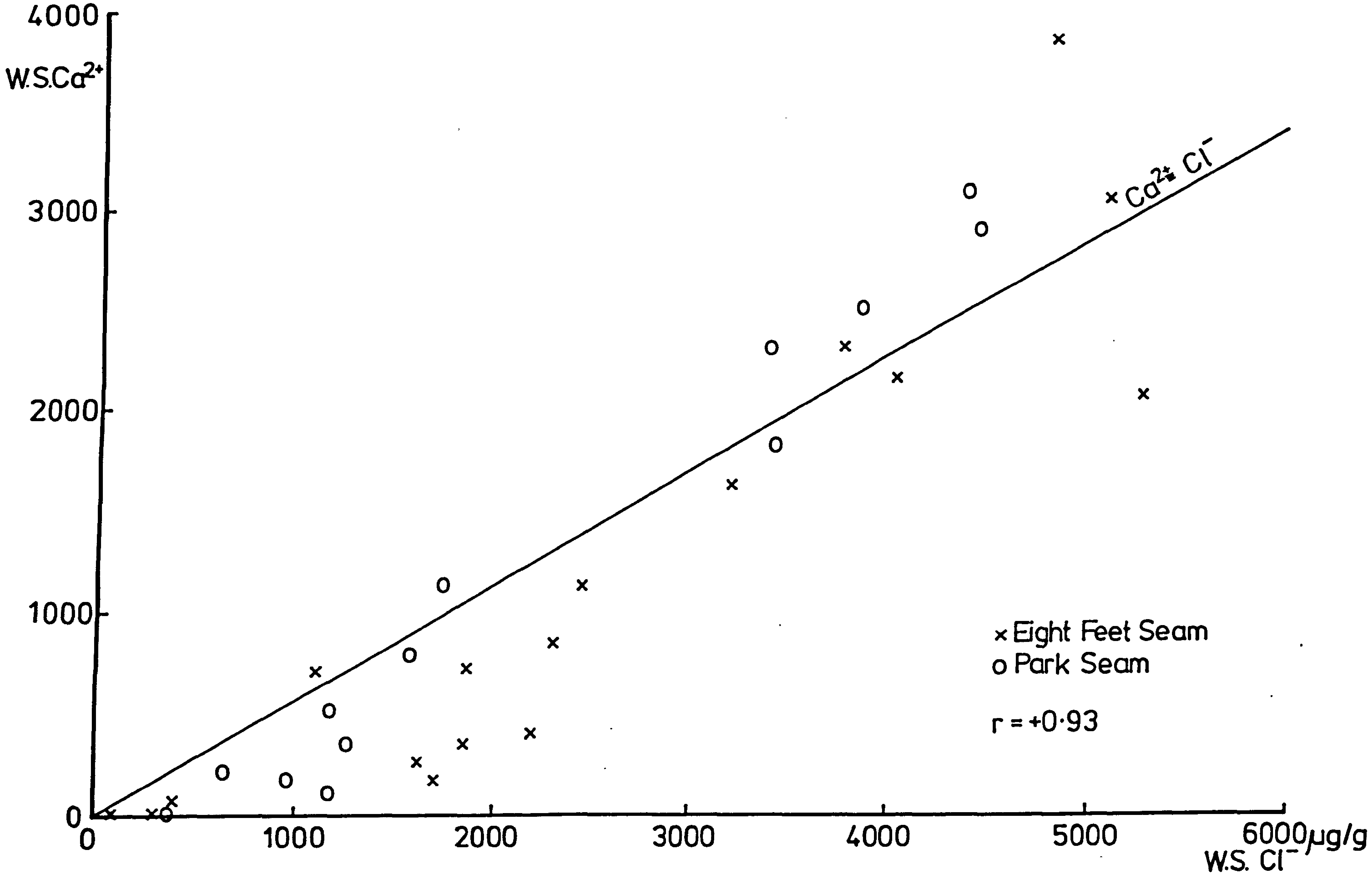
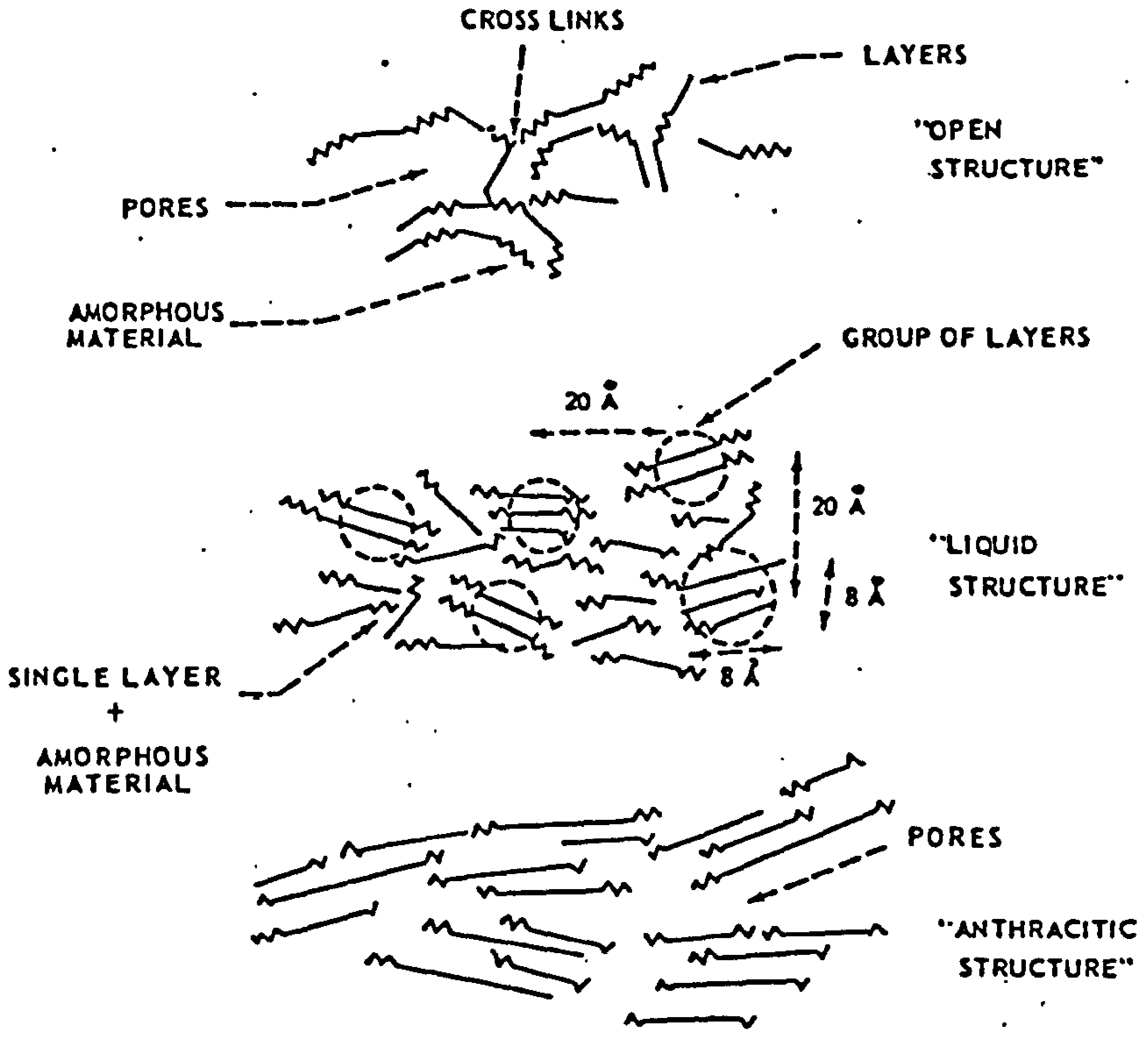
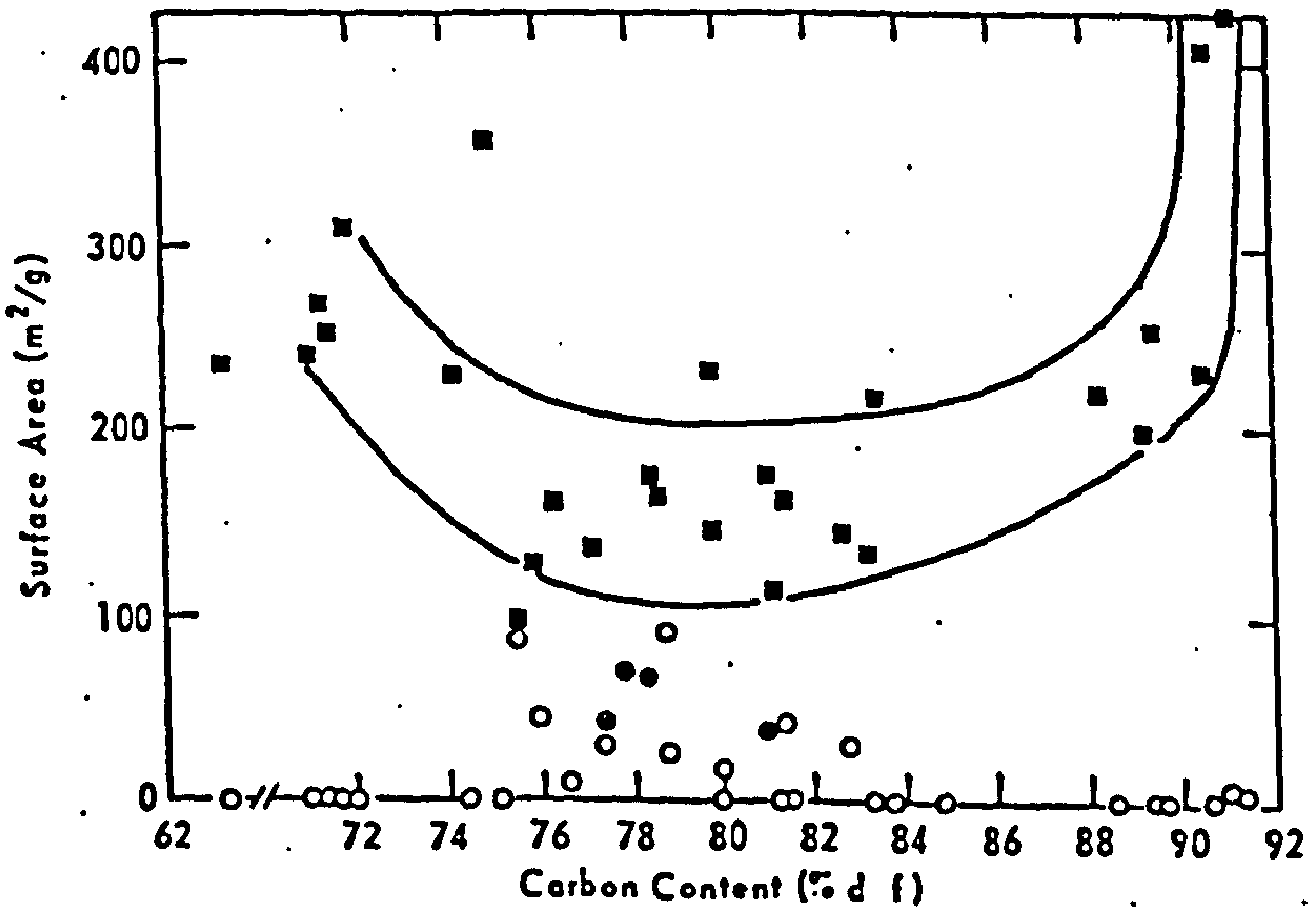


FIGURE 4.1 Schematic model of coal structure.



Schematic model of coal structure. (From Hirsch, 1954.)

FIGURE 4.2 Variation of N_2 and CO_2 surface areas of coals with carbon content (in Karr, 1978).



Variation of N_2 and CO_2 surface areas of coals with carbon content O, N_2; ■, CO_2; ●, N_2 (from Nandi and Walker, 1971).

FIGURE 4.3 Organic matter versus Chlorine.

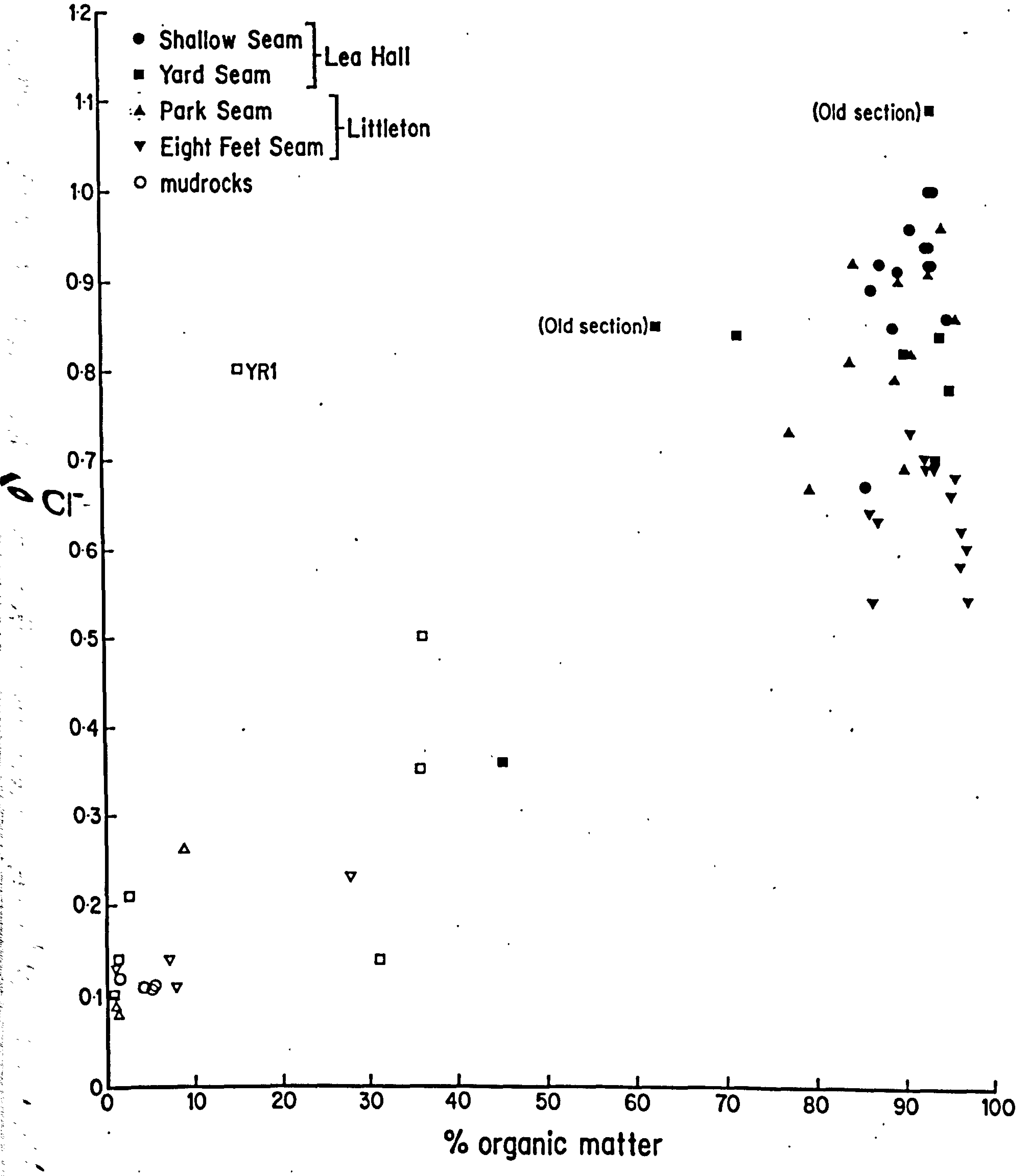


FIGURE 4.4 Total Cl$^-$% versus Moisture % (reduced major axis regression for coals only).

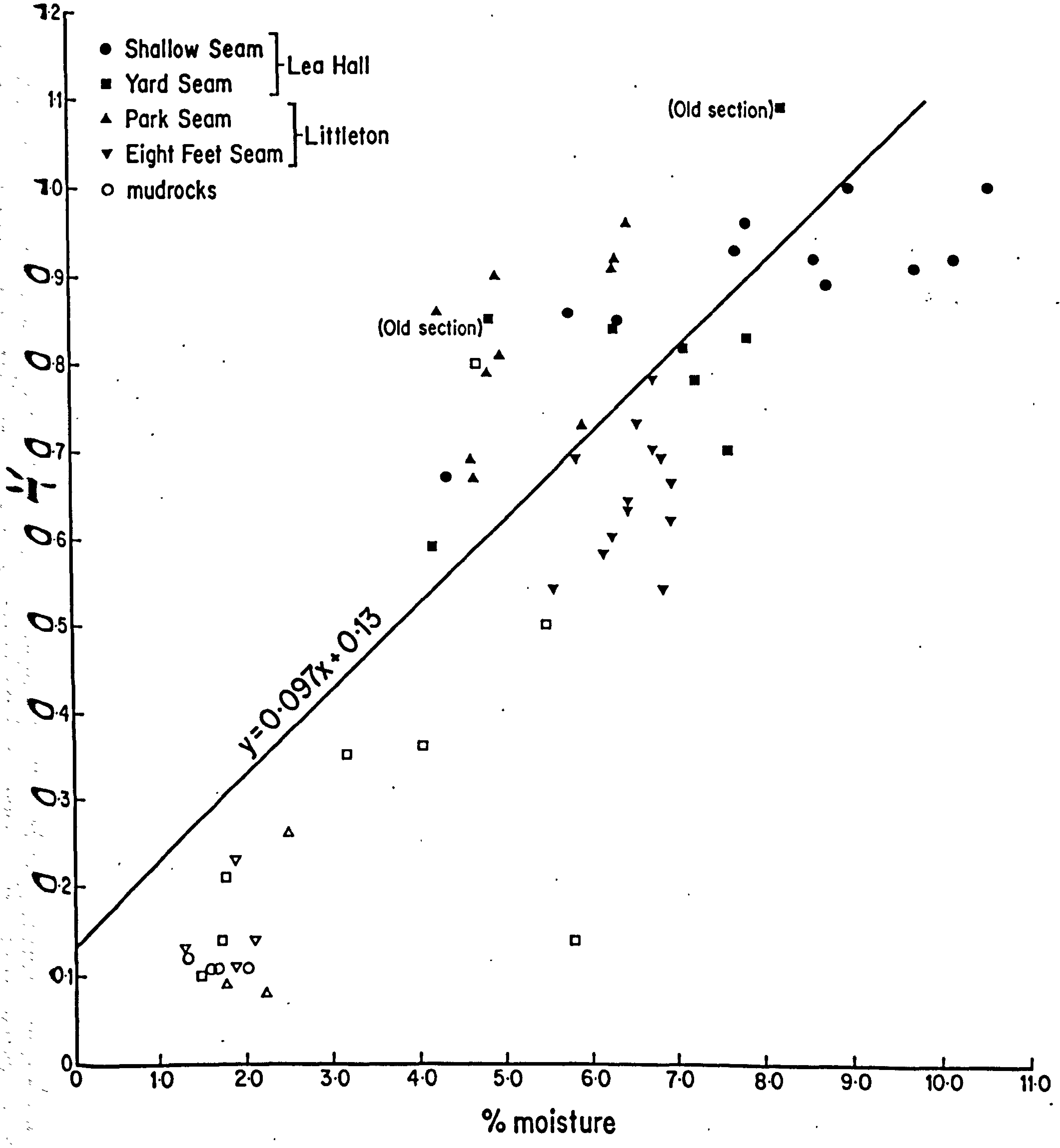
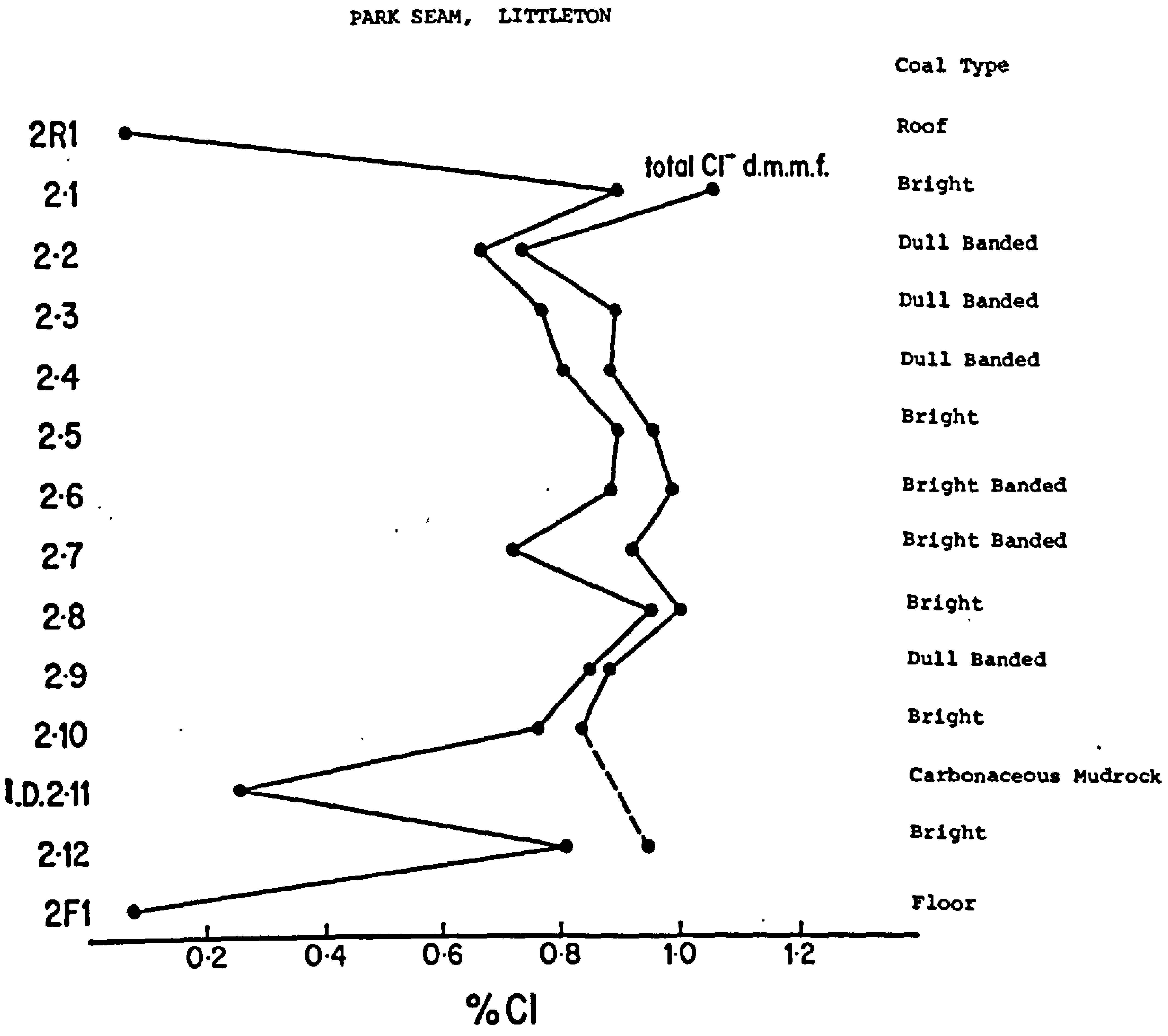


FIGURE 4.5 Total Cl^- percentage in the Park Seam section on a dry and dry mineral matter free basis.



d.m.m.f. = dry mineral matter free basis

FIGURE 4.6 Total Cl^- percentage in the Shallow Seam section on a dry mineral matter free basis.

FIGURE 4.7 Lea Hall and Littleton Colliery 'Organic Chlorine' profiles.

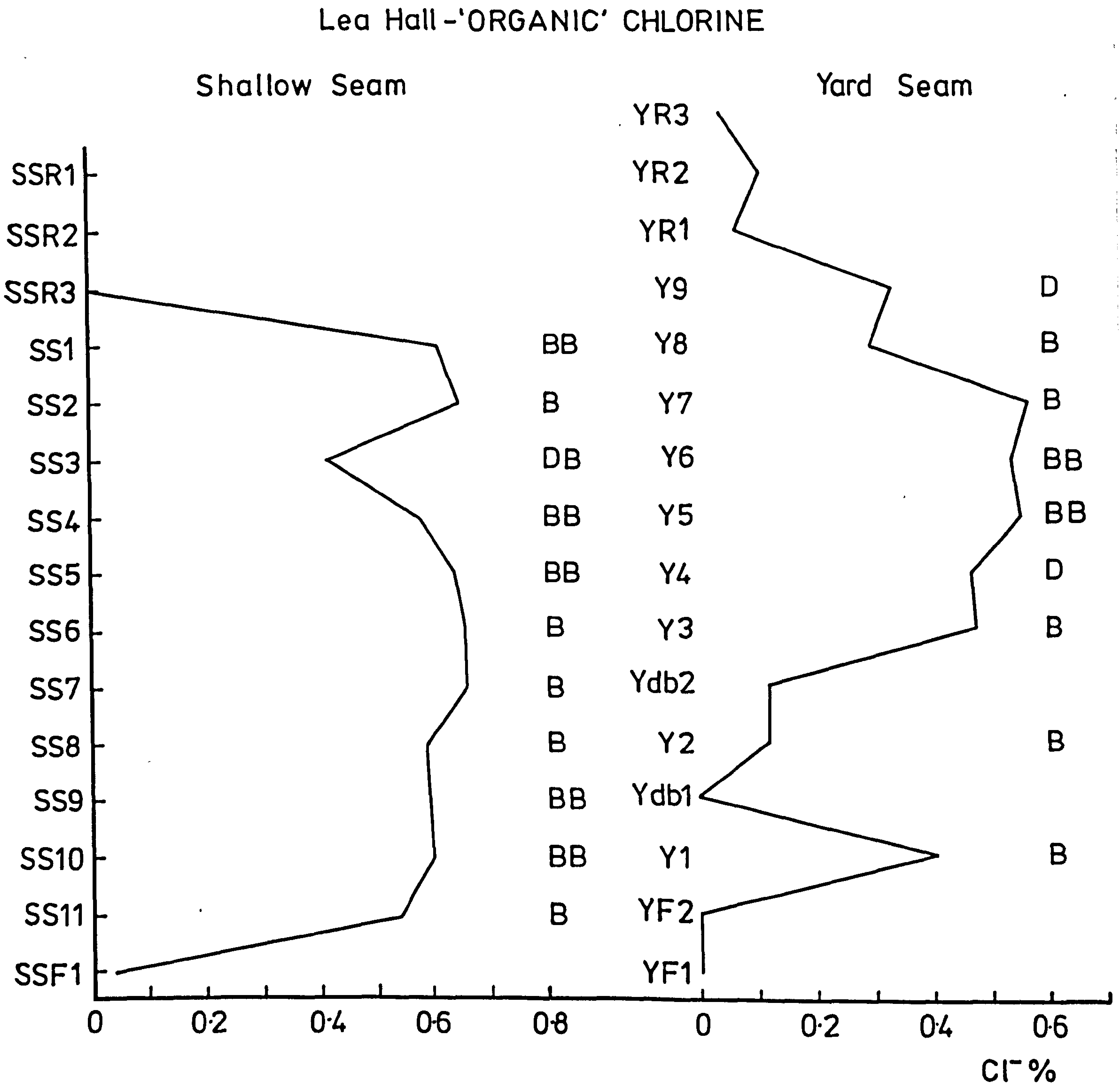


FIGURE 4.7 Lea Hall and Littleton Colliery 'Organic Chlorine' profiles.

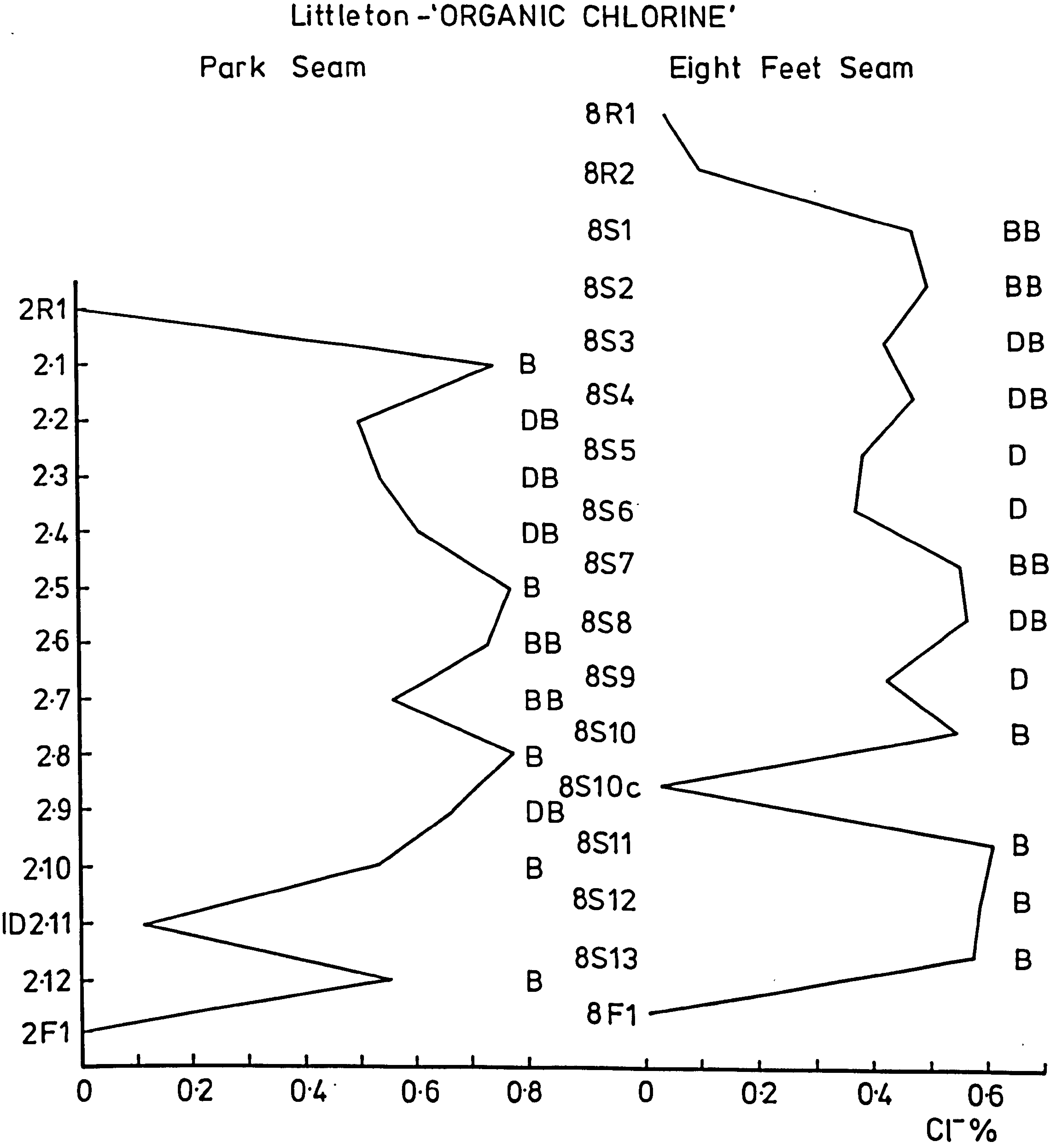


FIGURE 5.1 Lea Hall Shallow Seam L.T.A. Profile (moisture free).

FIGURE 5.2 Lea Hall Yard Seam L.T.A. Profile (moisture free).

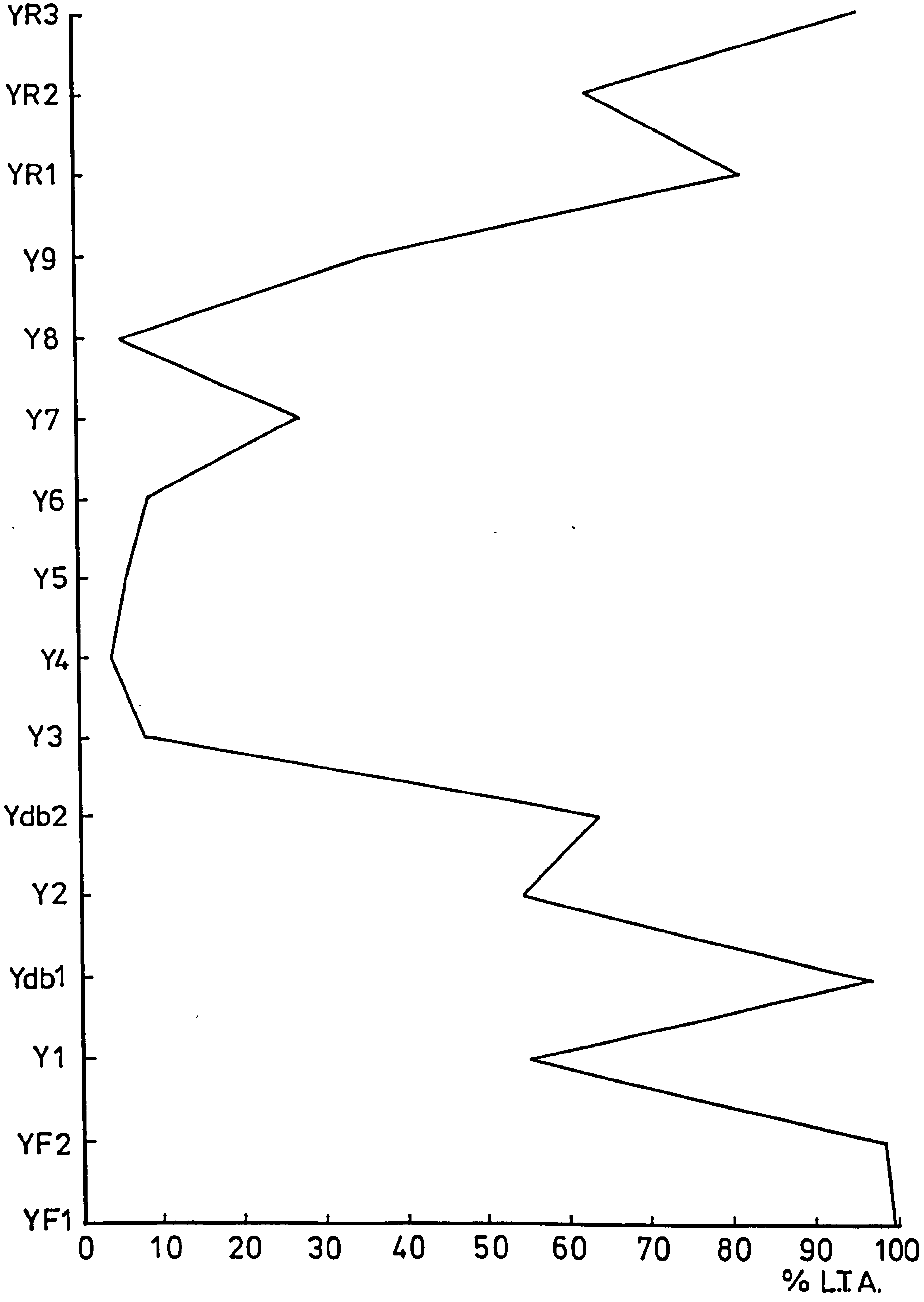


FIGURE 5.3 Littleton Park Seam L.T.A. Profile (moisture free).

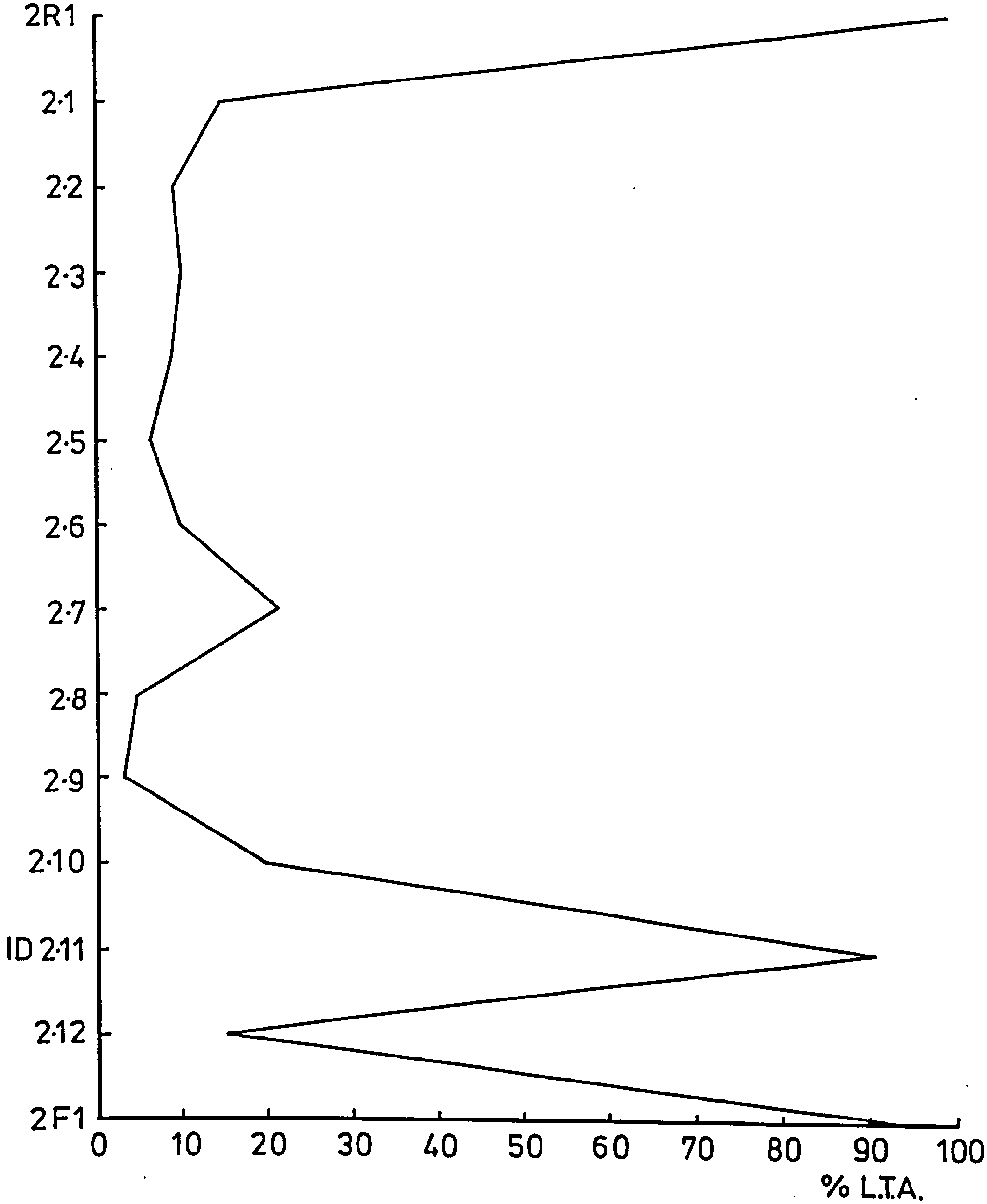


FIGURE 5.4 Littleton Eight Feet Seam L.T.A. Profile (moisture free).

FIGURE 6.1 Quartz, TiO_2, Zr (whole rock) and Quartz/TiO_2 variations through the mudrock profiles.

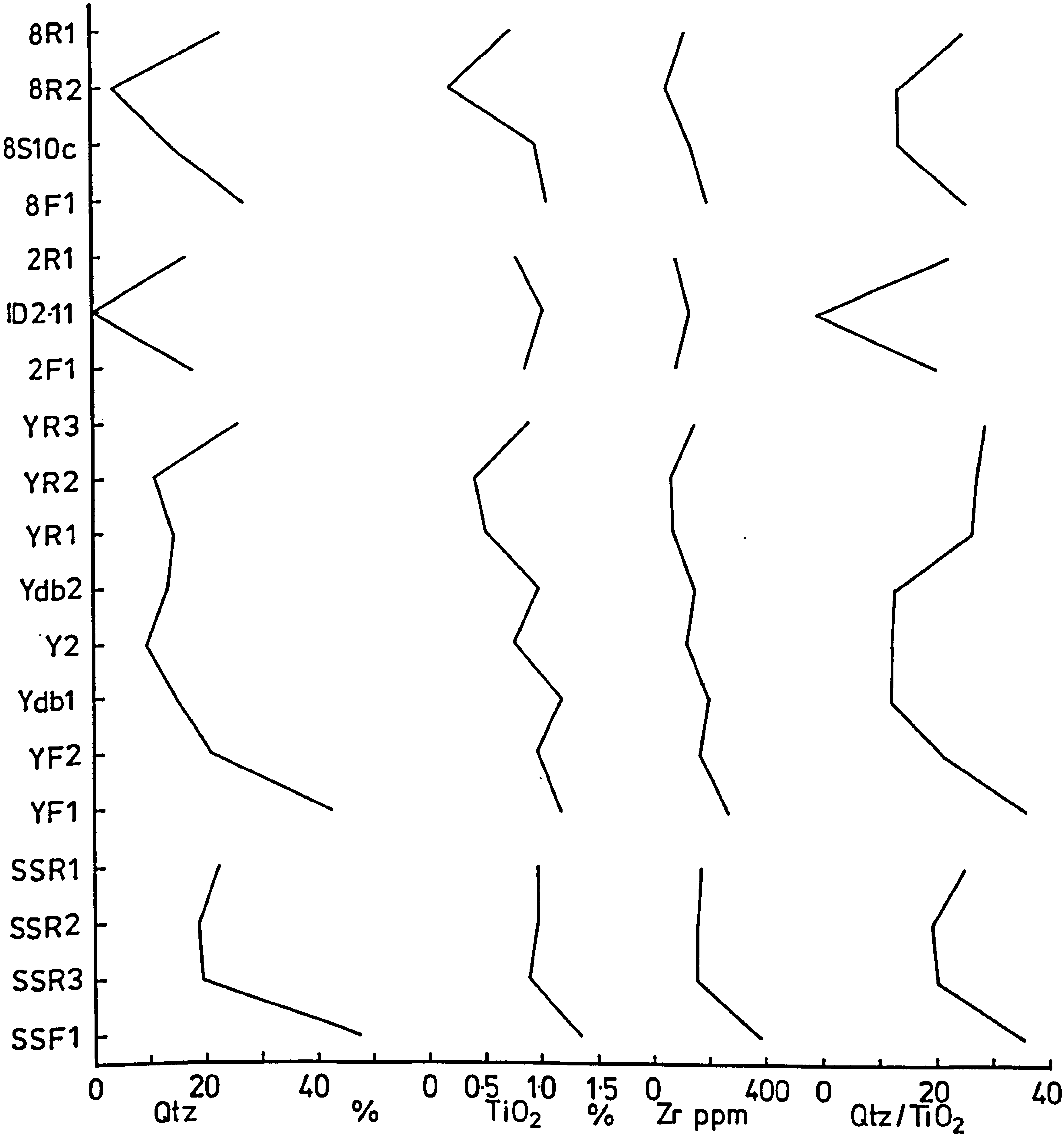


FIGURE 6.2 Al_2O_3/Combined Silica and K_2O/Al_2O_3 ratio variations through the mudrock profiles.

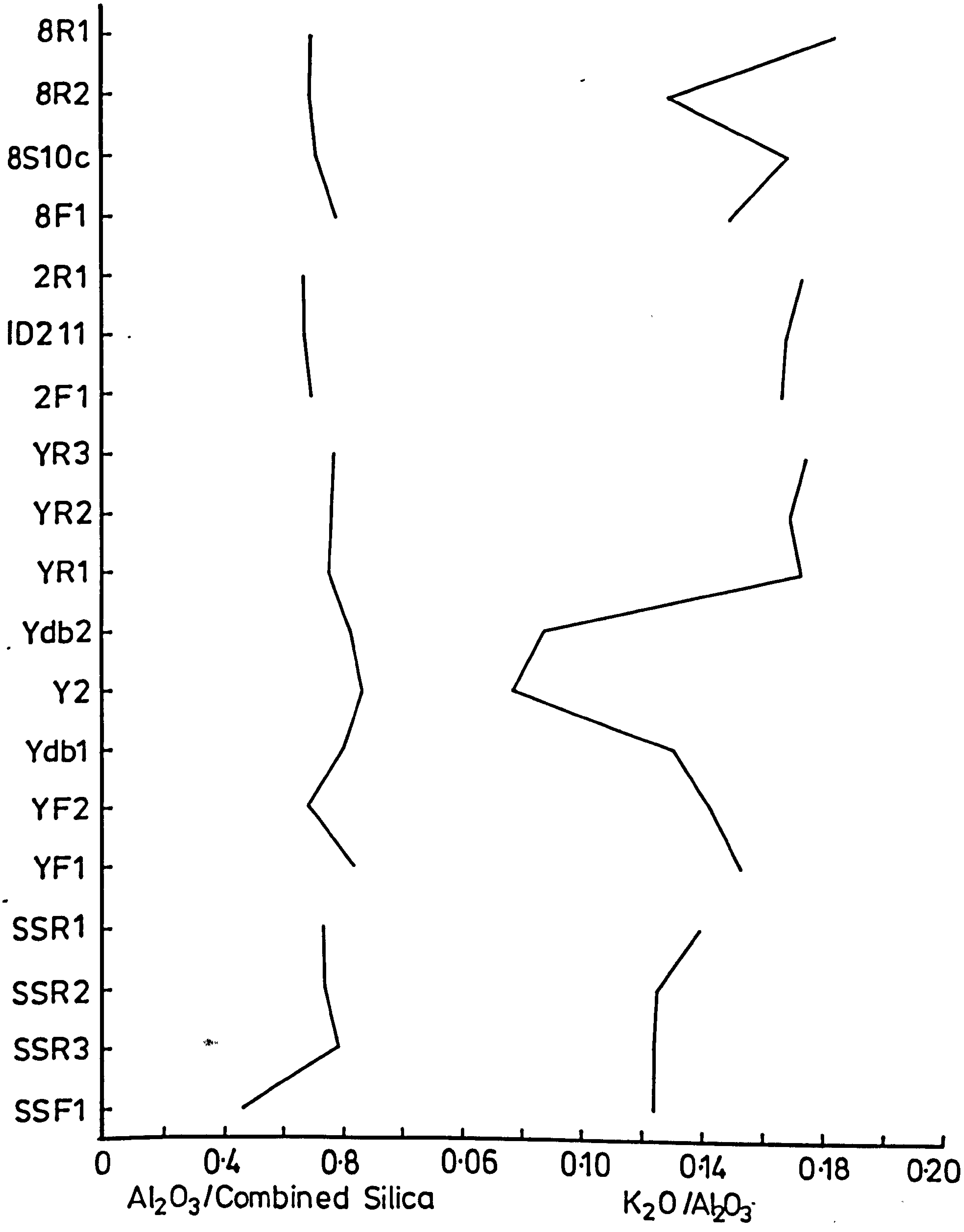
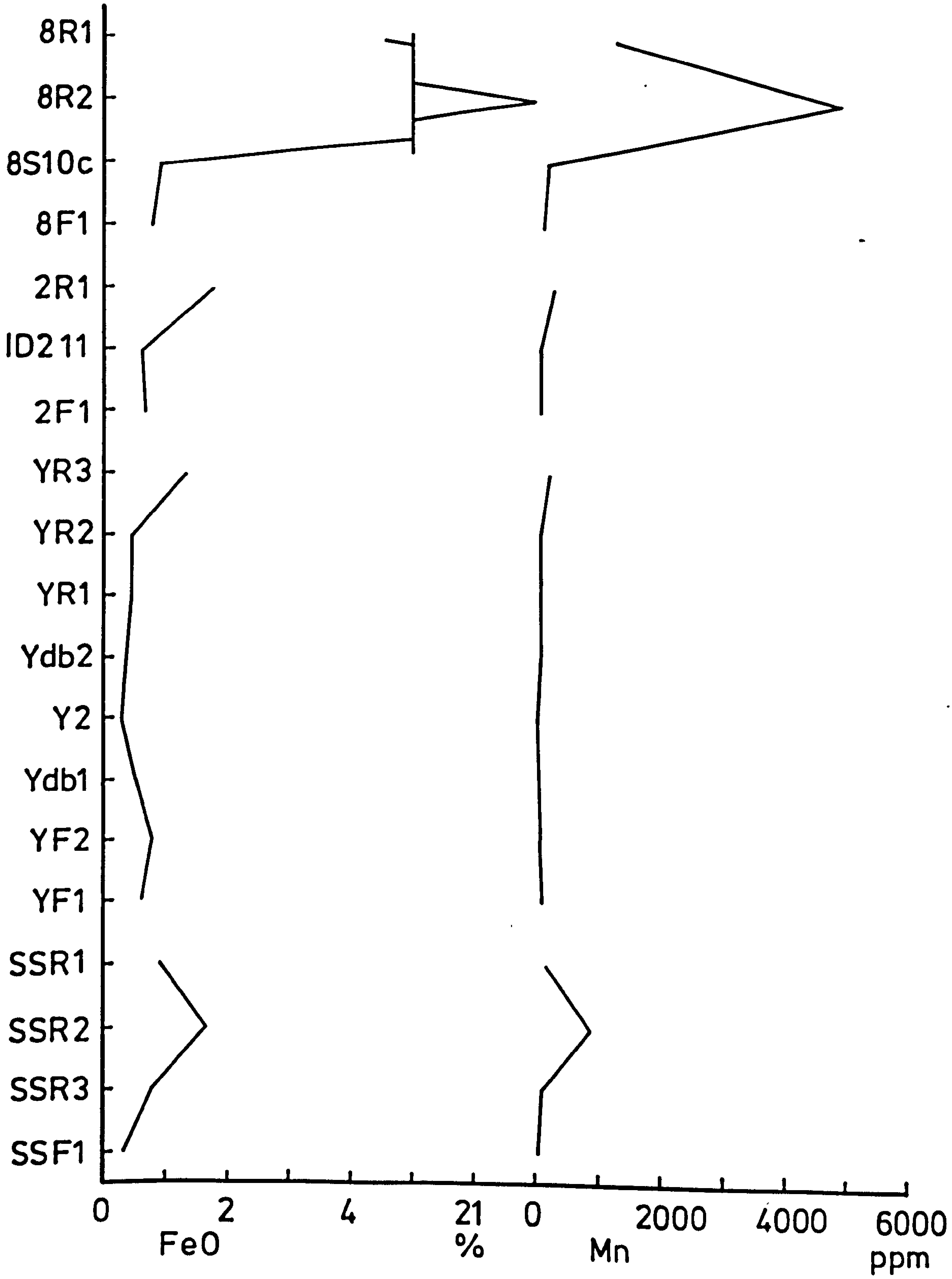


FIGURE 6.3 FeO and Mn (whole rock) variations through the mudrock profiles.



6.4 Normative siderite, MnO (whole rock) and Mn/FeO ratio through the mudrock profiles.

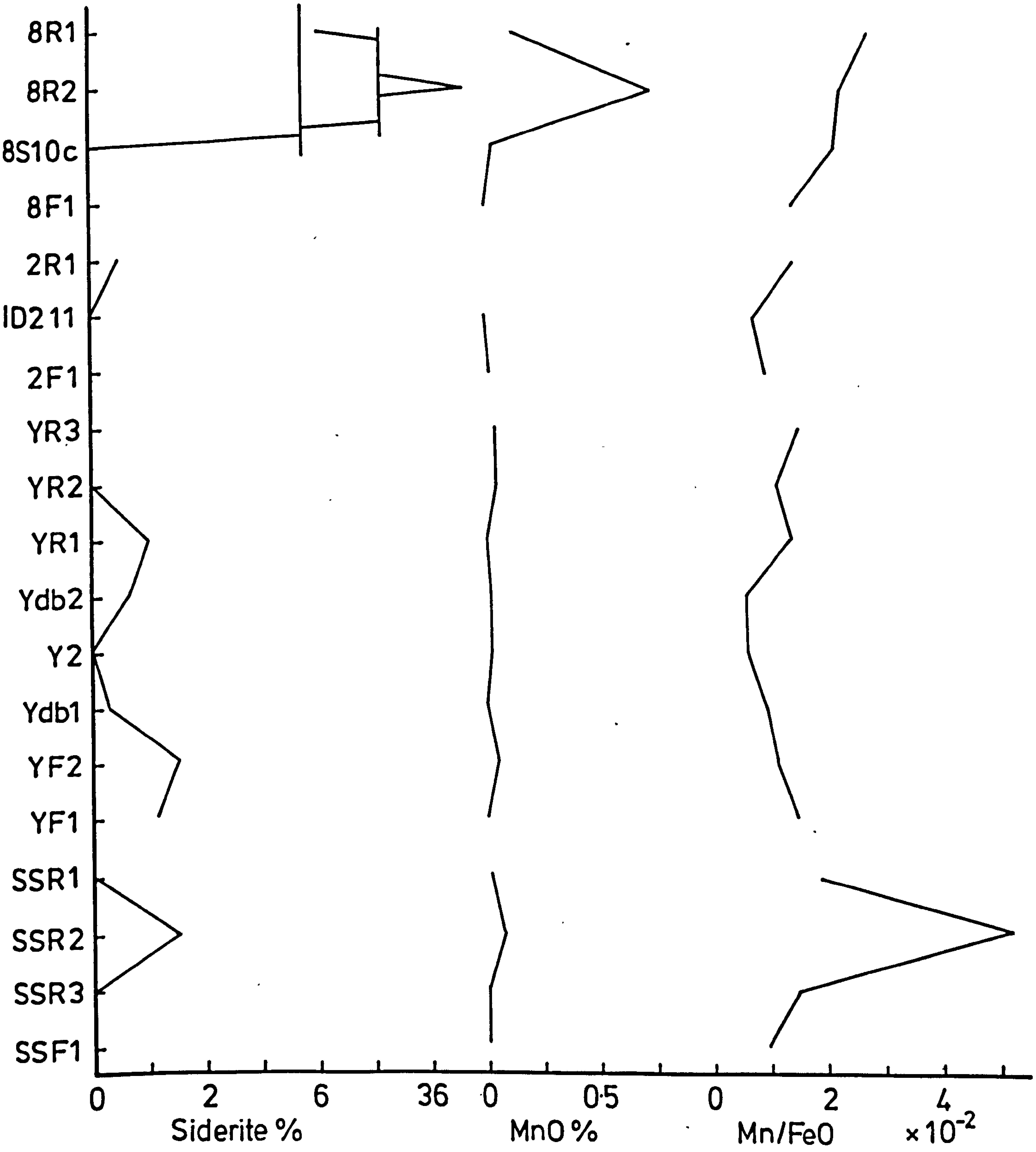


FIGURE 6.5 Fe_2O_3, S and normative pyrite (whole rock) through the mudrock profiles.

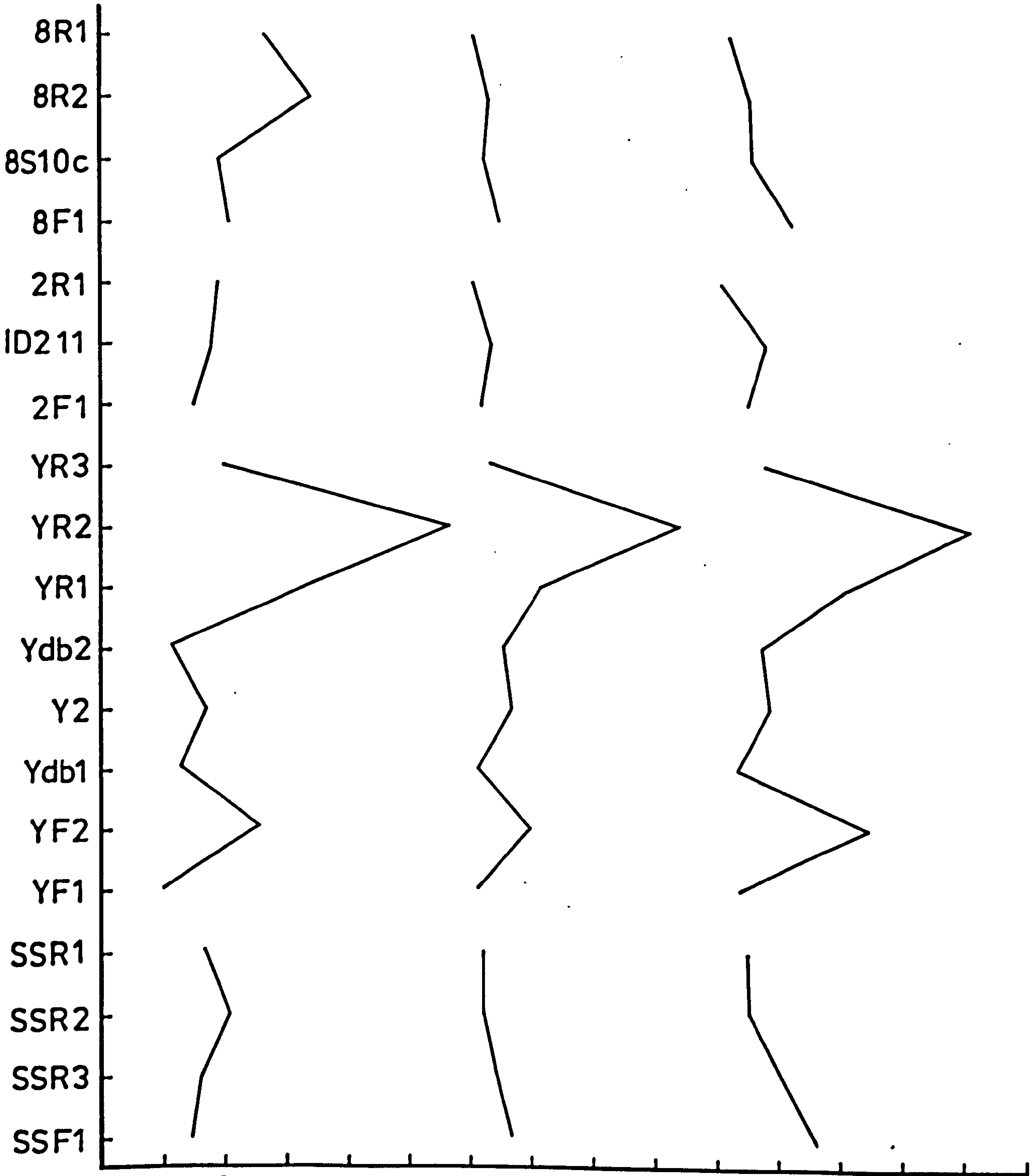


FIGURE 6.6 CaO, MgO and CO_2 (whole rock) through the mudrock profiles.

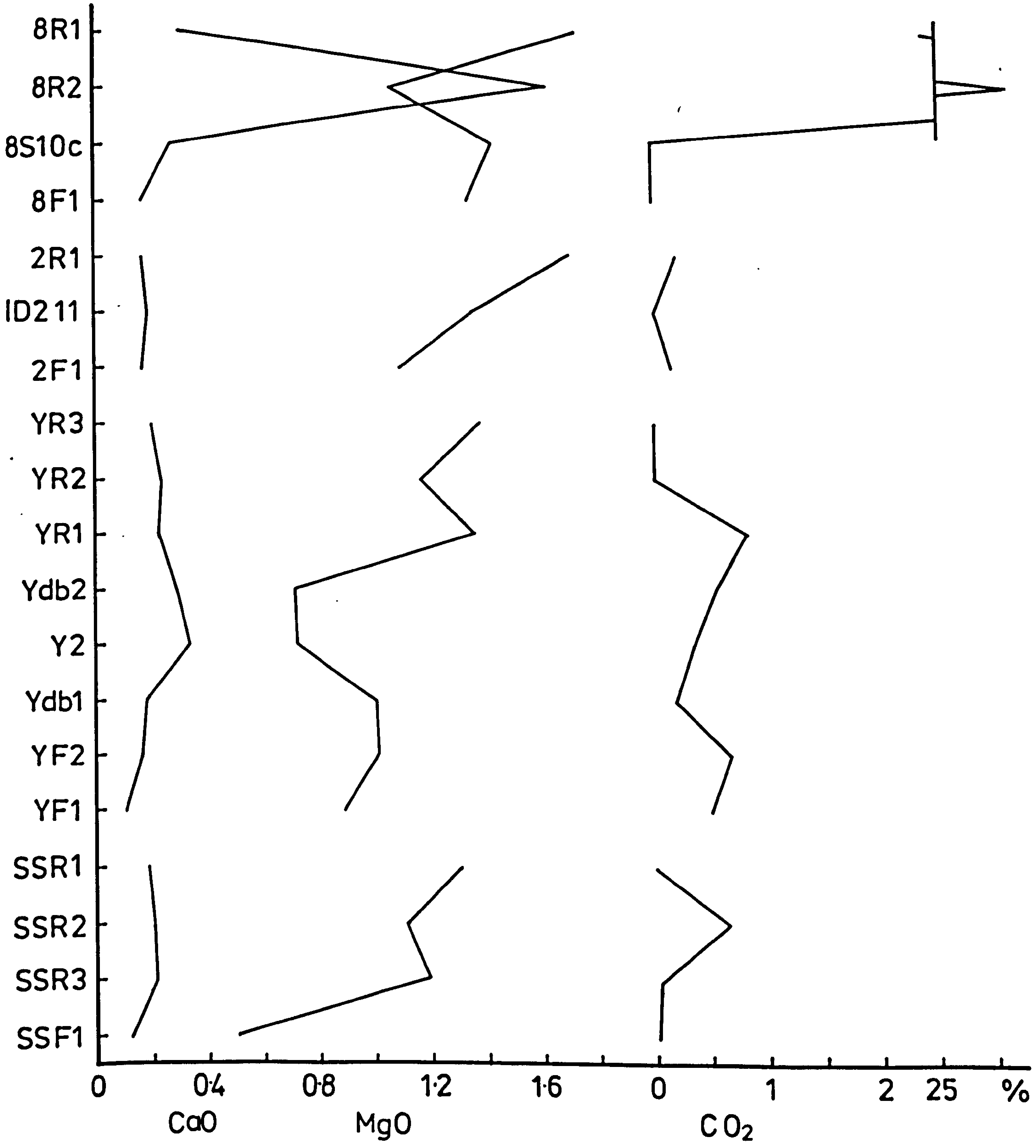


FIGURE 6.7 MgO/Al_2O_3 ratio, and normative dolomite and calcite (whole rock) through the mudrock profiles..

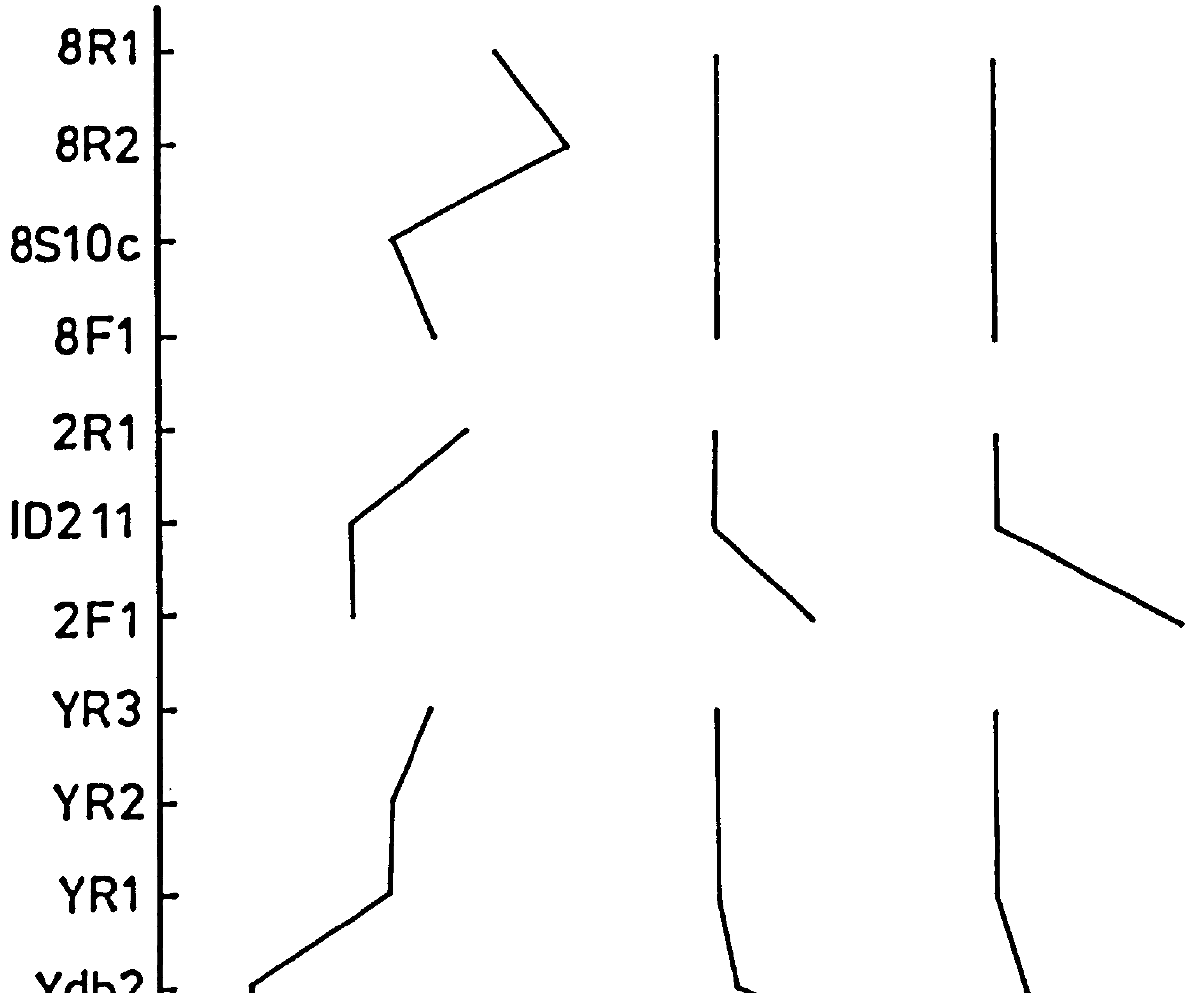


FIGURE 6.8 Carbonate CaO versus CO_2 showing different trends between Lea Hall and Littleton Colliery samples.

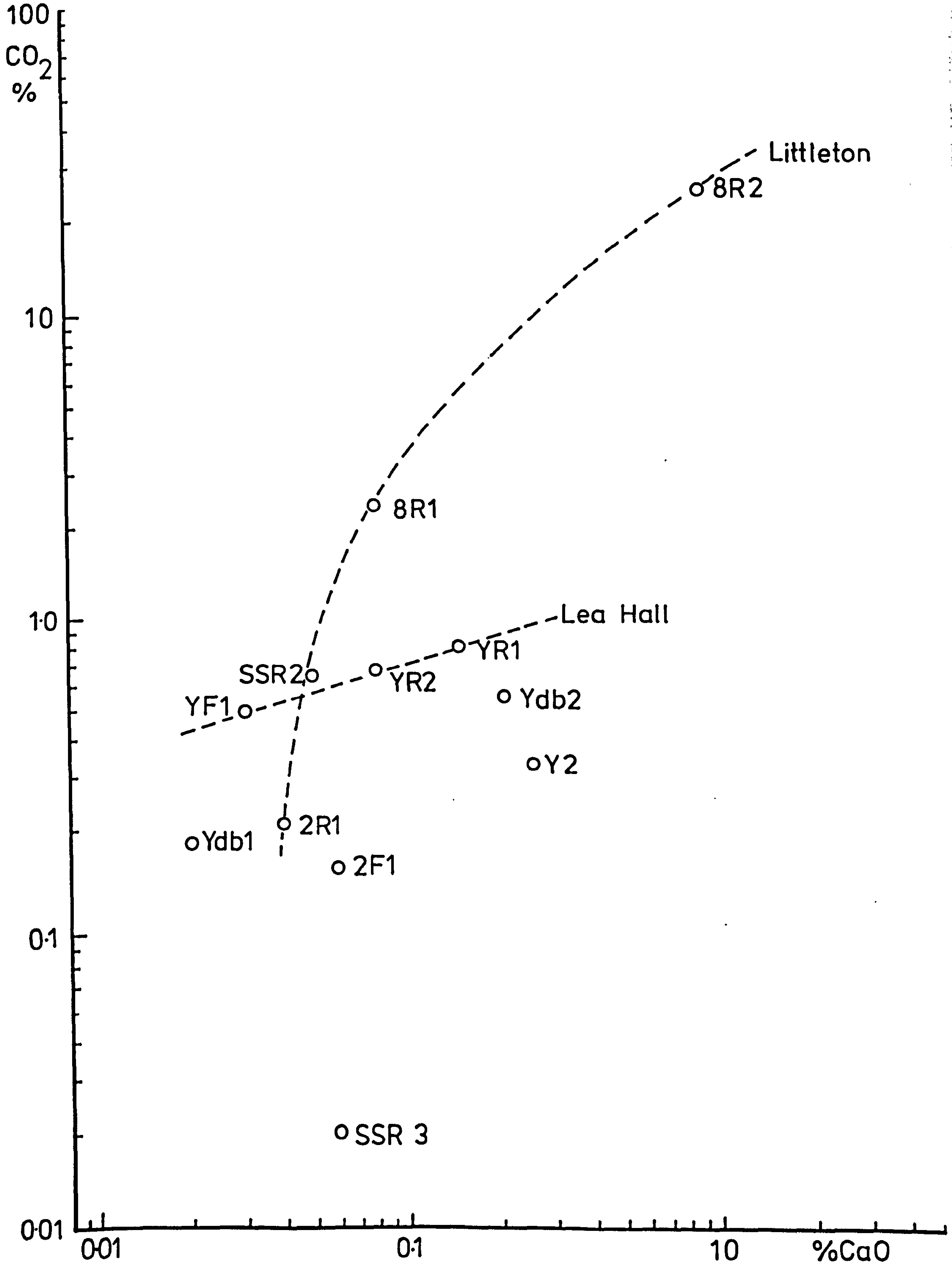


FIGURE 6.9 Na_2O and K_2O (whole rock) and Na_2O/K_2O and Na_2O/Al_2O_3 ratios through the mudrock profiles.

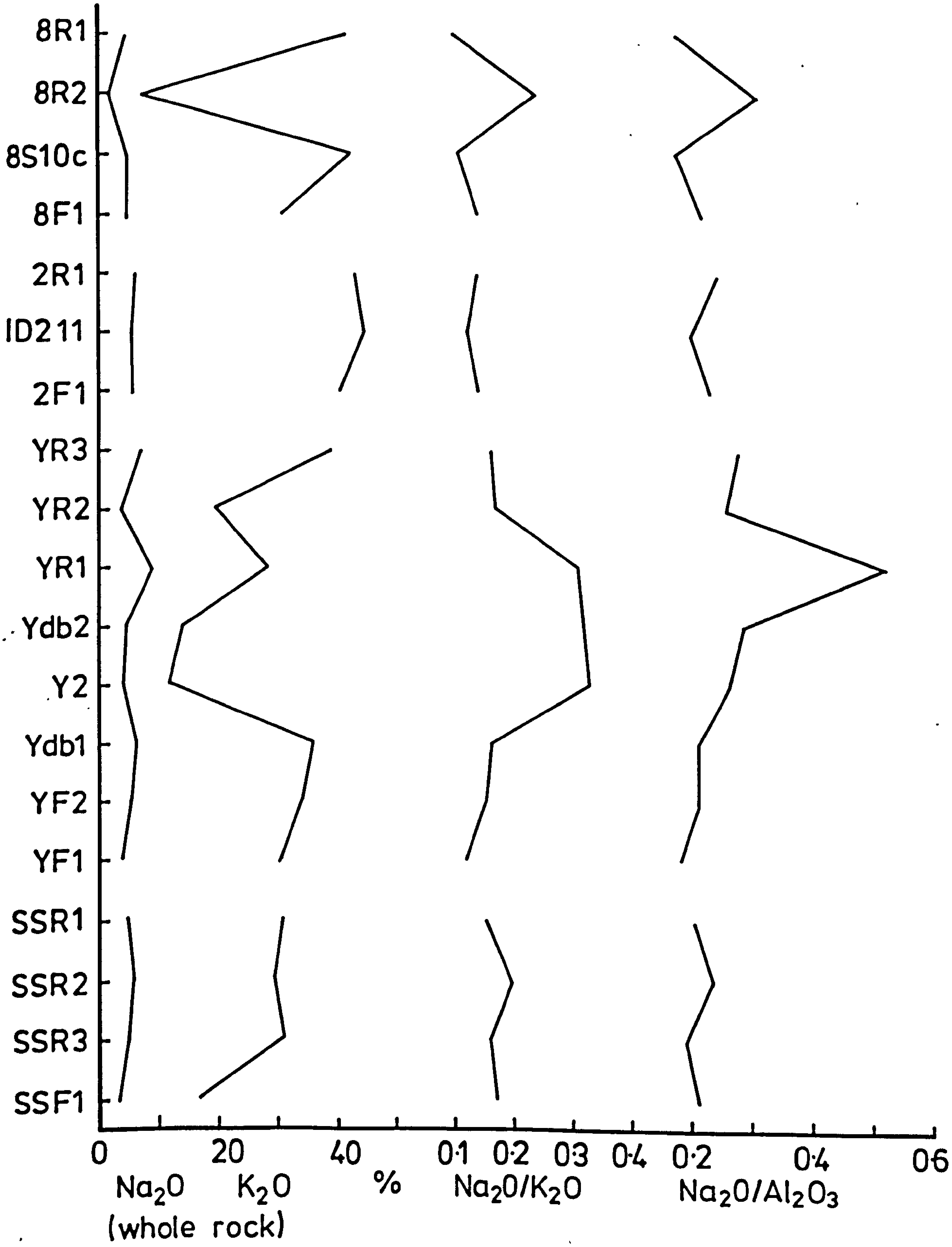


FIGURE 6.10 P_2O_5 (whole rock) and P_2O_5/CaO ratios through the mudrock profiles.

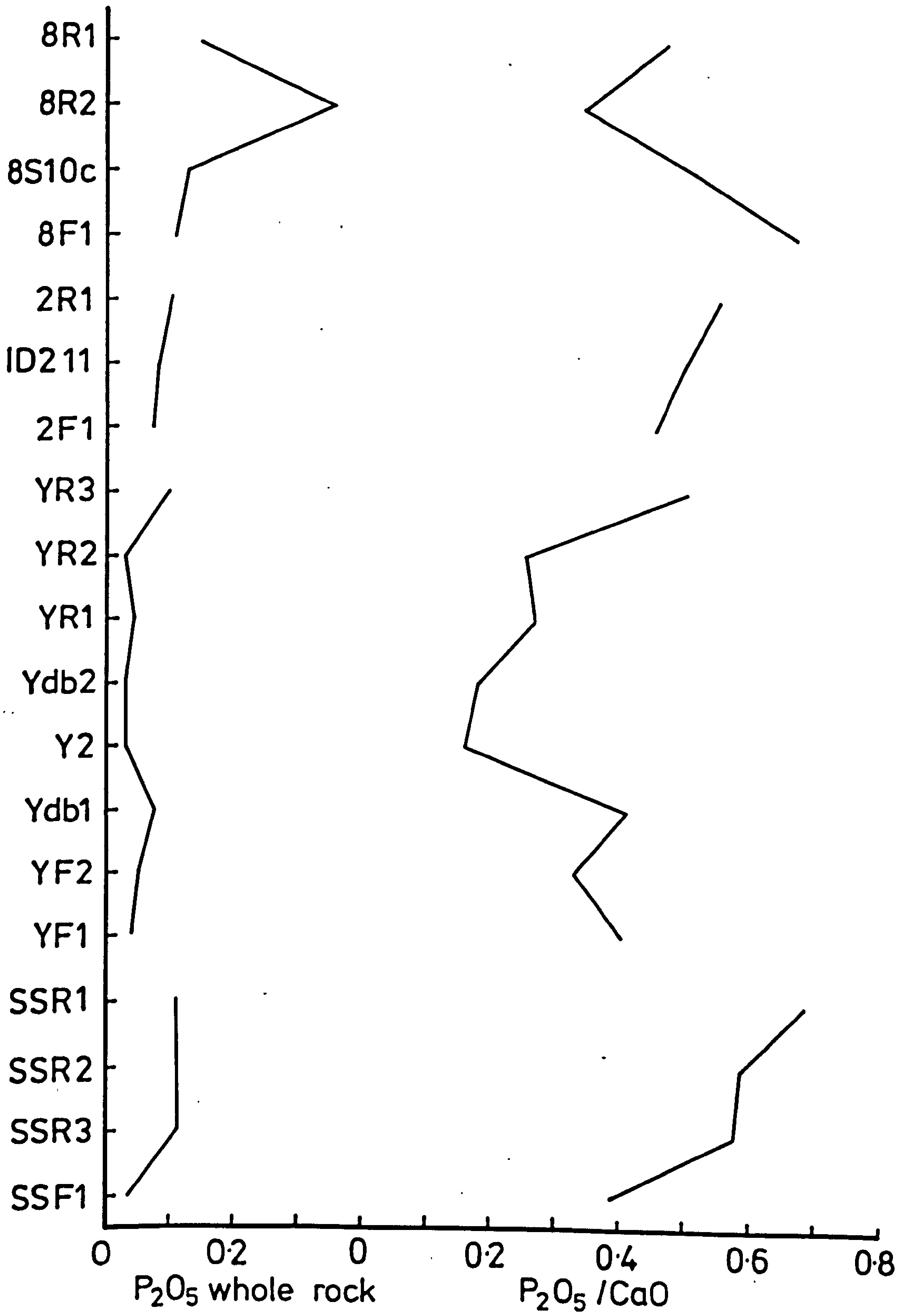


FIGURE 6.11 Rationalised XRD diffraction trace of glycolated and air dried clay minerals (SSR2).

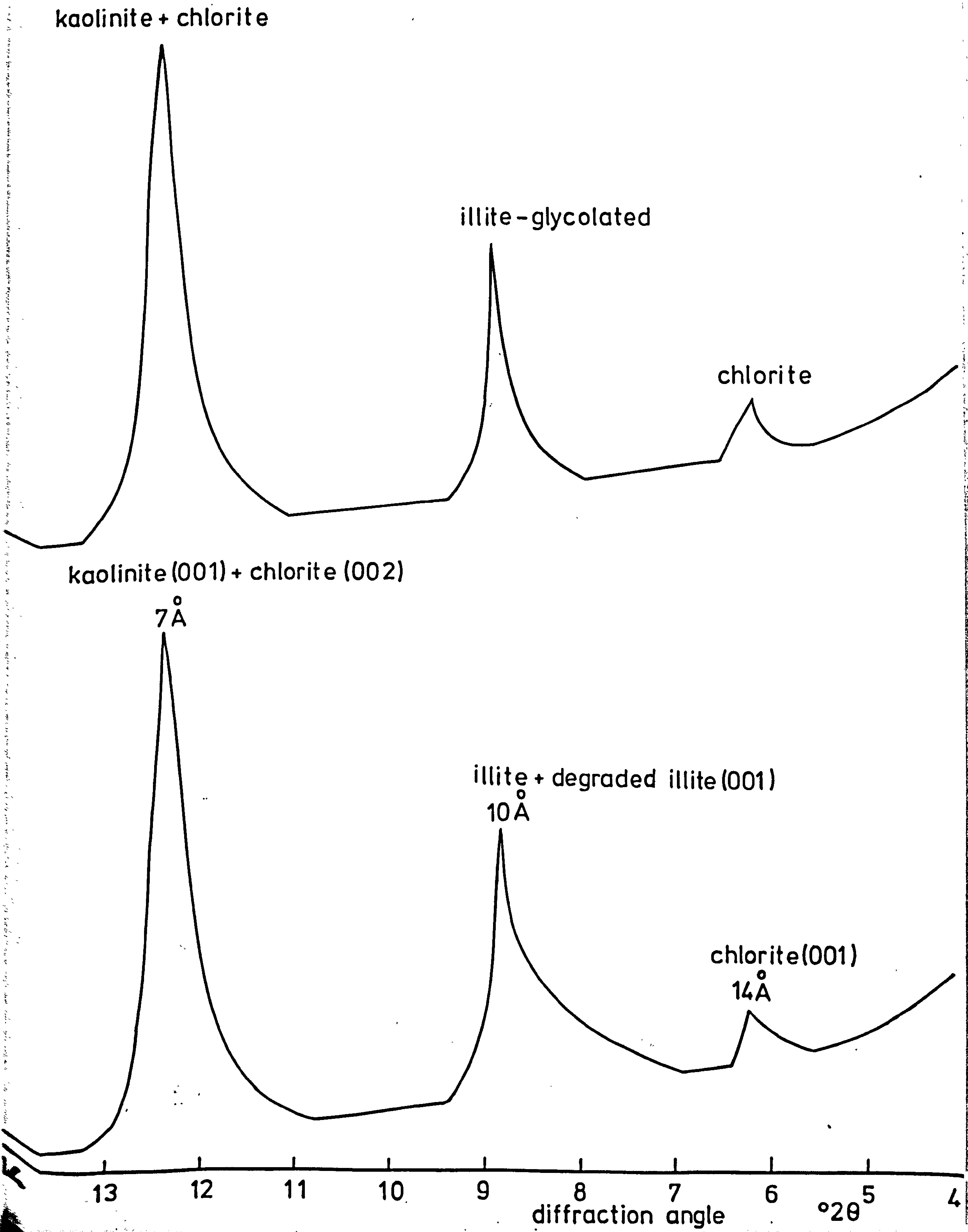


FIGURE 6.12 Relative Clay percentages.

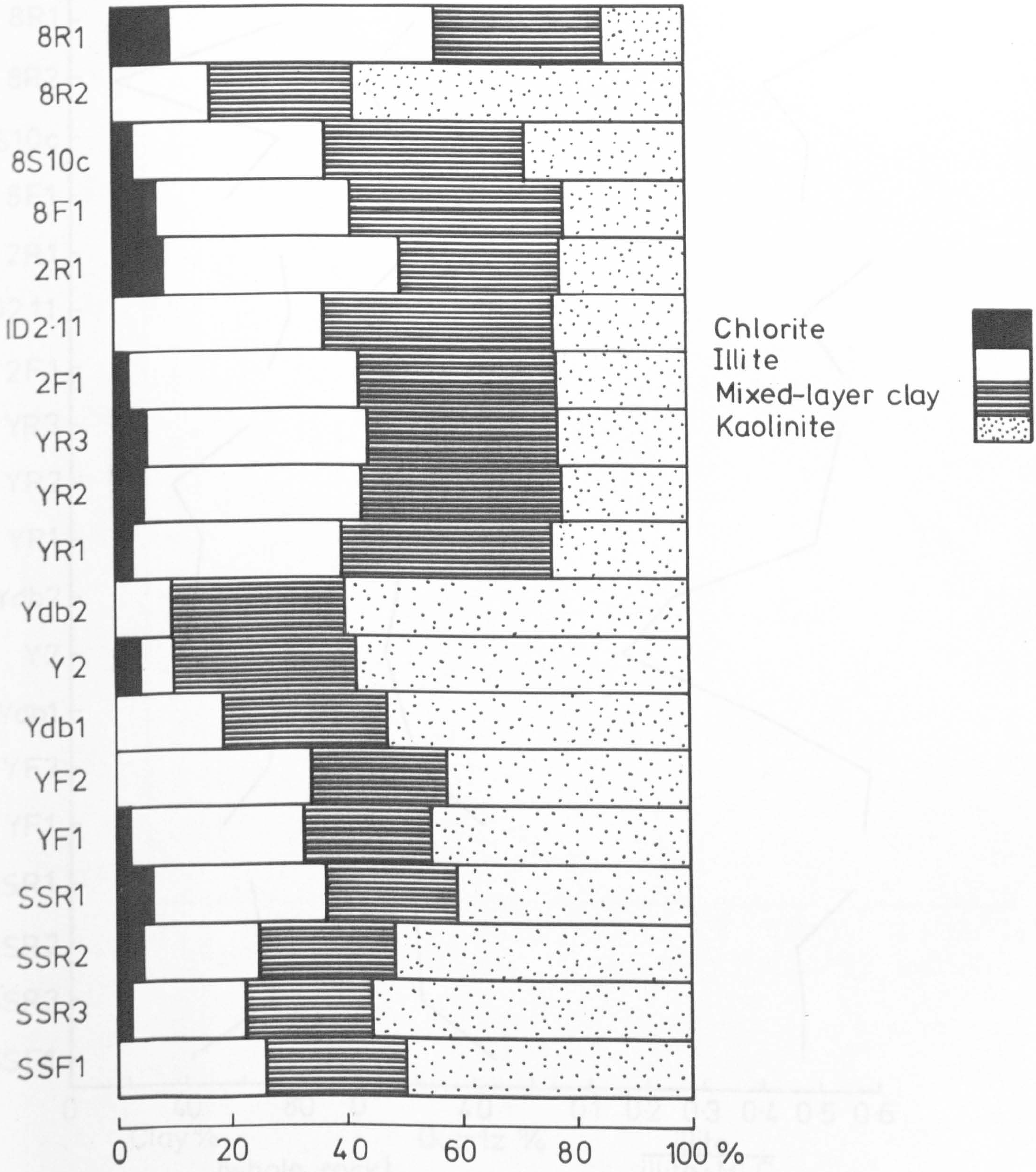


FIGURE 6.13 Clay and quartz percentages (whole rock) and the illite/illite+ mixed-layer clay ratio through the mudrock profiles.

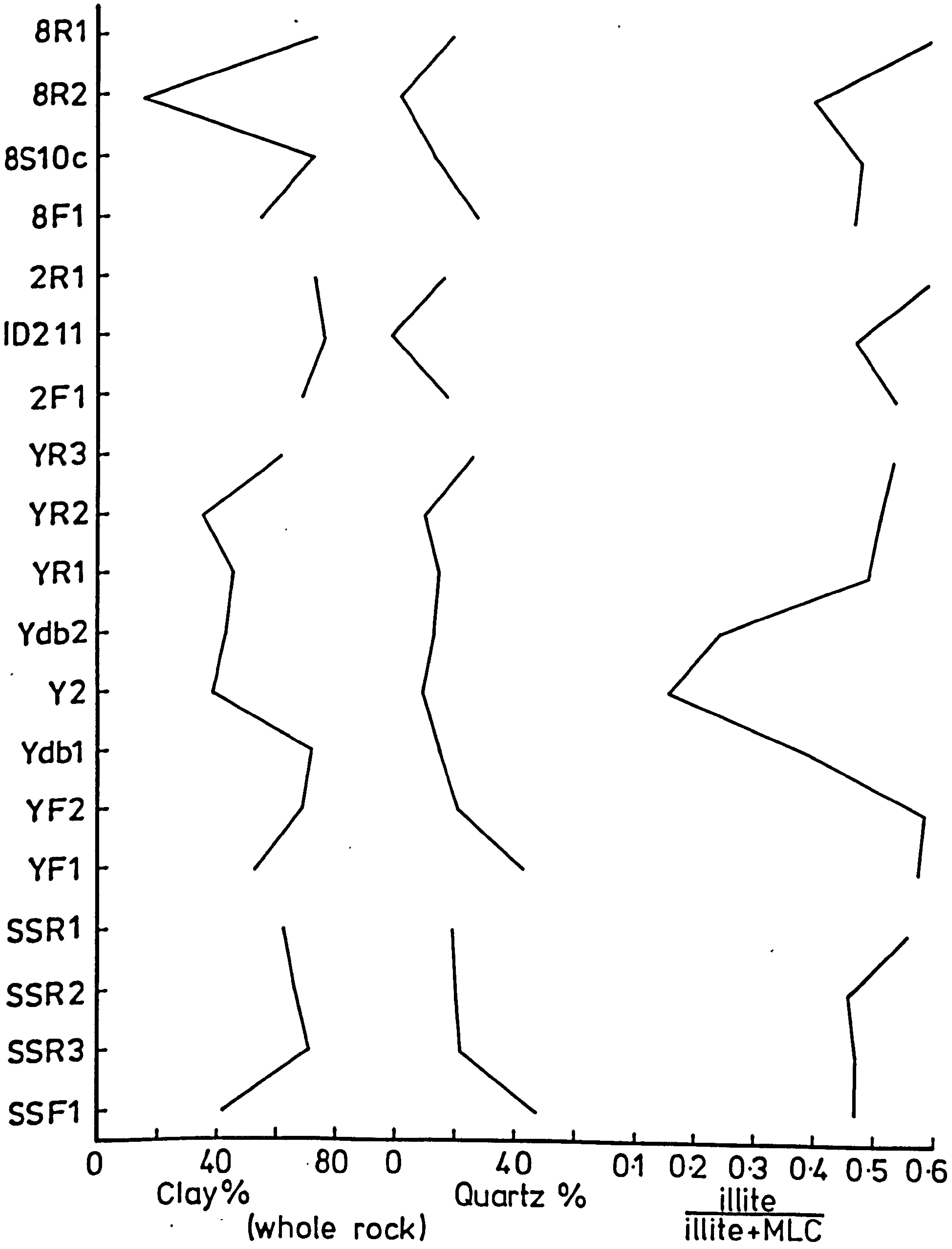


FIGURE 6.14 Illite Crystallinity (selected samples).

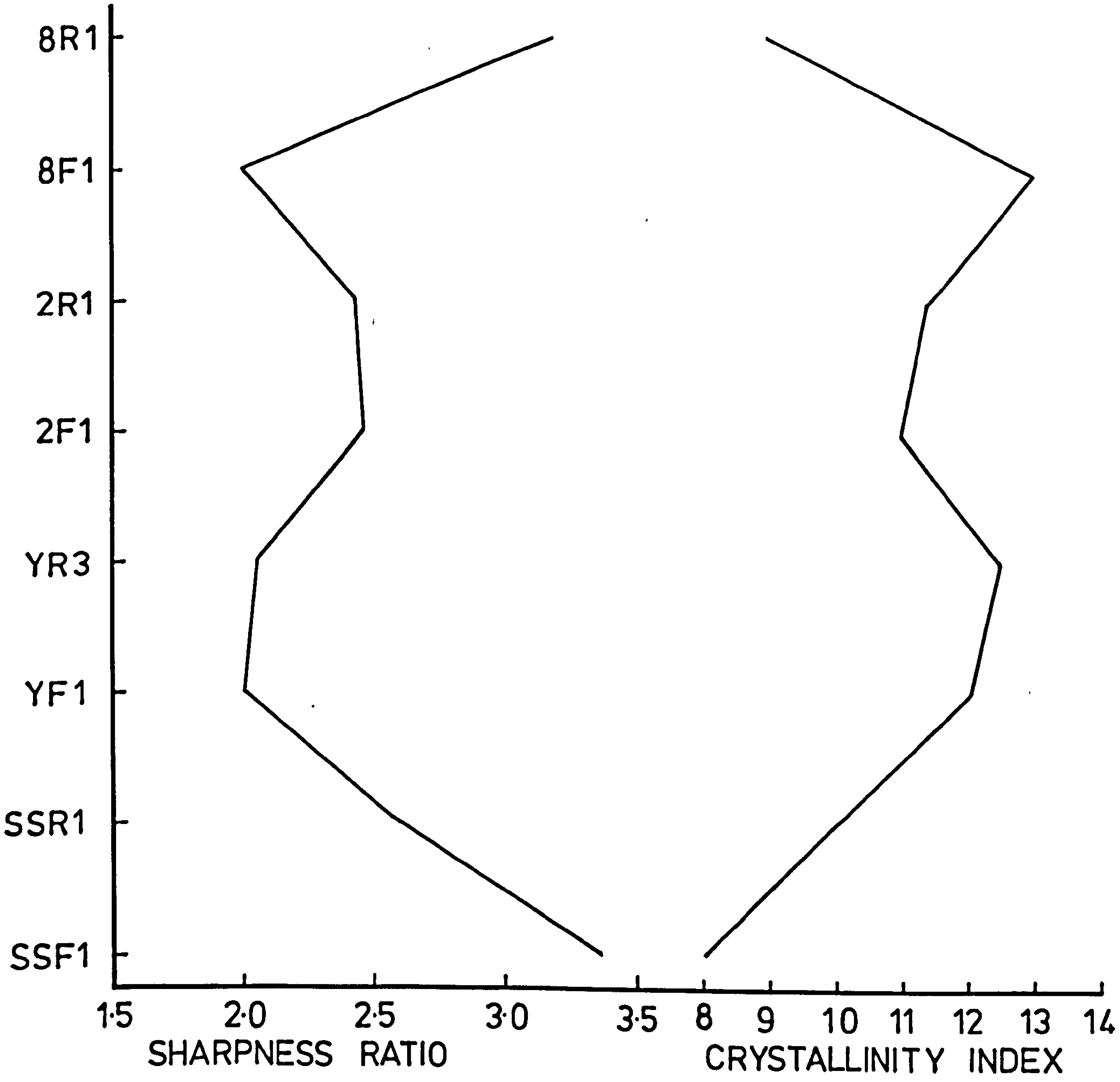


FIGURE 6.15 The relative intensity of the 002/001 illite peak ratios through the mudrock profiles.

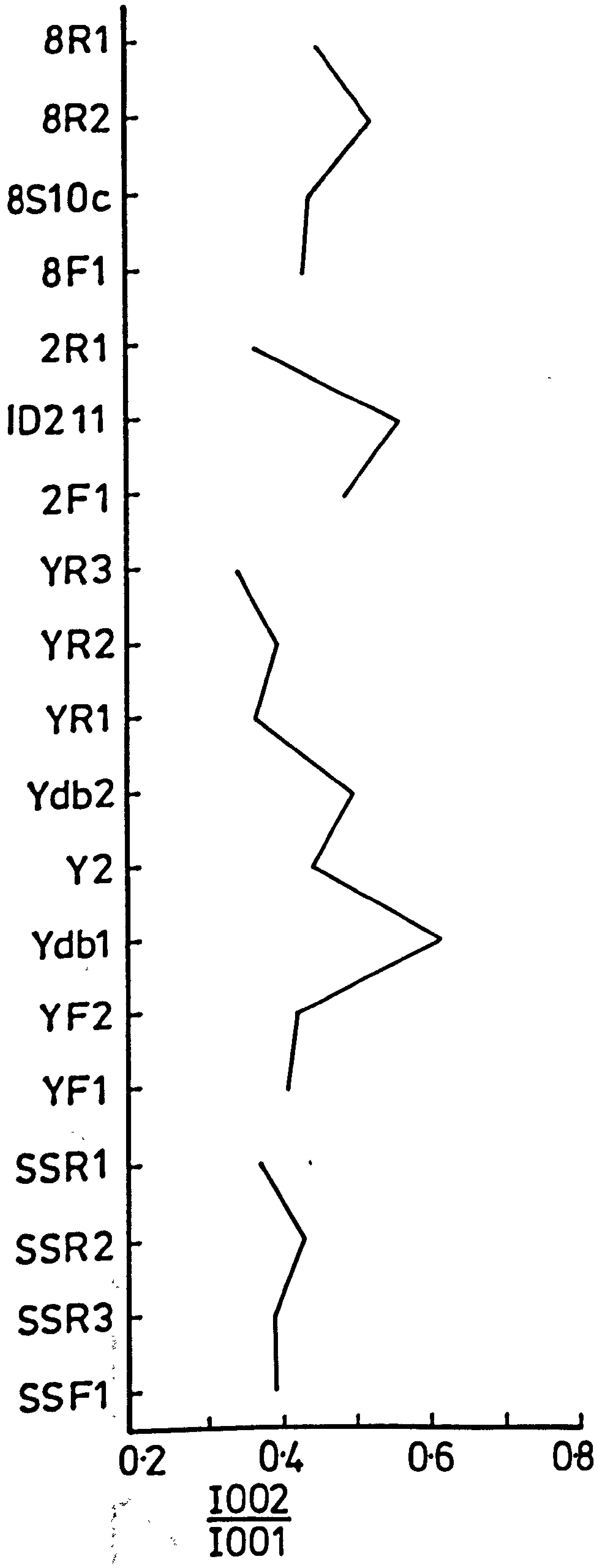


FIGURE 6.16 Kaolinite Crystallinity and Ash Content (L.T.A.) through the seam profiles.

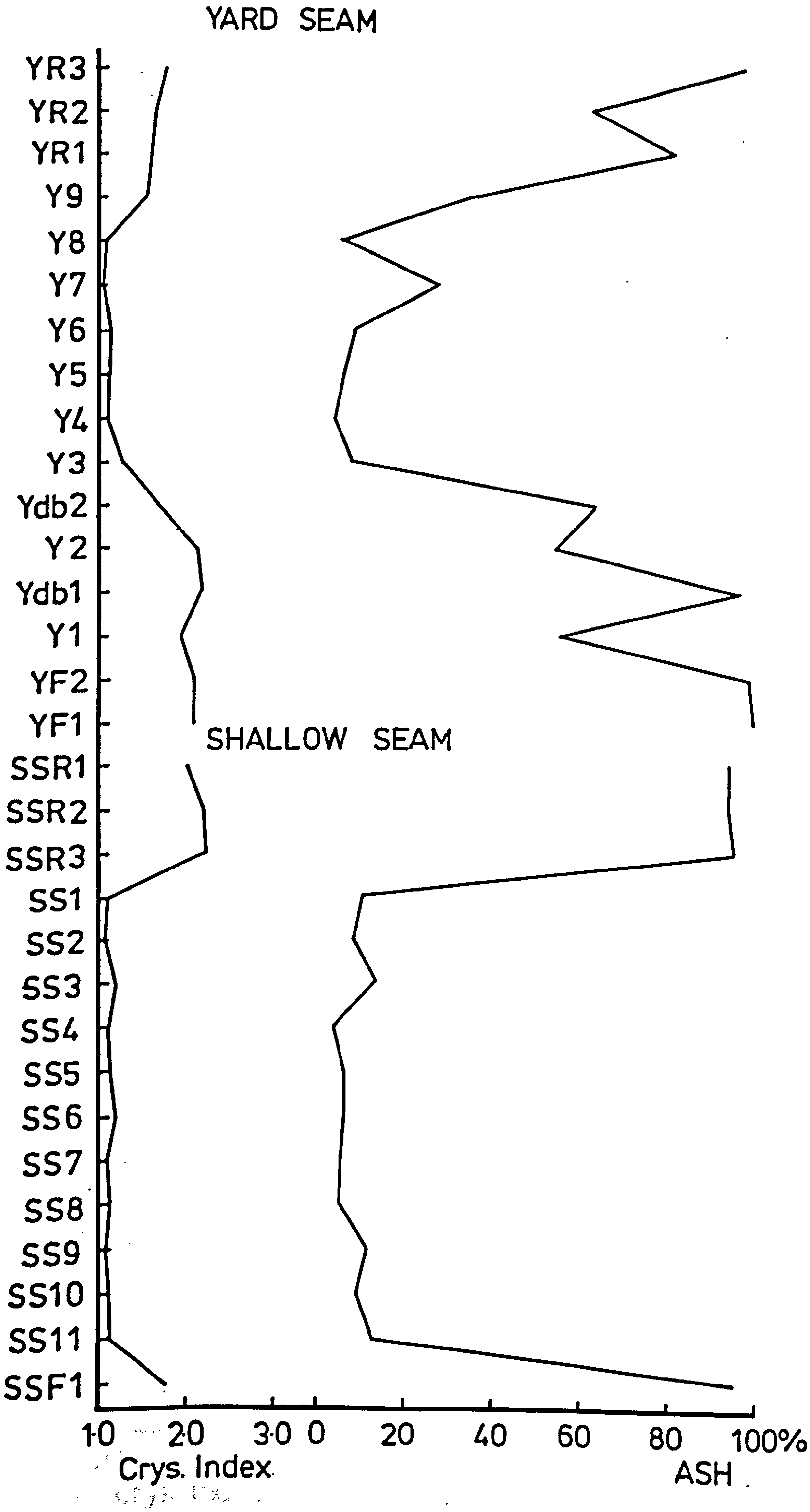


FIGURE 6.16A Kaolinite Crystallinity and Ash Content (I.T.A.) through the seam profiles.

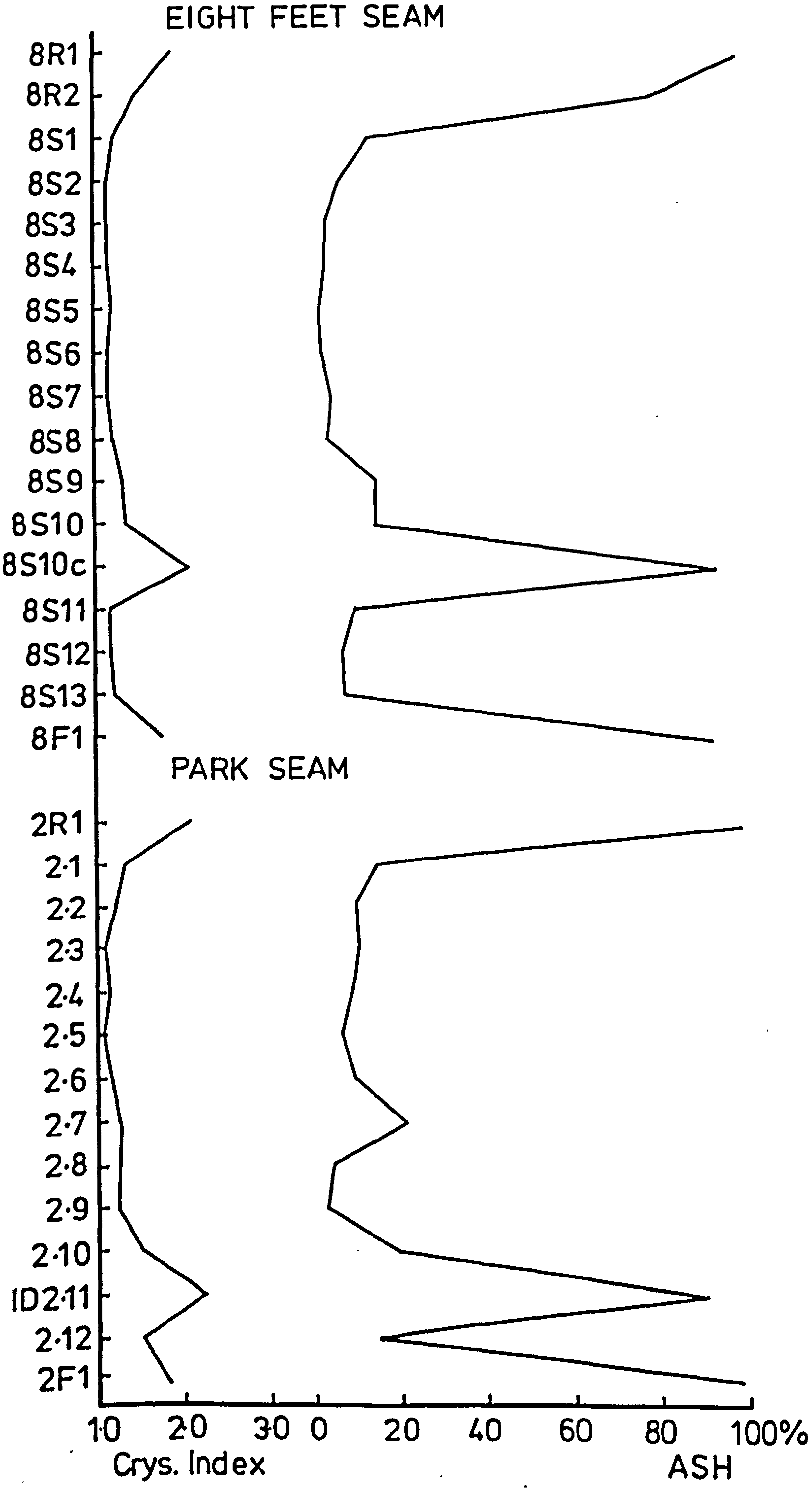


FIGURE 6.17 Ba, Mn, R, Sr and Zr through the mudrock profiles.

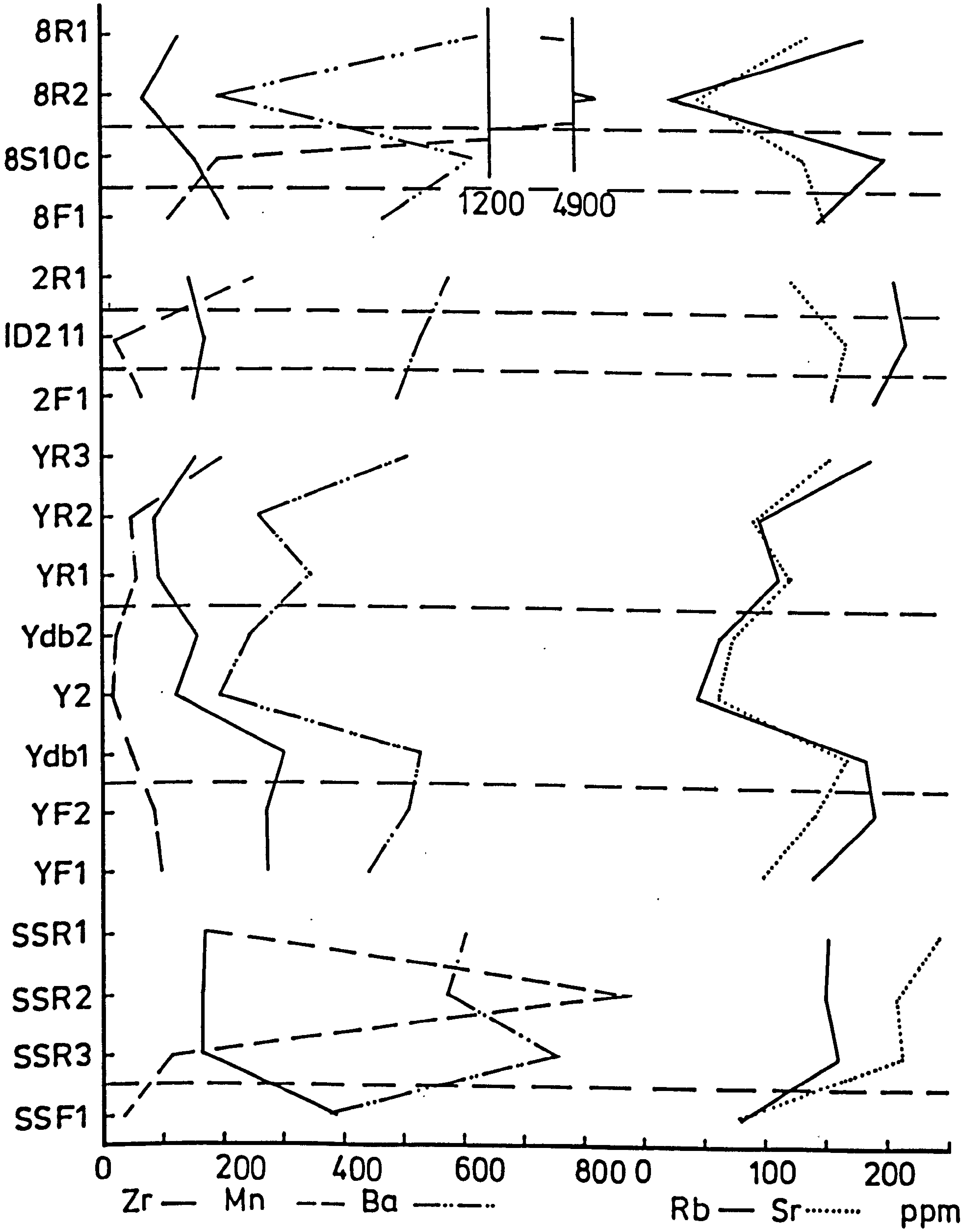


FIGURE 6.18 Co, Cr, Ni and V through the mudrock profiles.

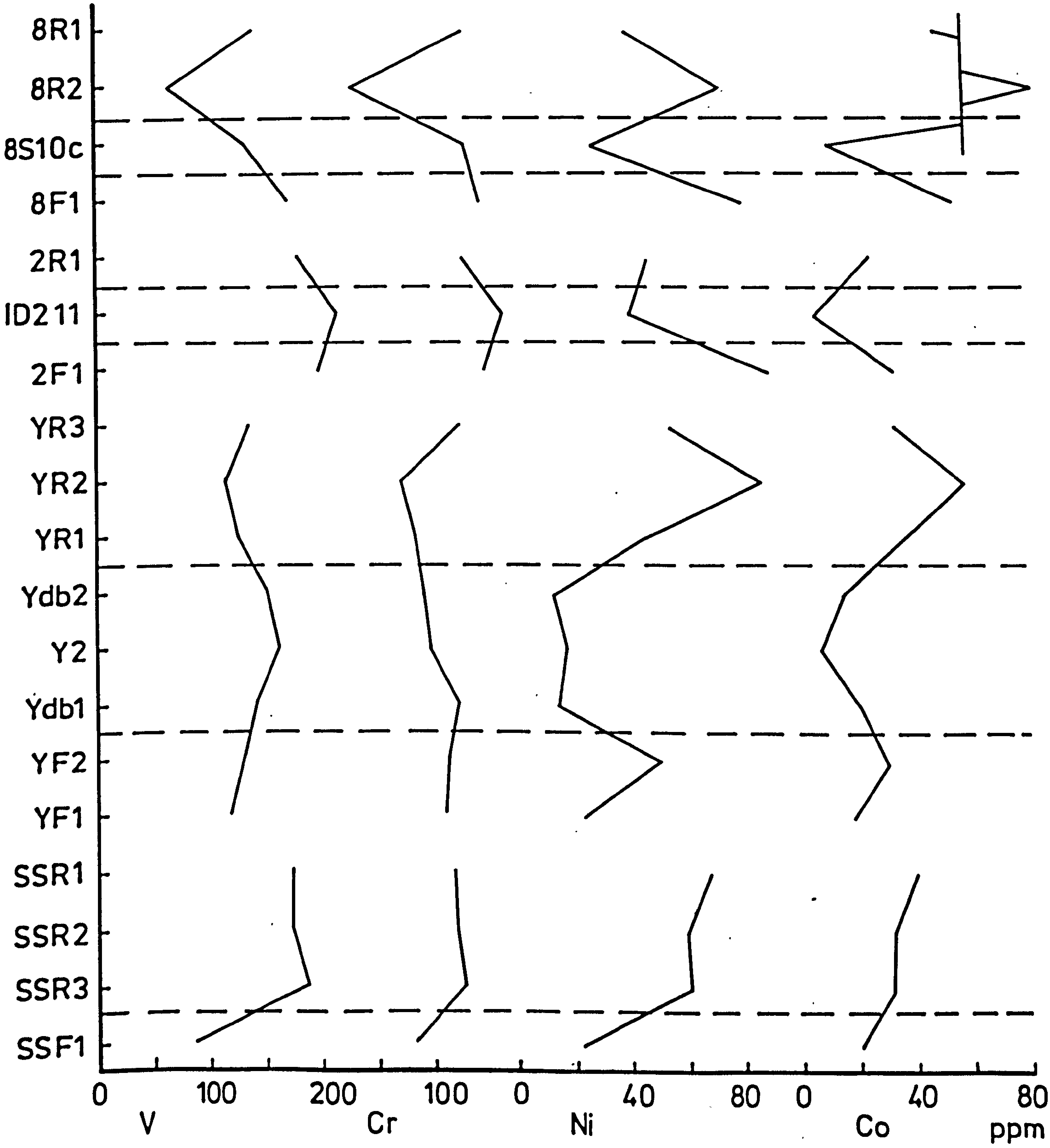


FIGURE 6.19 Cu, Pb, Y and Zn through the mudrock profiles.

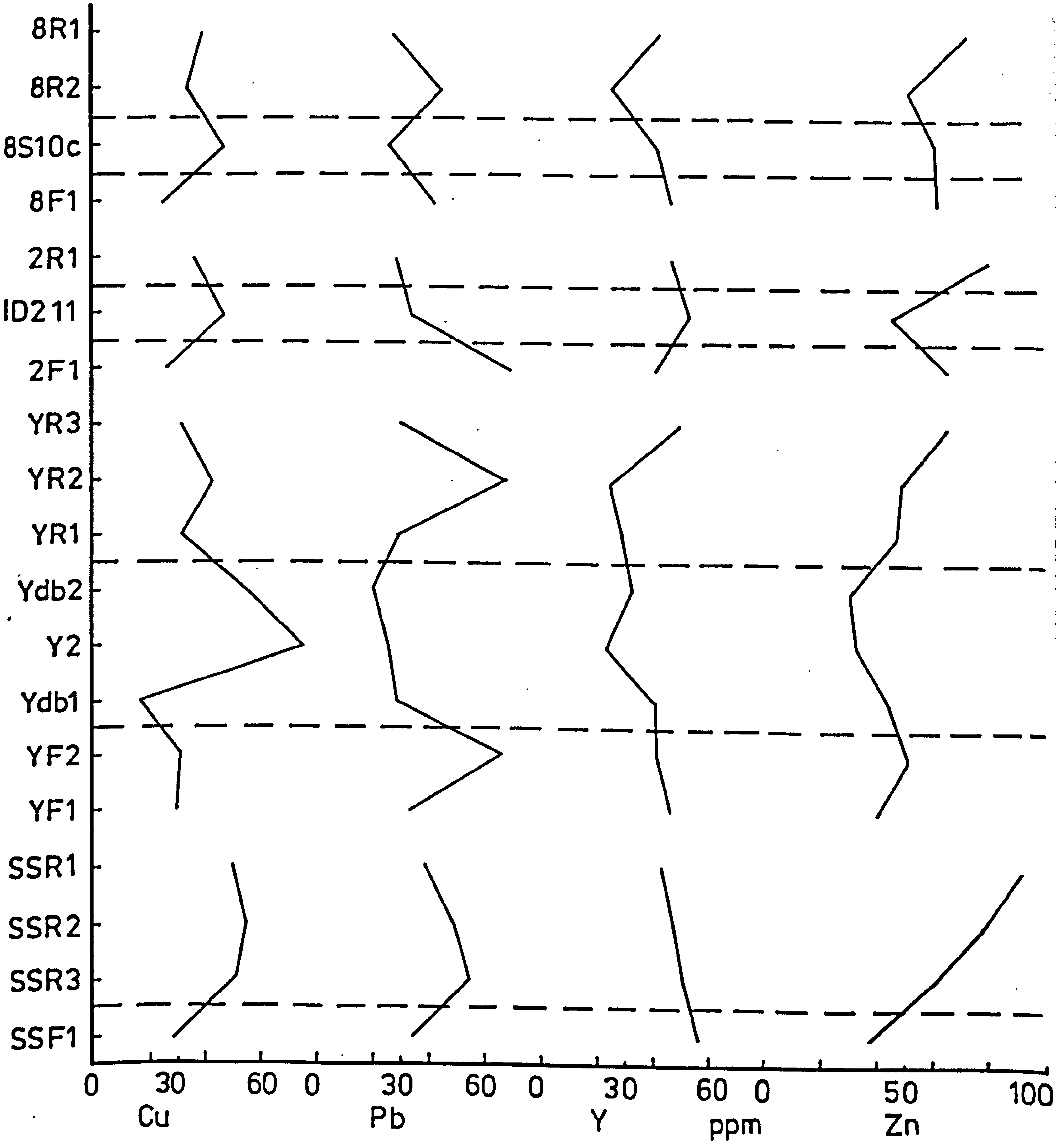


FIGURE 6.20 The ratios of K_2O to Ba, Rb and Sr through the mudrock profiles.

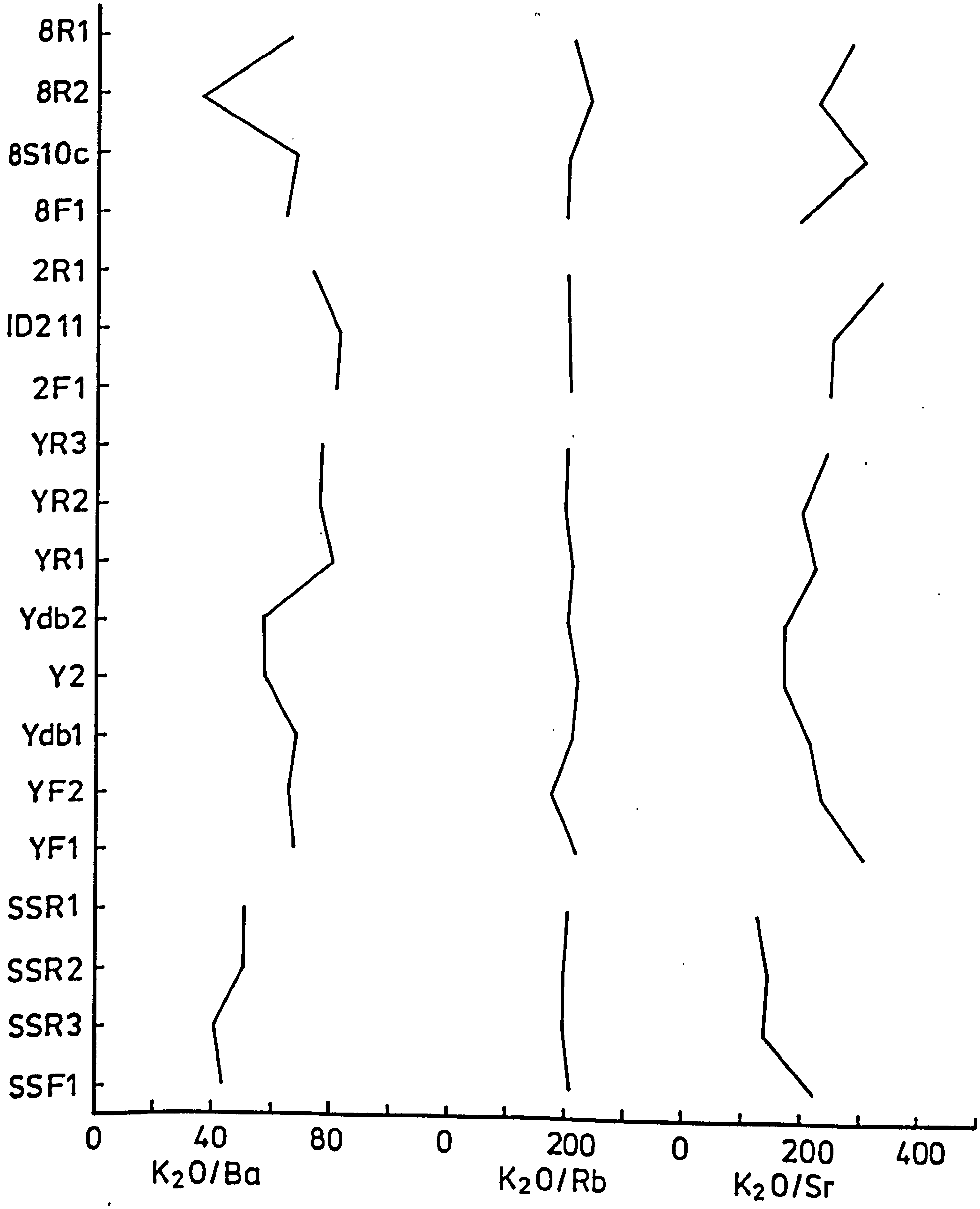


FIGURE 6.21 The ratios of K_2O to Cr, V and Y through the mudrock profiles.

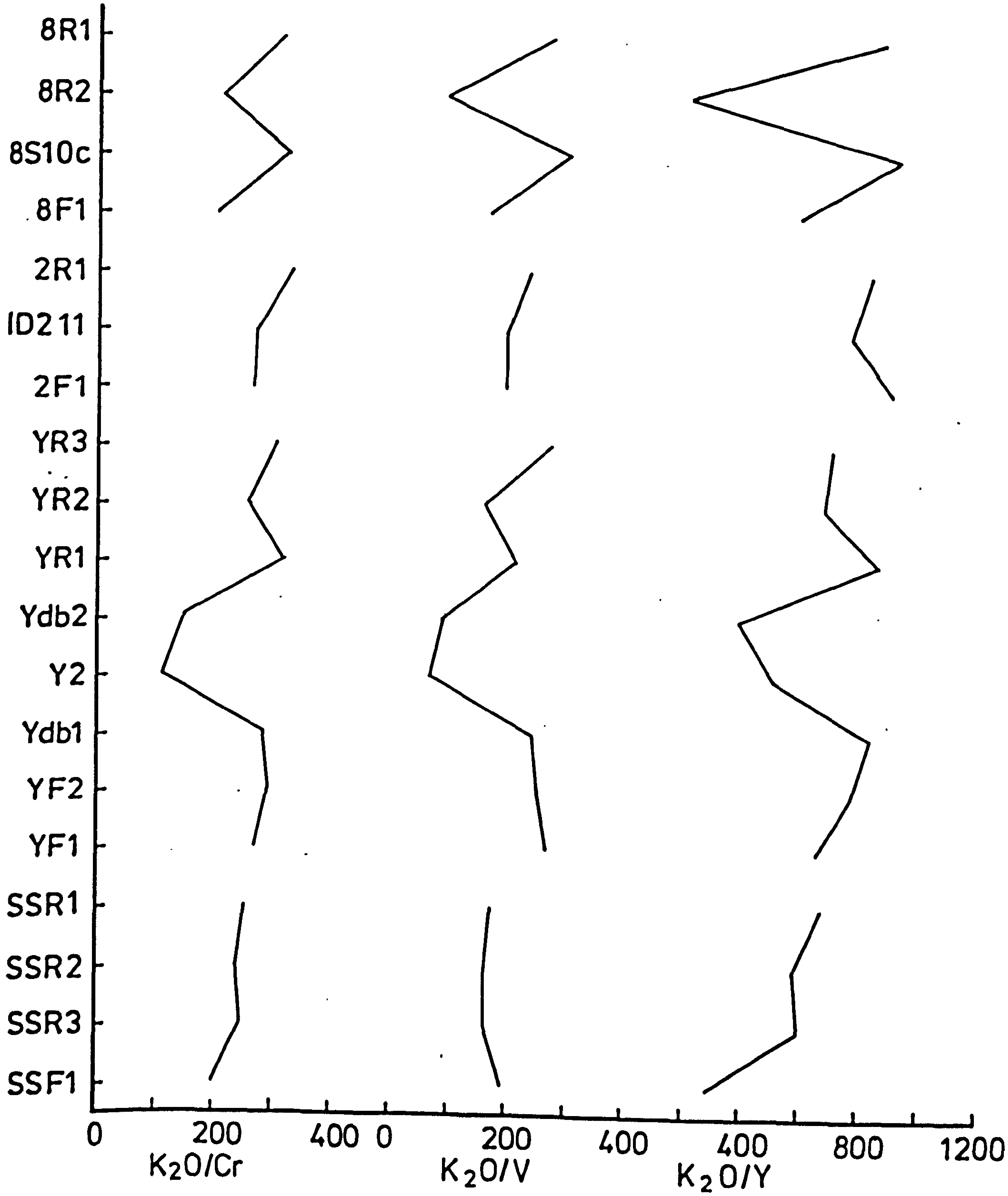


FIGURE 6.22 The ratios of Total Clay/Co and Organic Matter/Cu through the mudrock profiles.

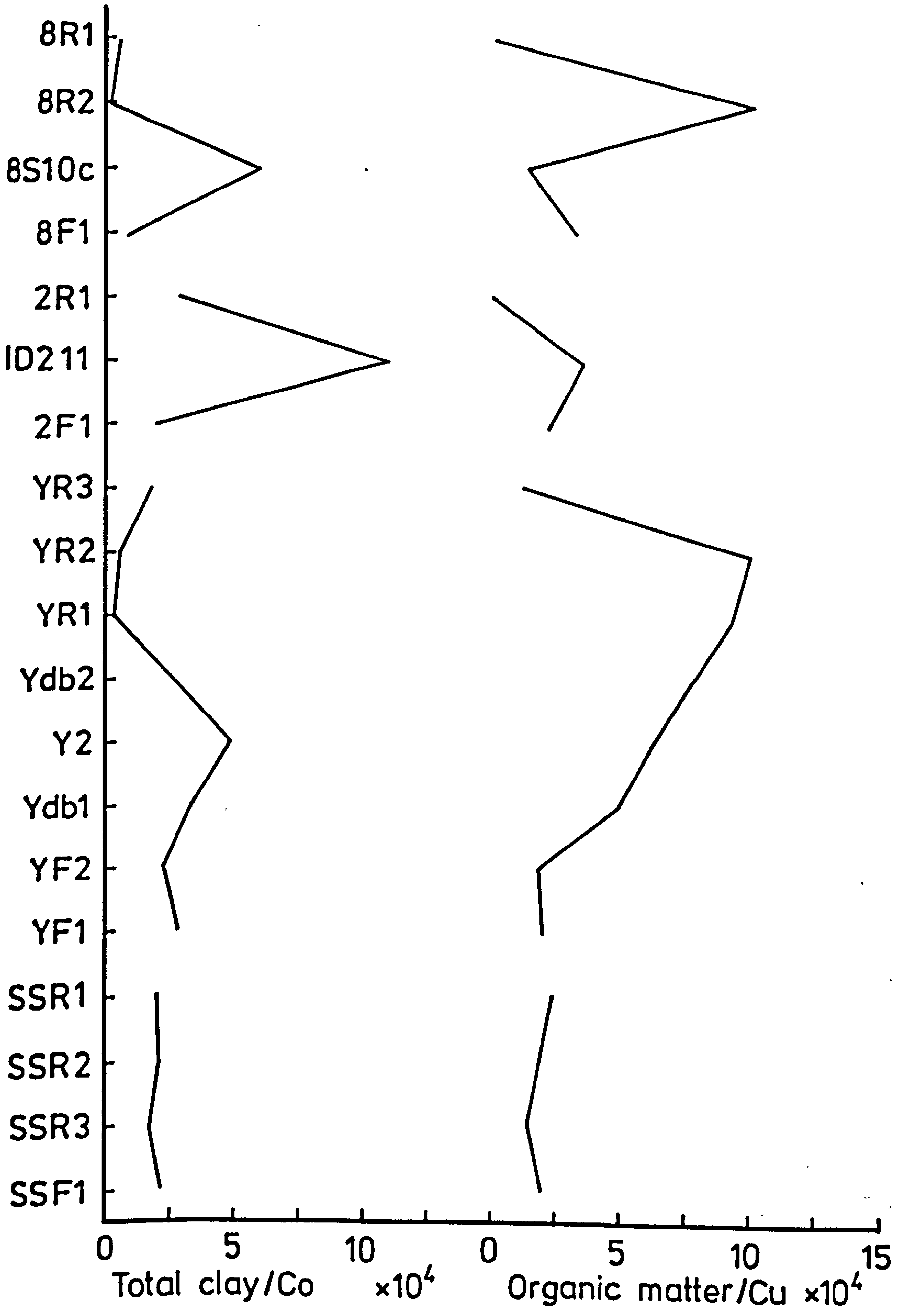


FIGURE 6.23 Standard versus Weak Cone Indenter Numbers on selected mudrock samples (r = + 0.93, 99.9% significance level).

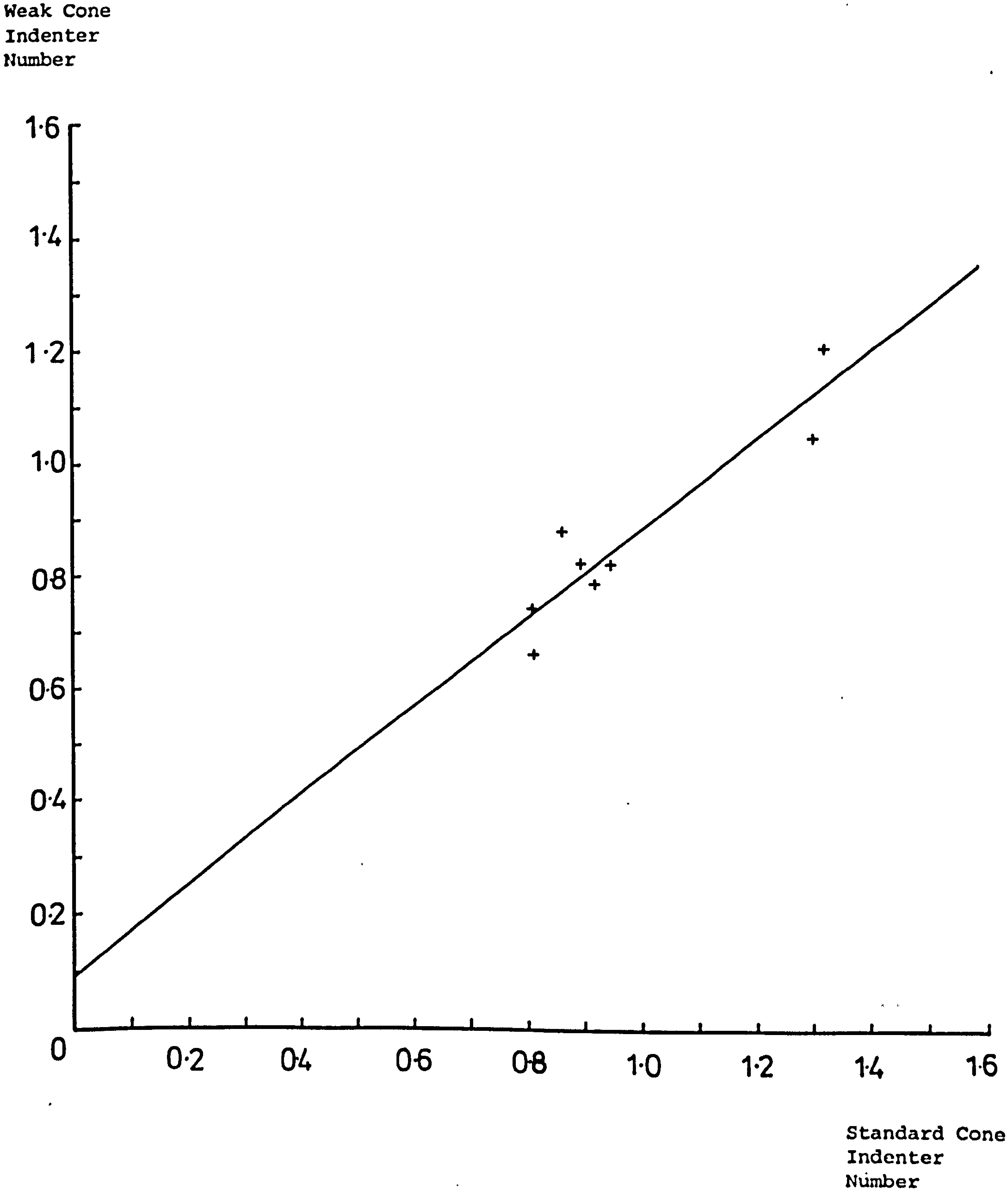


FIGURE 7.1 Exchangeable cation profiles through the Shallow Seam.

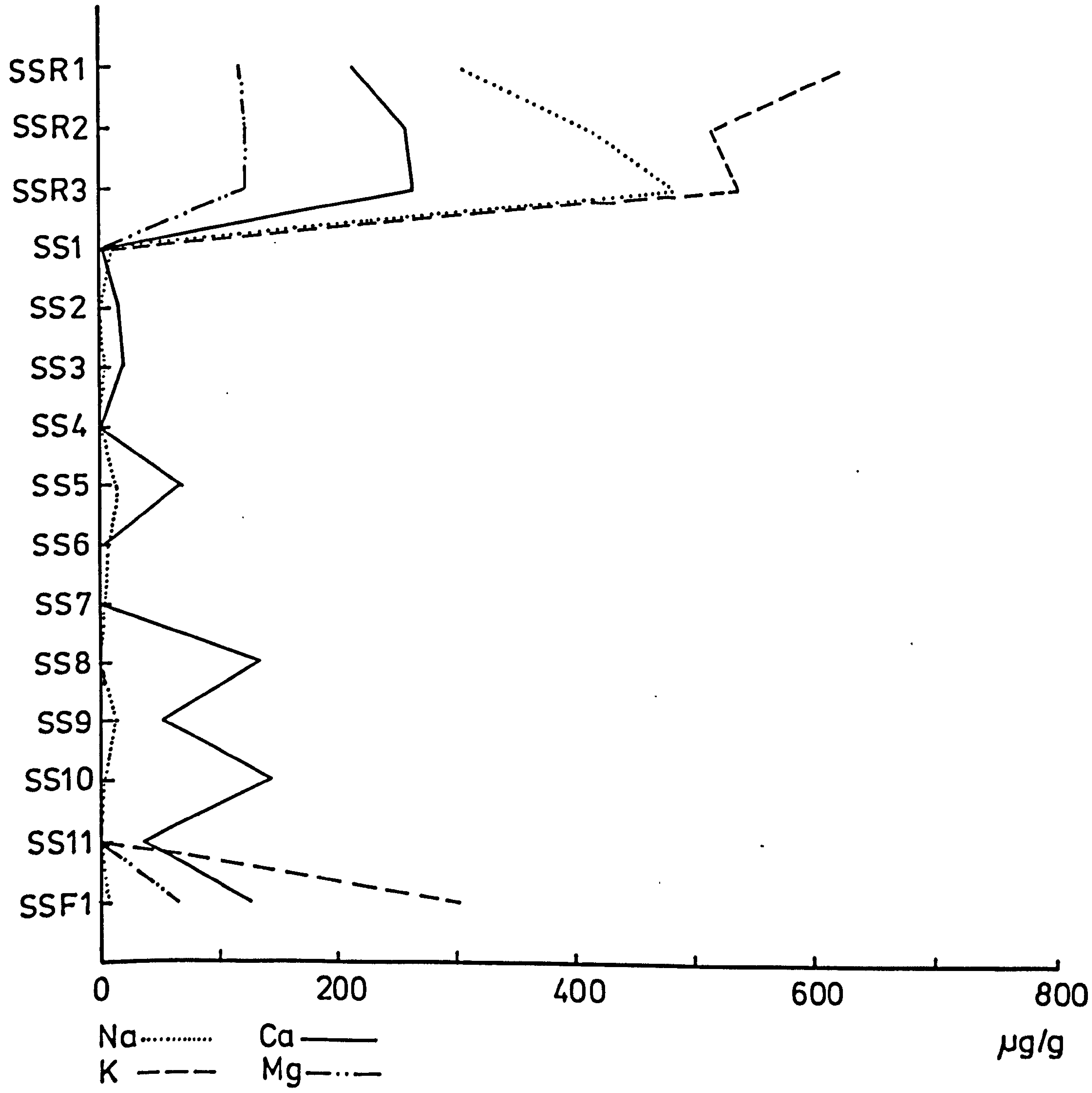


FIGURE 7.2 Exchangeable cation profiles through the Yard Seam.

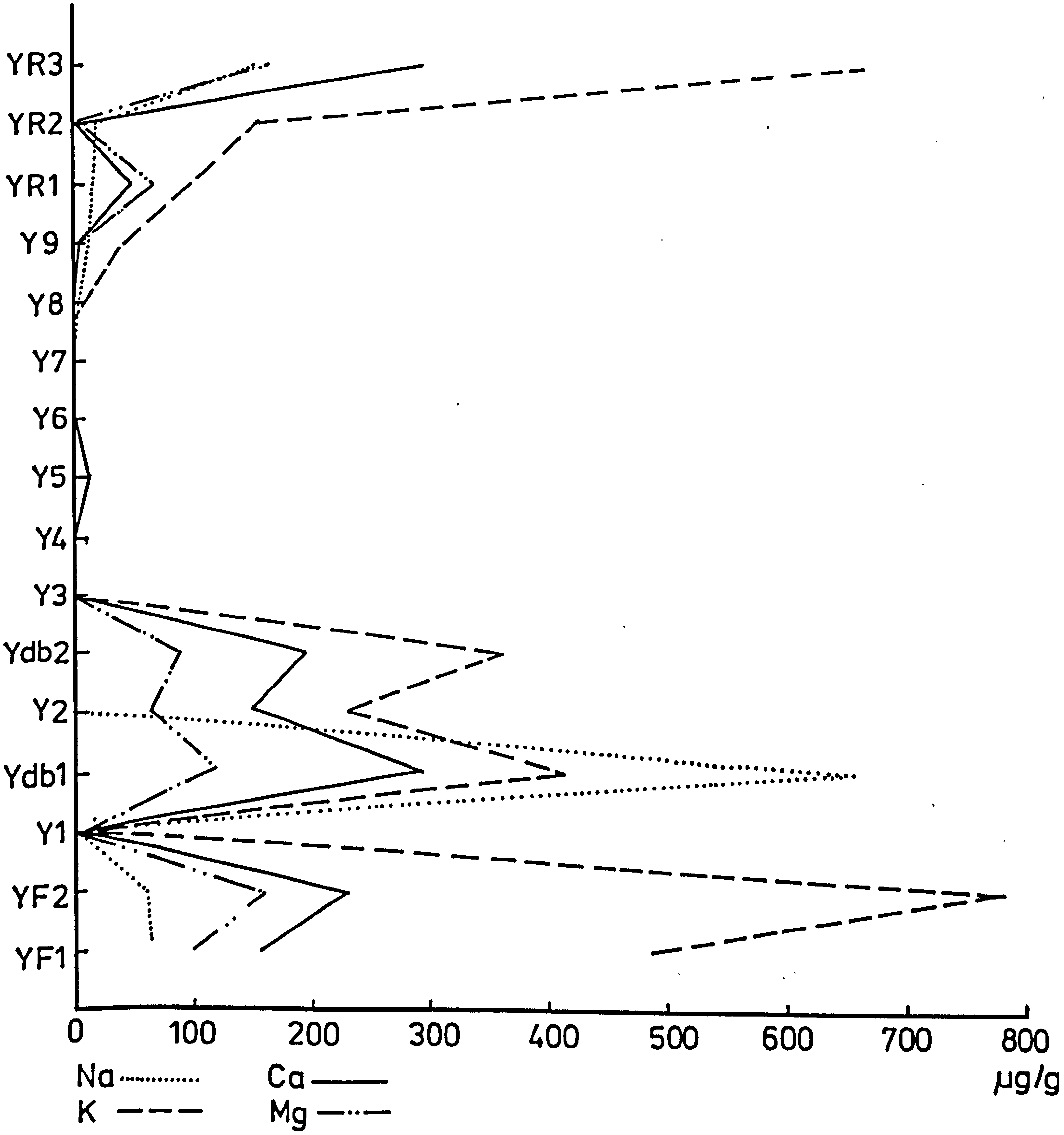


FIGURE 7.3 Exchangeable cation profiles through the Park Seam.

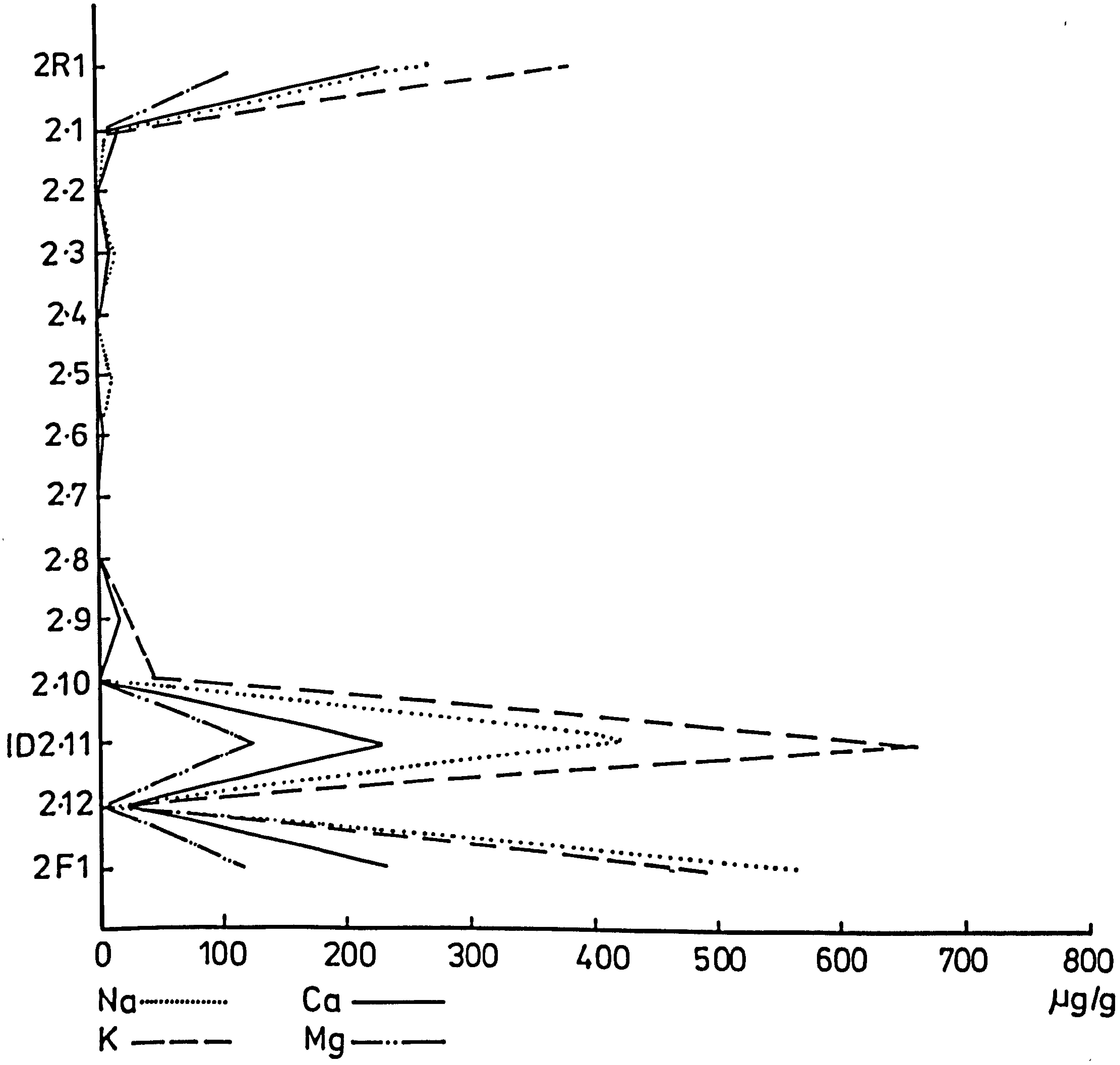


FIGURE 7.4 Exchangeable cation profiles through the Eight Feet Seam.

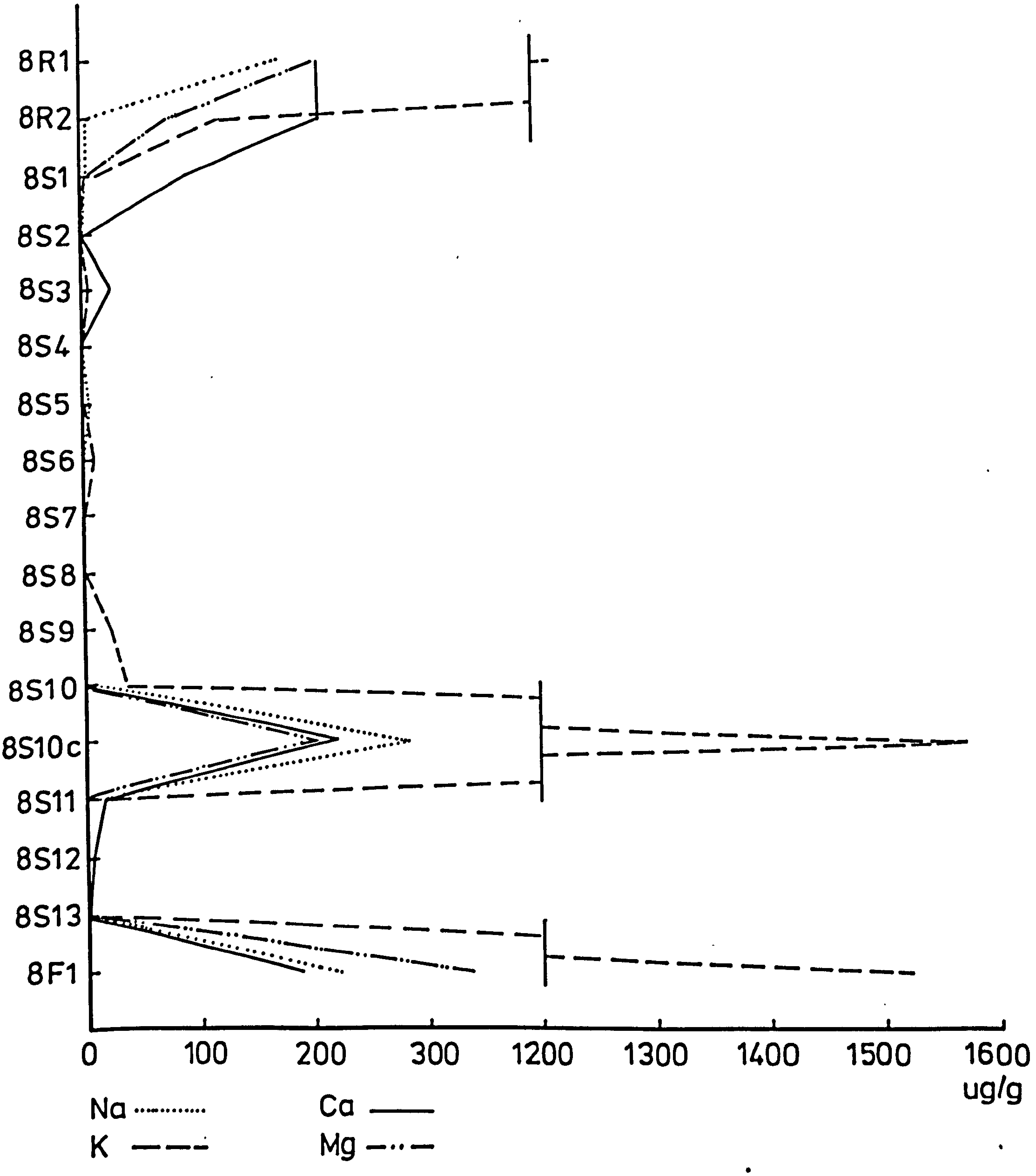


FIGURE 7.5 Exchangeable Mg/Ca and Na/K cation ratios through the mudrock profiles.

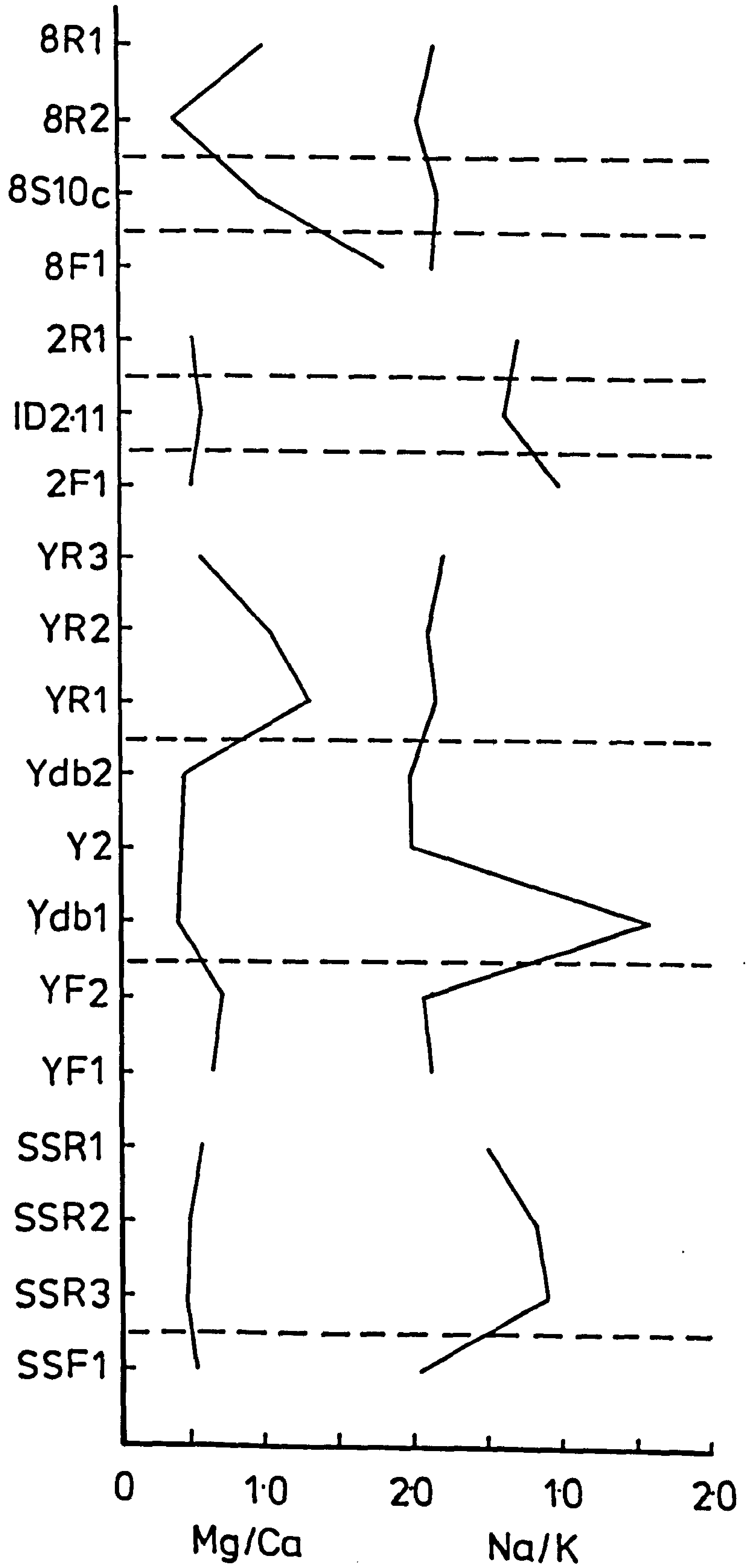


FIGURE 7.6 Cation exchange capacity and percentage clay minerals across the mudrock profiles (whole rock).

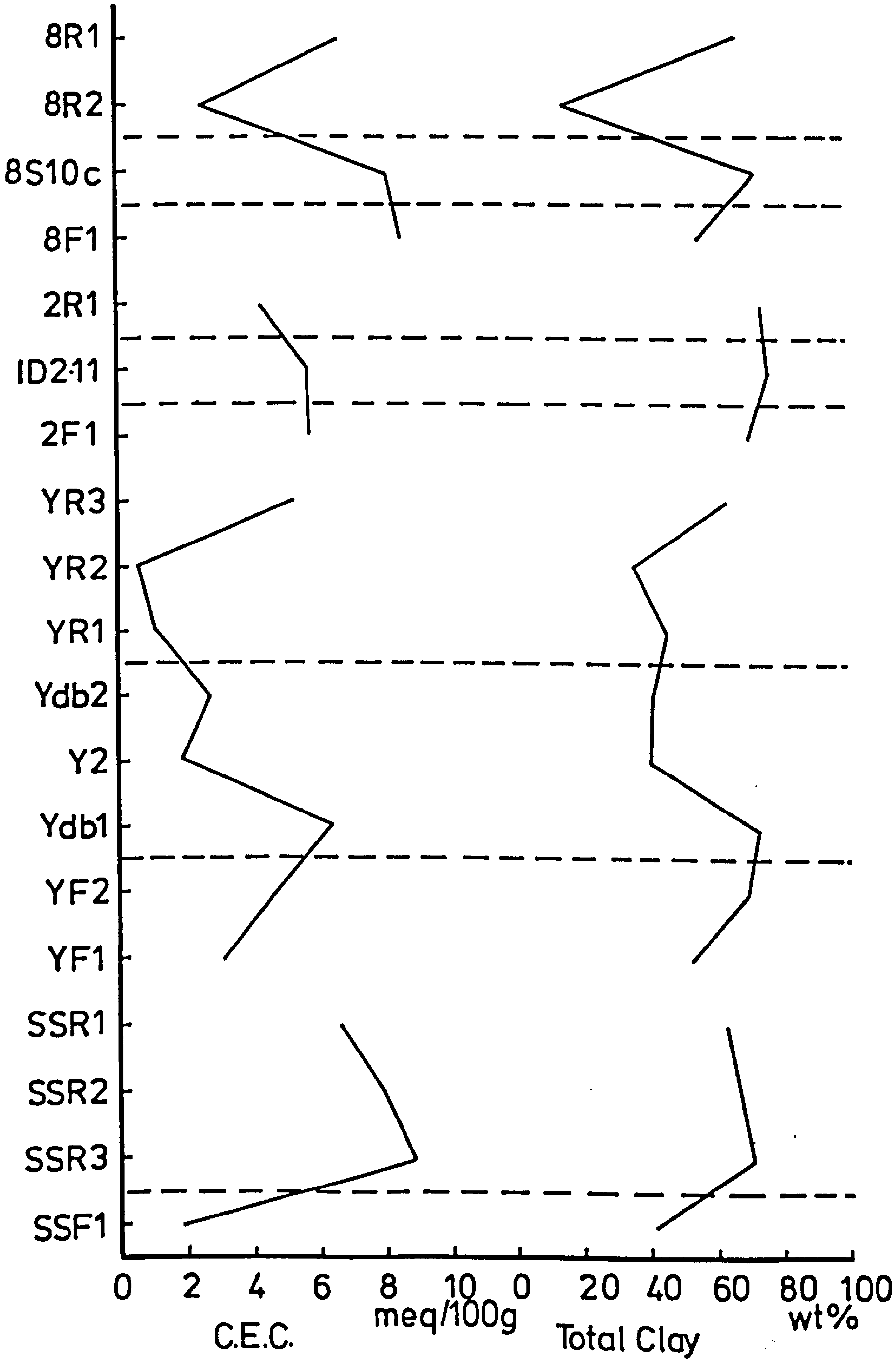


FIGURE 8.1 Mineral abundance in the coal ash (XRD peak height), carbonates and coal type, Lea Hall Colliery.

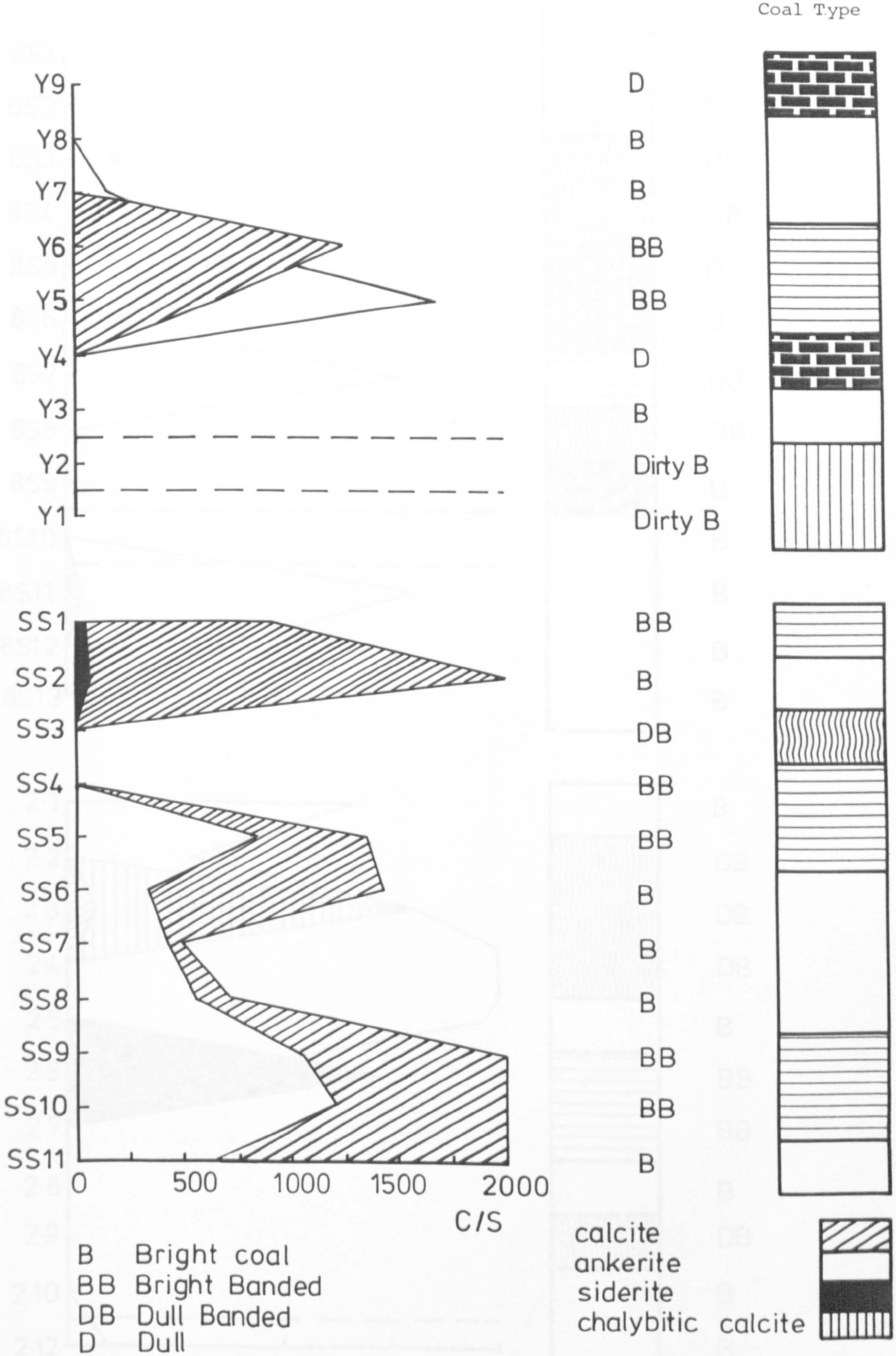


FIGURE 8.2 Mineral abundance in the coal ash (XRD peak height), carbonates and coal type, Littleton Colliery.

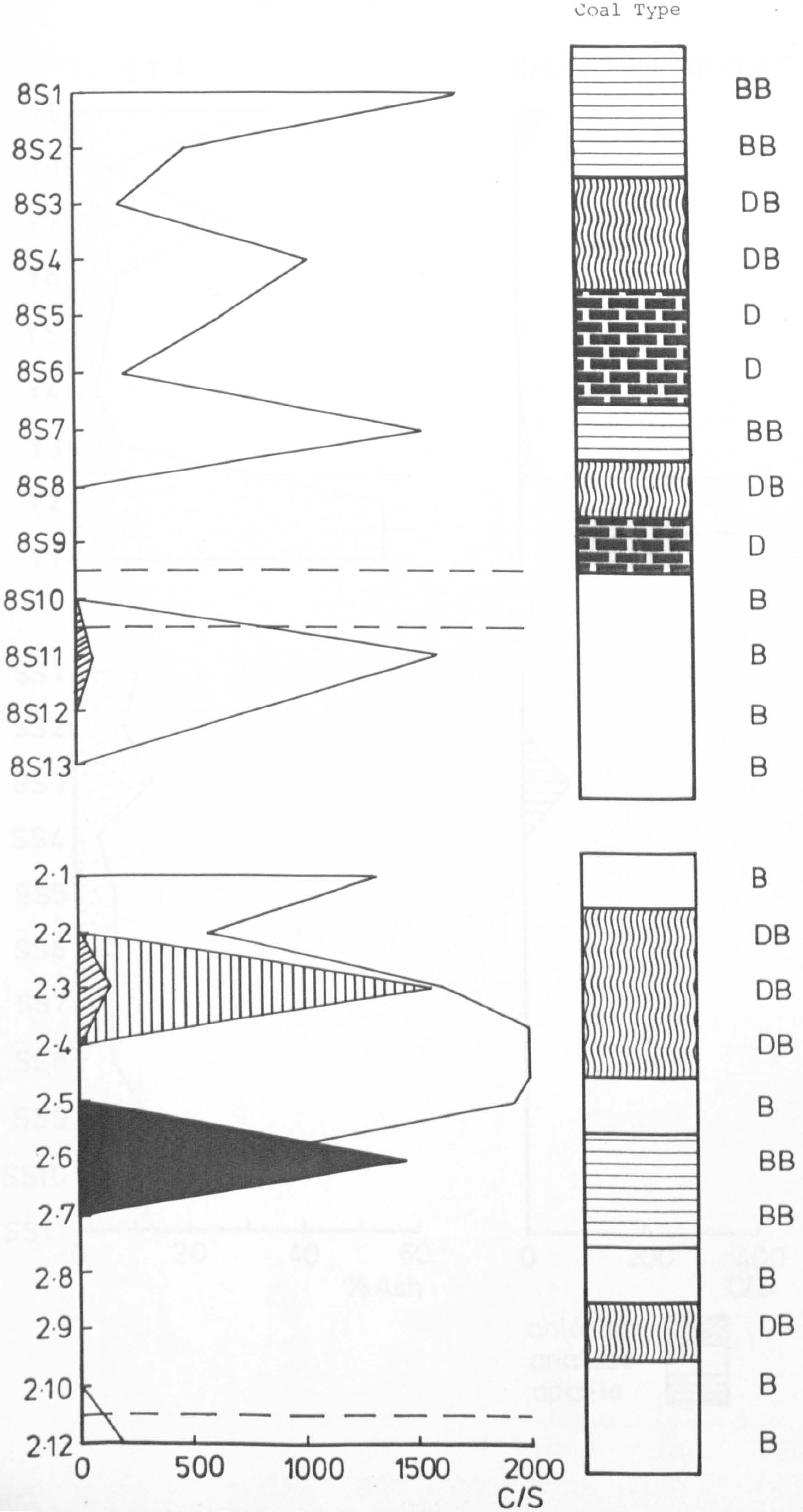


FIGURE 8.3 Mineral abundance in the coal ash (XRD peak height), chlorite, apatite and L.T.A. profiles, Lea Hall Colliery.

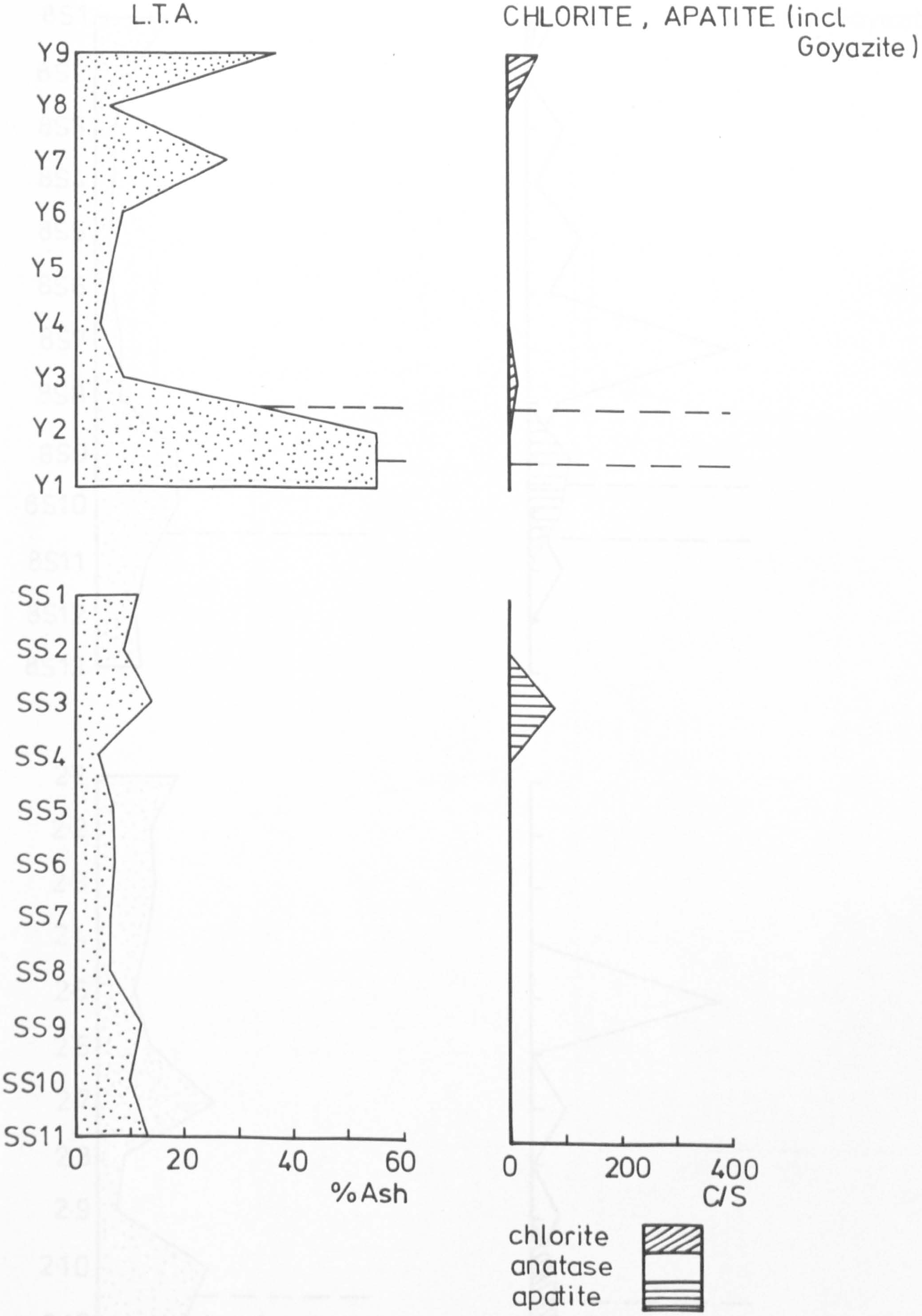


FIGURE 8.4 Mineral abundance in the coal ash (XRD peak height), chlorite, apatite and L.T.A. profiles, Littleton Colliery.

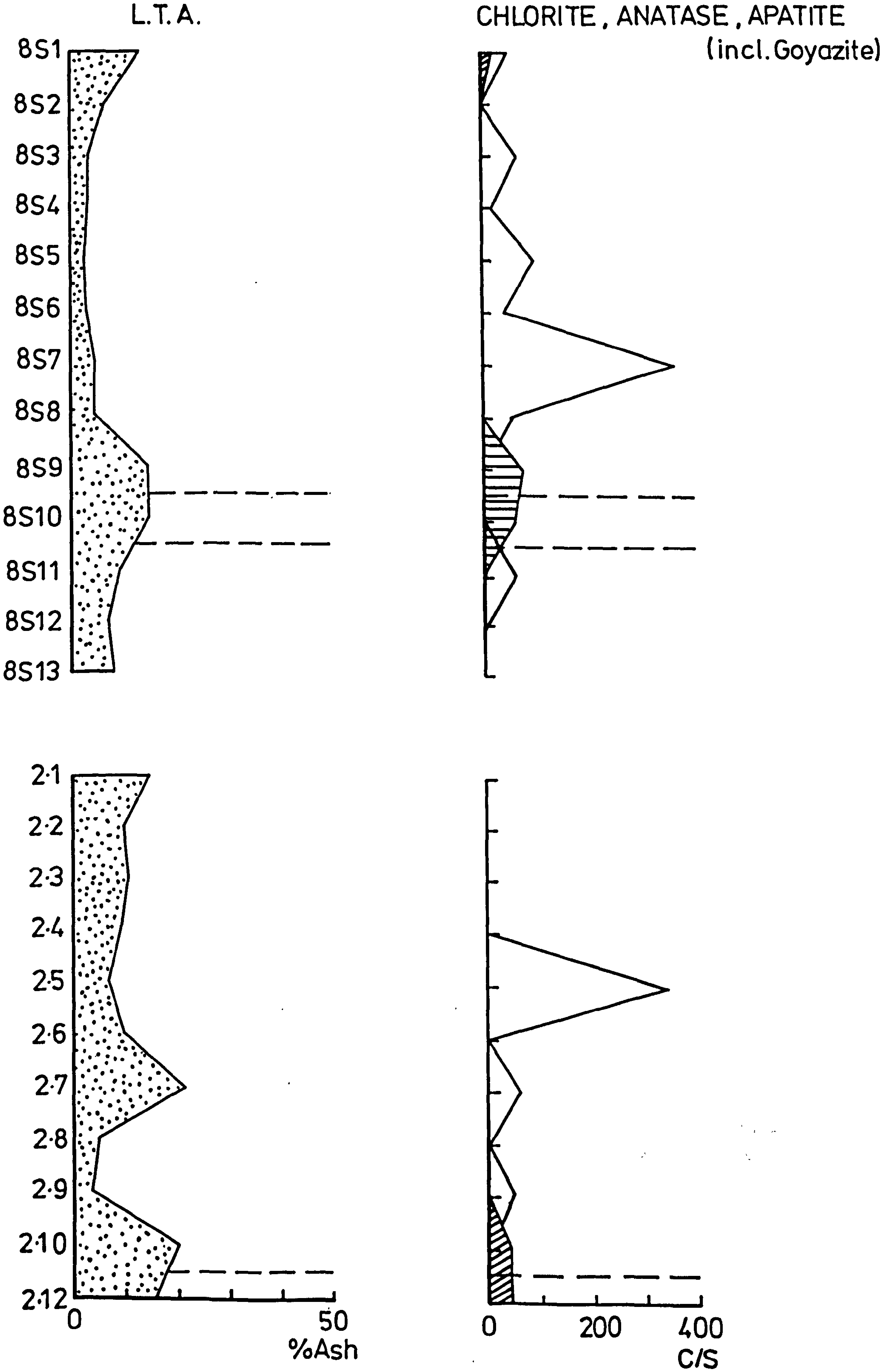


FIGURE 8.5 Mineral abundance in the coal ash (XRD peak height), illite, kaolinite and quartz, Lea Hall Colliery.

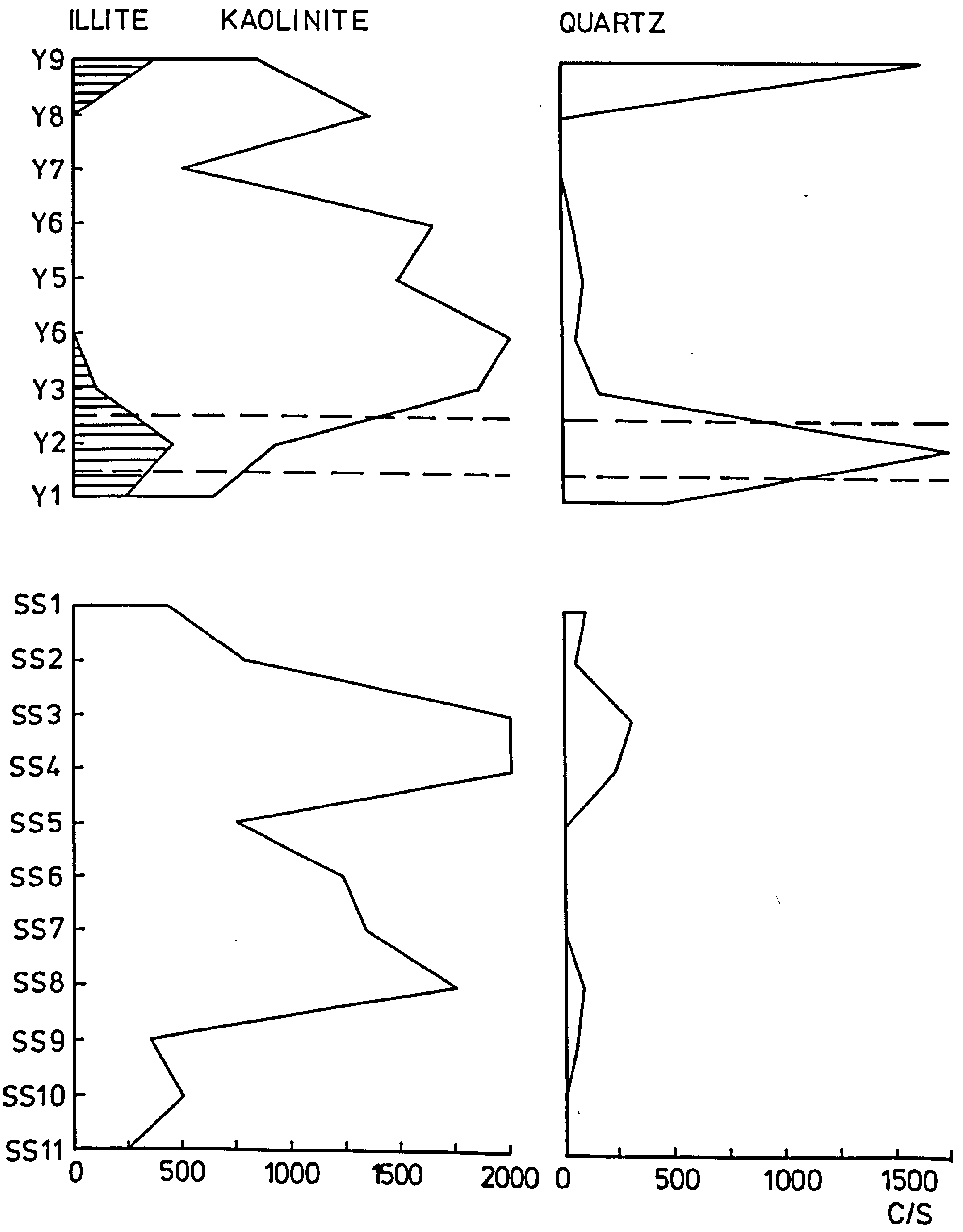


FIGURE 8.6 Mineral abundance in the coal ash (XRD peak height), illite, kaolinite and quartz, Littleton Colliery.

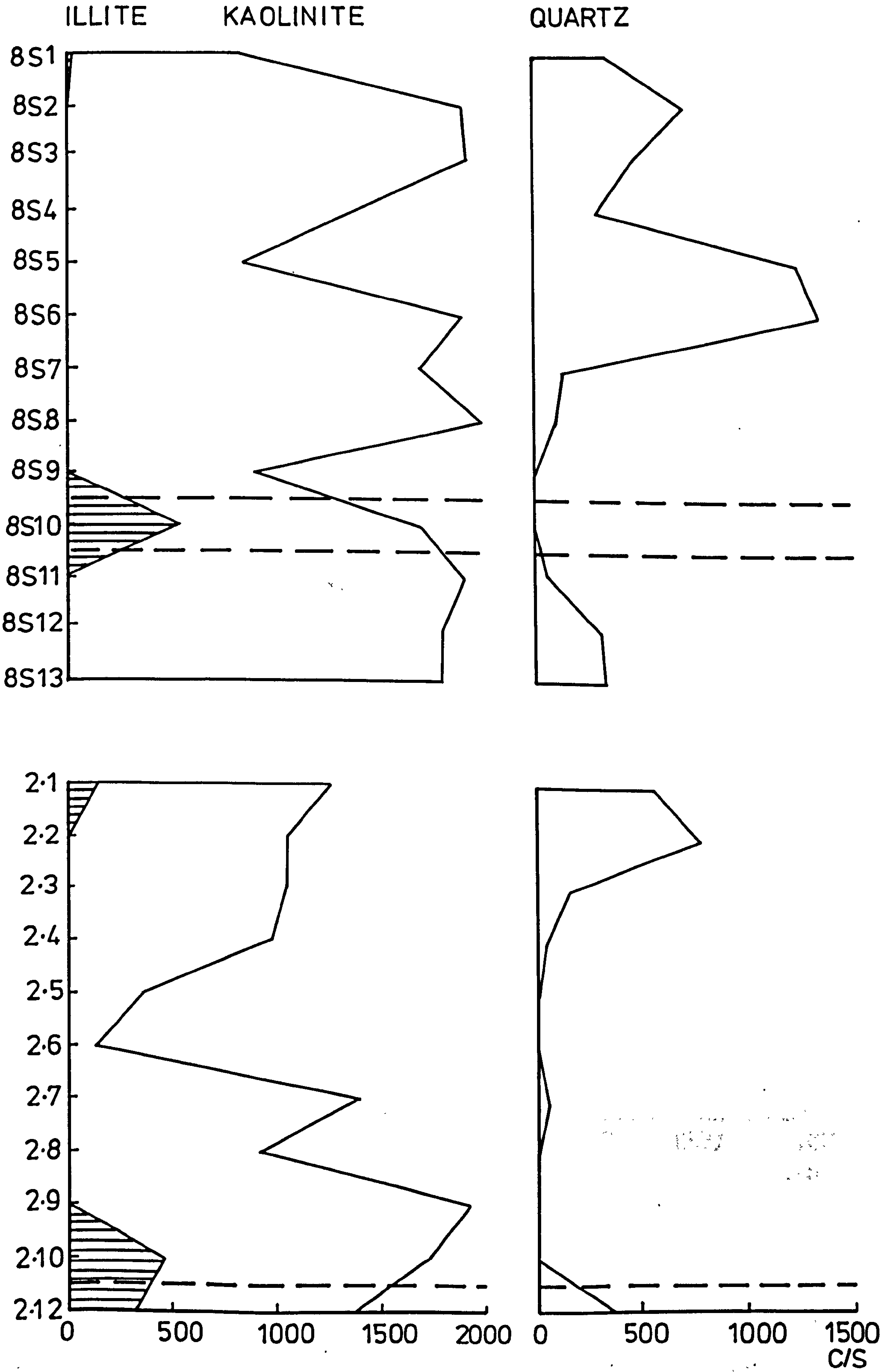


FIGURE 8.7 Mineral abundance in the coal ash (XRD peak height), marcasite, pyrite and gypsum, Lea Hall Colliery.

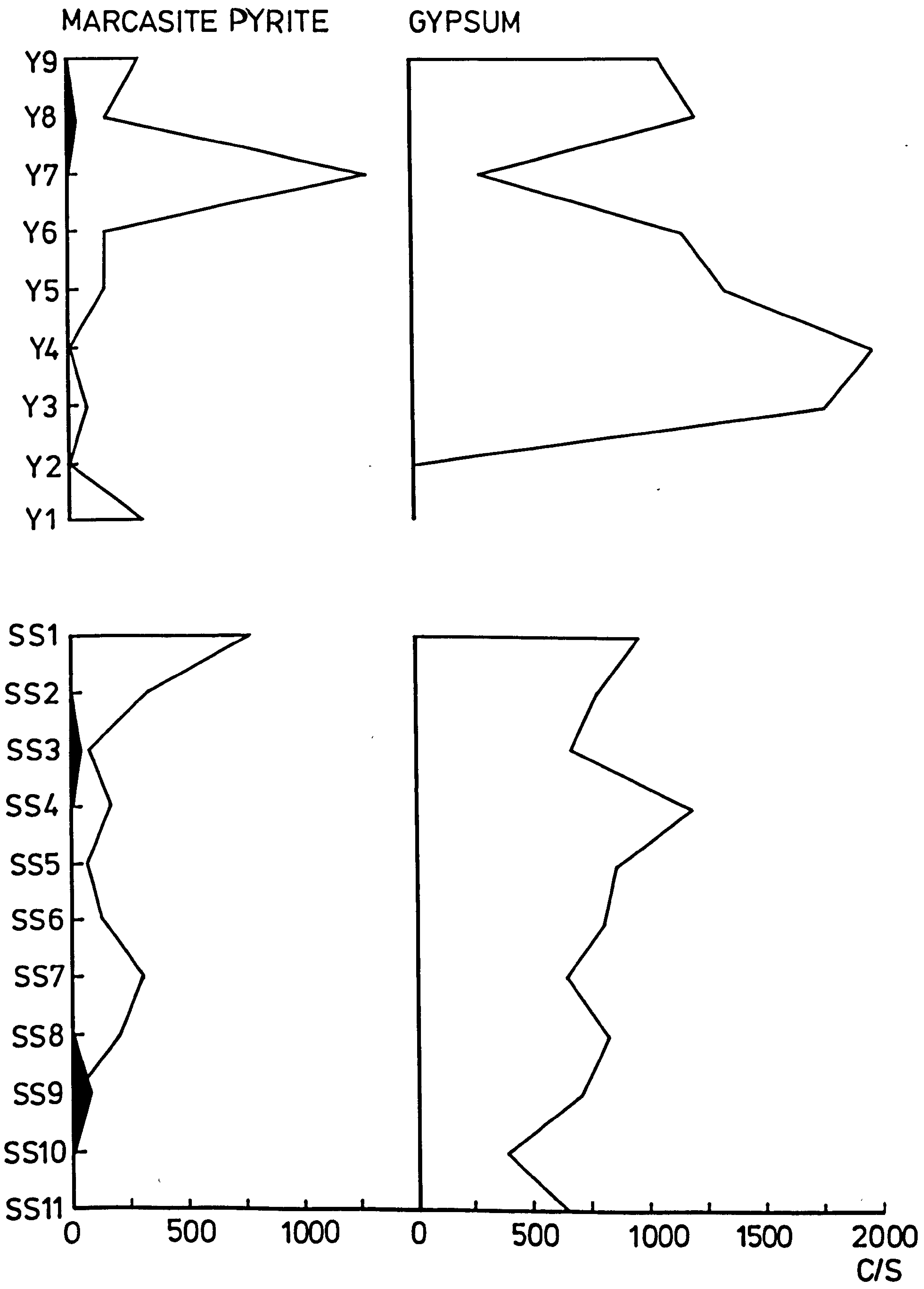


FIGURE 8.8 Mineral abundance in the coal ash (XRD peak height), marcasite, sphalerite, pyrite and gypsum, Littleton Colliery.

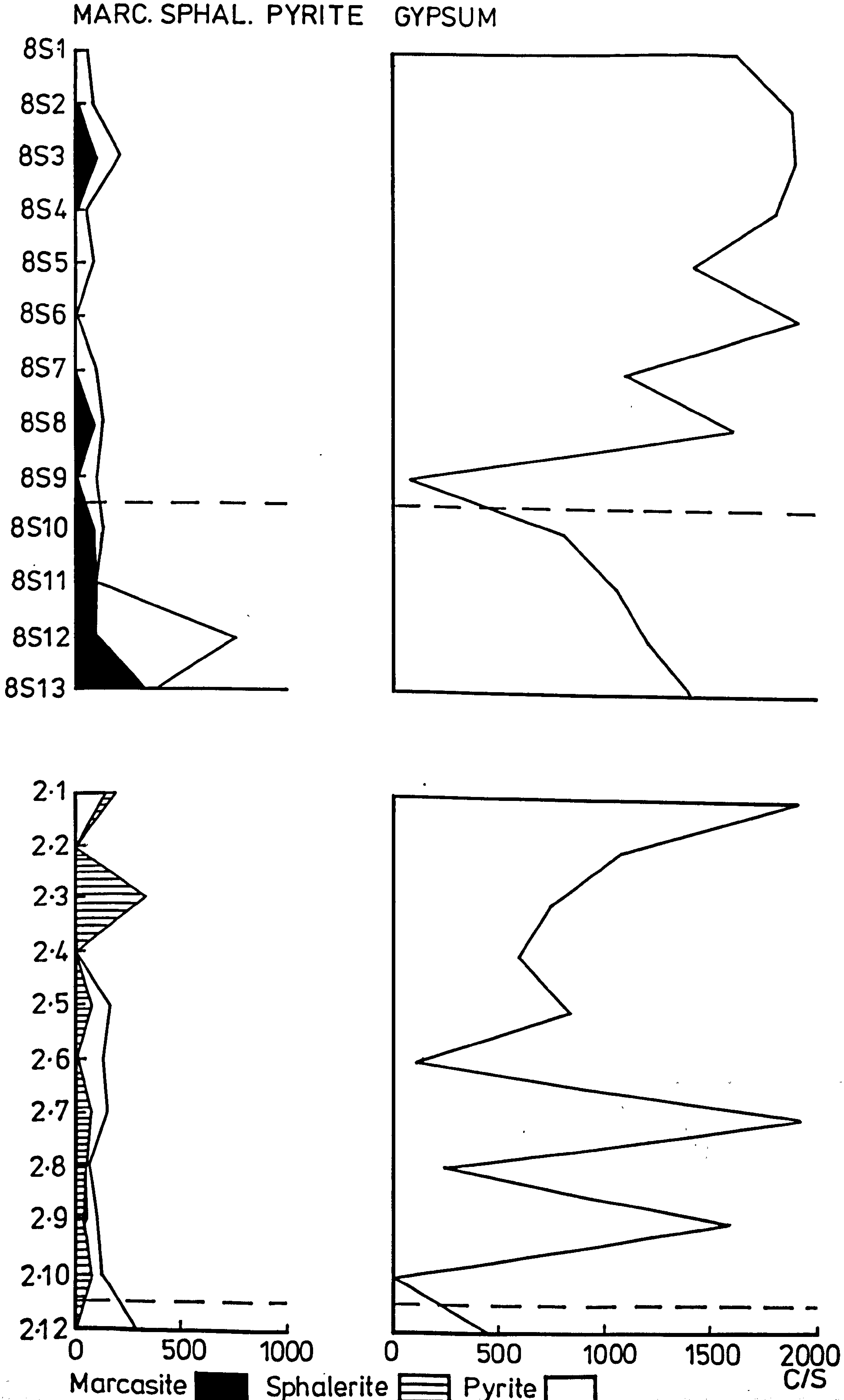


FIGURE 8.9 Al_2O_3. SiO_2 and K_2O profiles through the grouped coal samples.

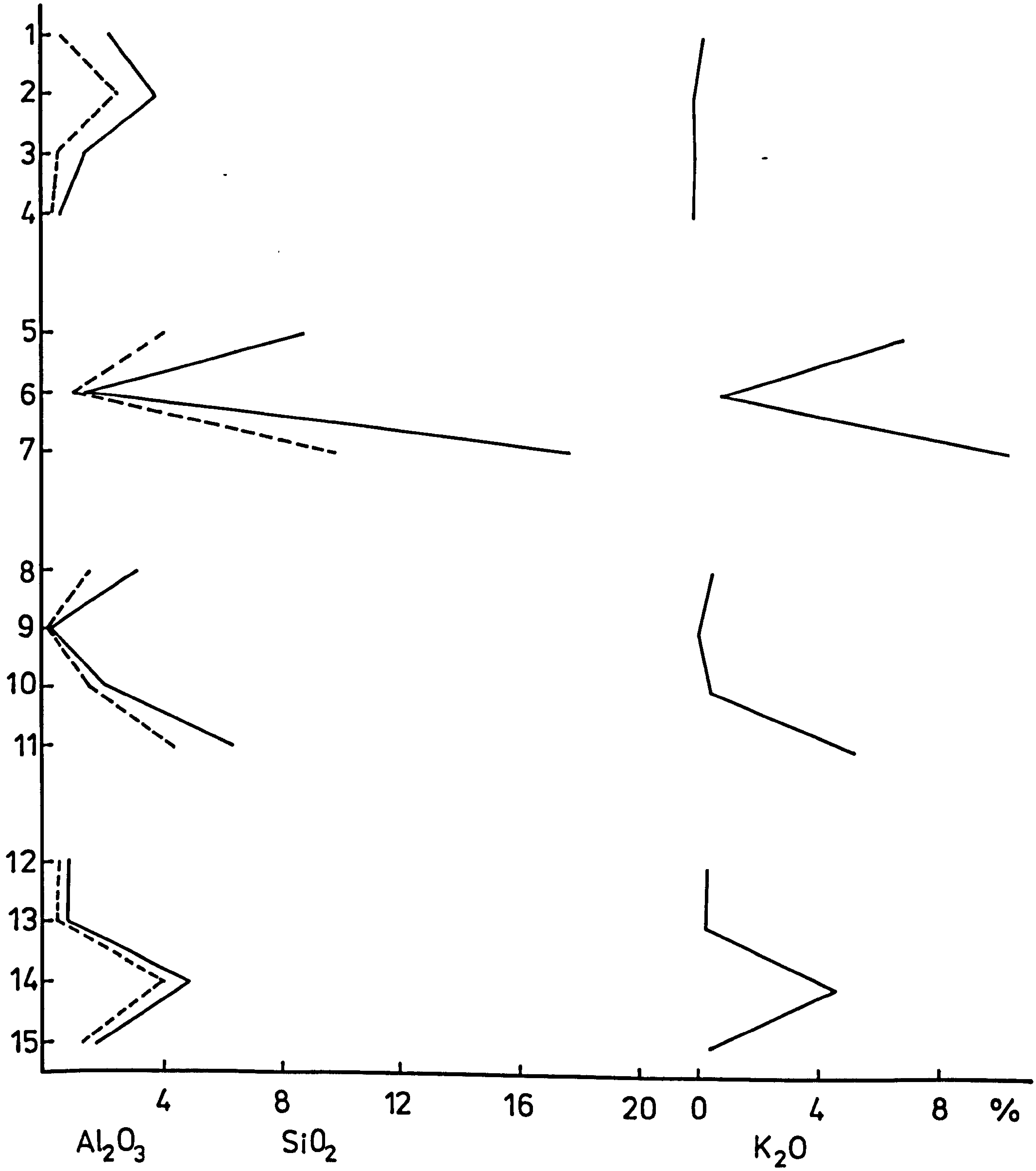


FIGURE 8.10 Na_2O, TiO_2 and 'calculated quartz' profiles through the grouped coal samples.

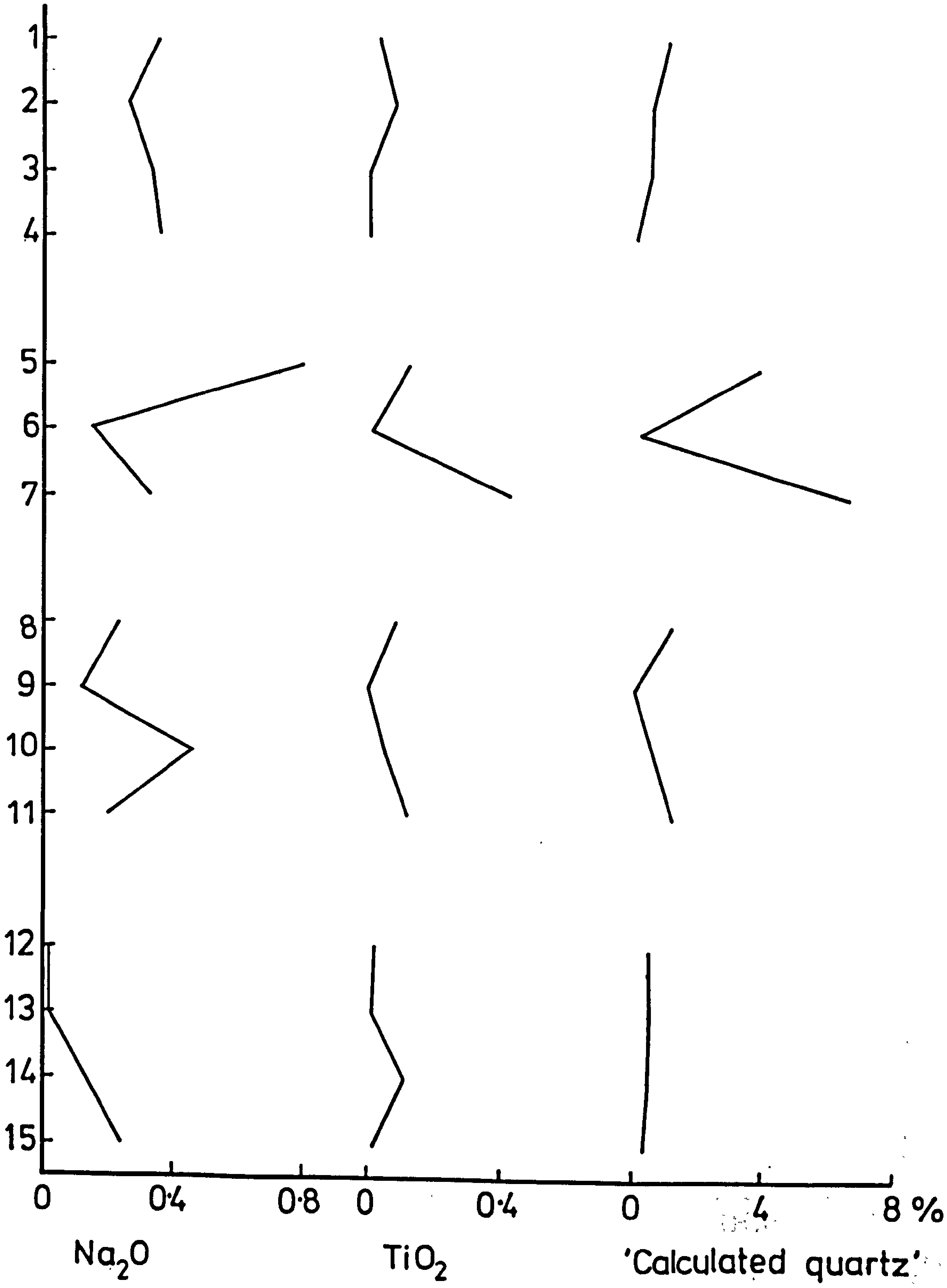


FIGURE 8.11 SiO_2/Al_2O_2, K_2O/Al_2O_3, TiO_2/Al_2O_3 and MgO/CaO ratios through the grouped coal samples.

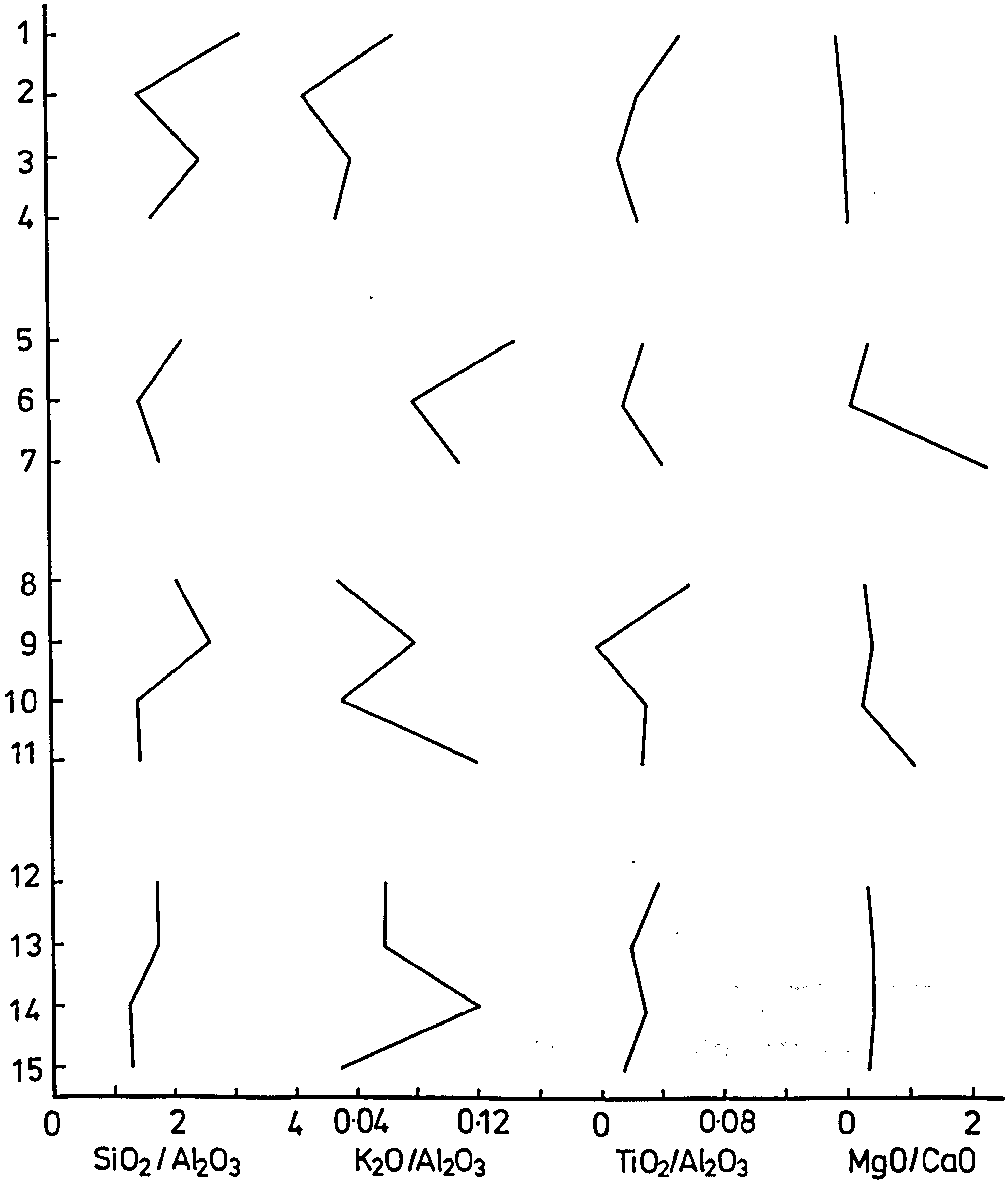


FIGURE 8.12 CaO, MnO, MgO and total Fe_2O_3 profiles through the grouped coal samples.

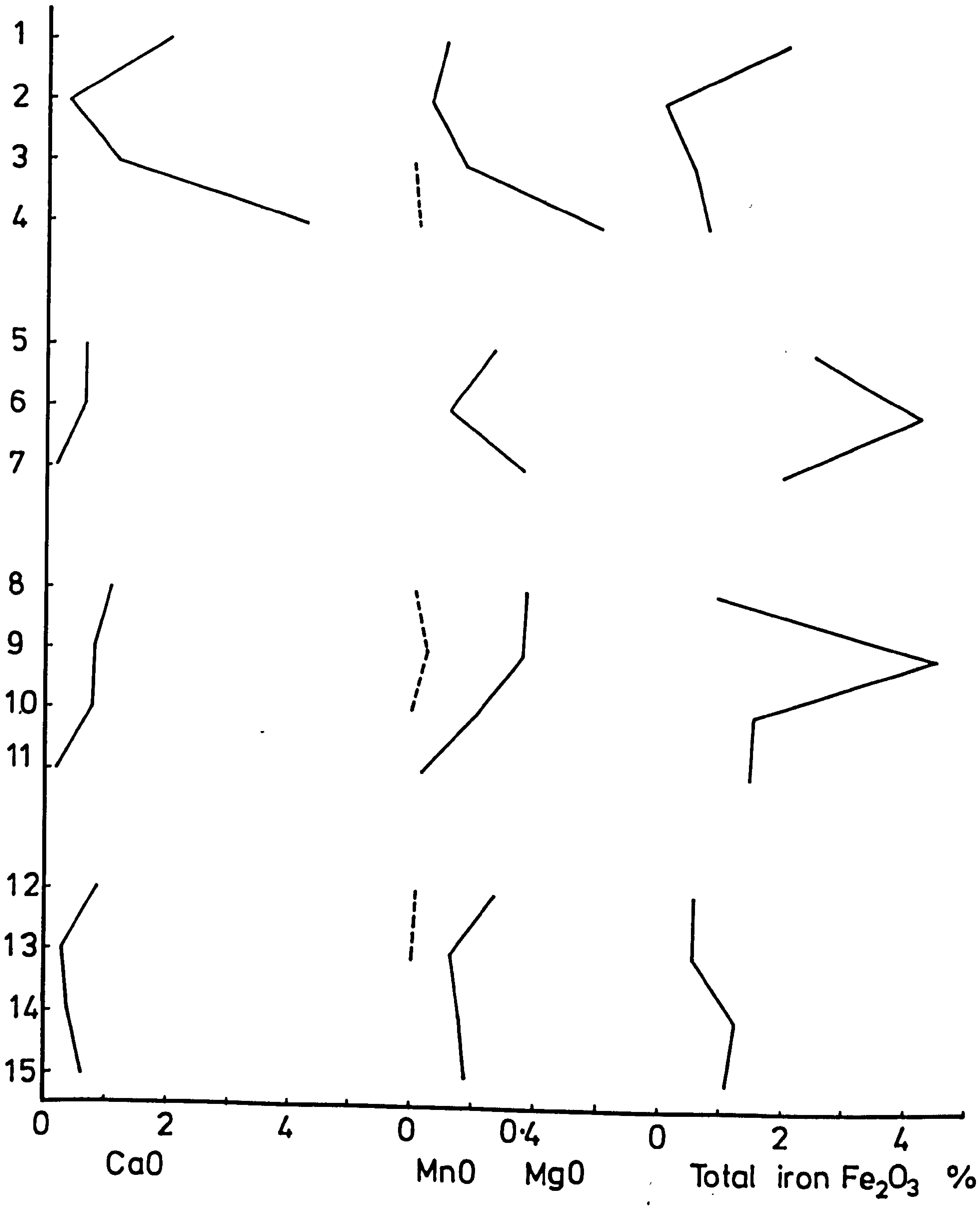


FIGURE 8.13 SO_3, CO_2 and FeO (selected) profiles through the grouped coal samples.

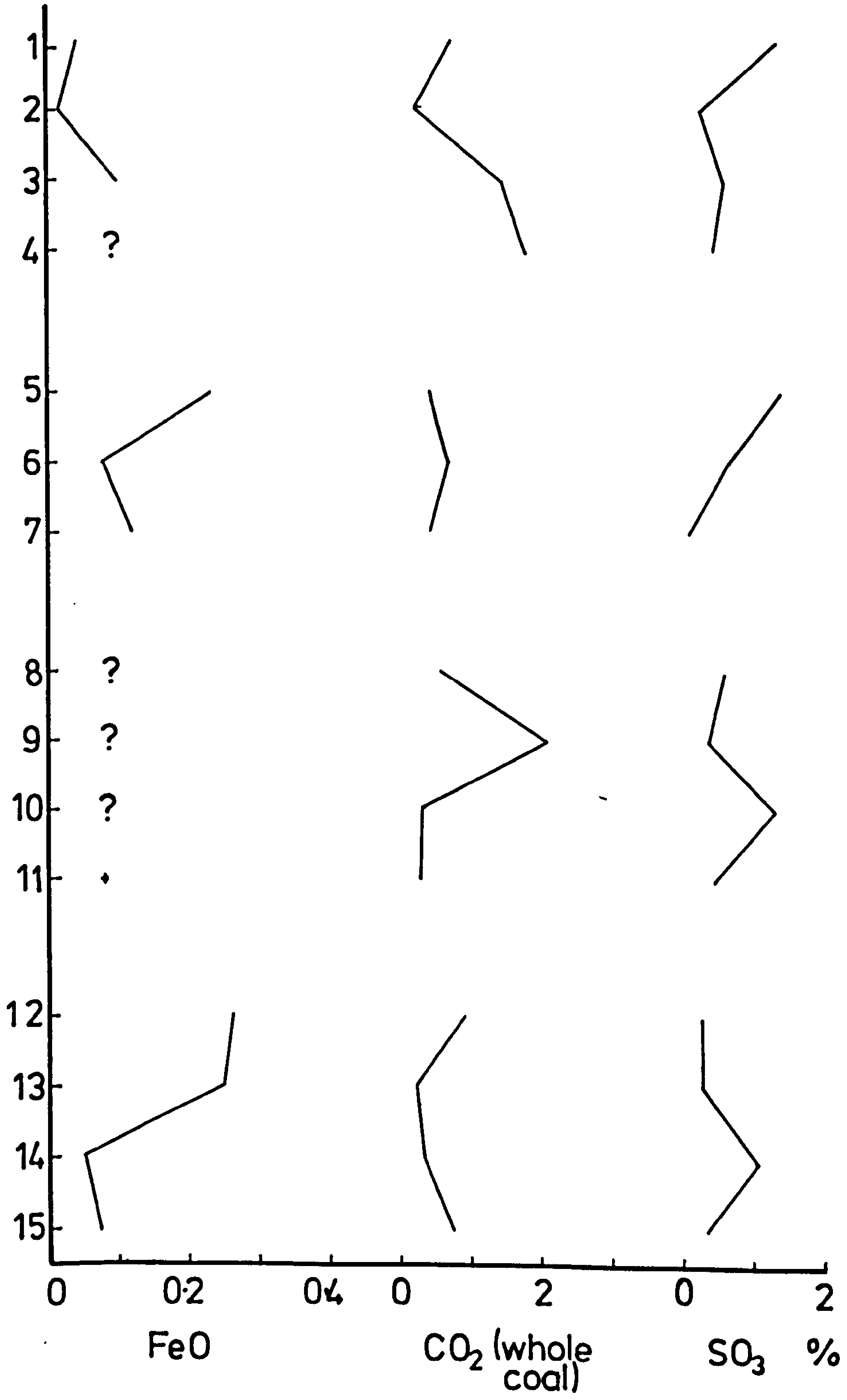


FIGURE 8.14 Losses and L.T.A. profiles through the grouped coal samples.

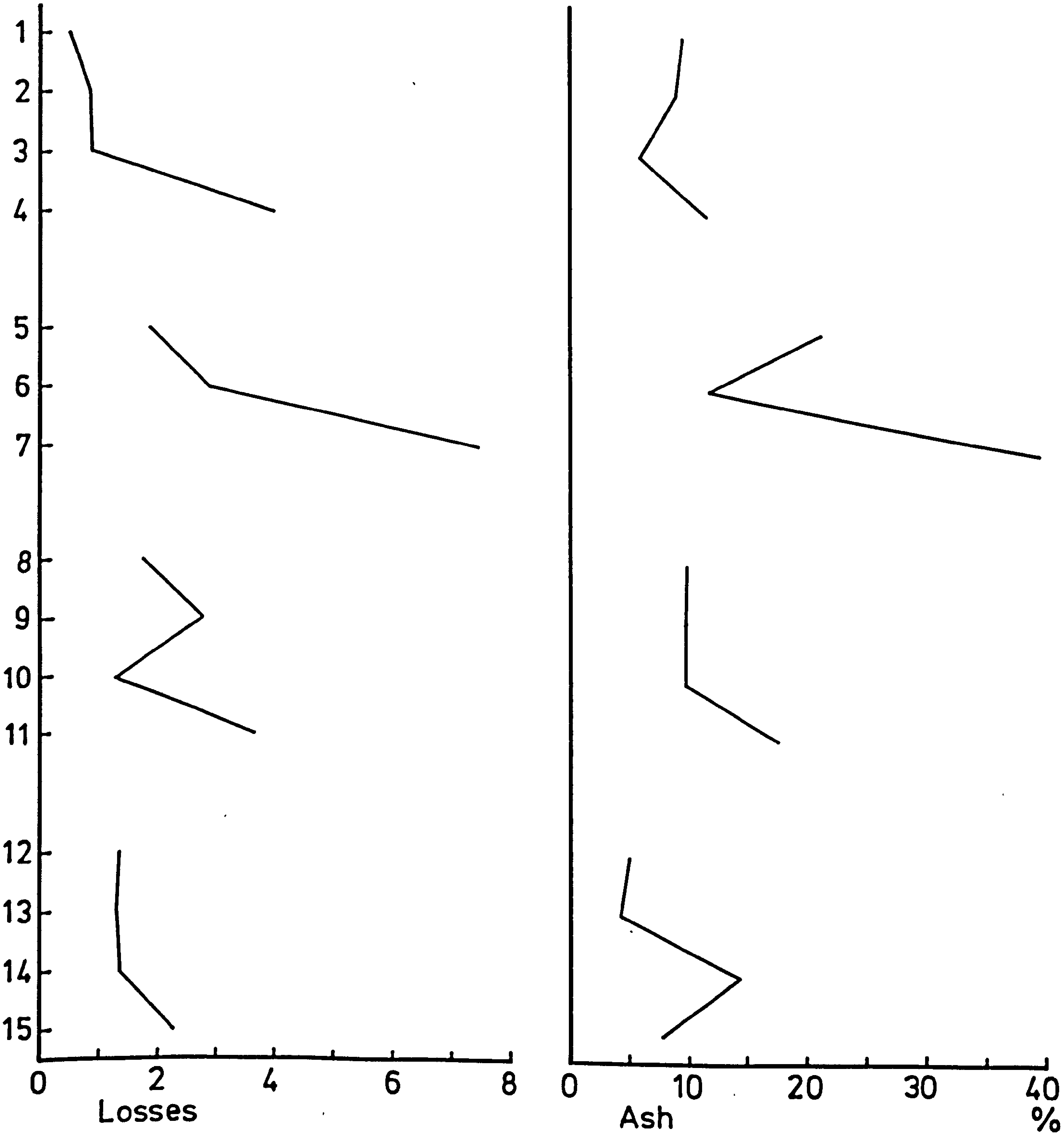


FIGURE 8.15 P_2O_5 profiles through the grouped coal samples.

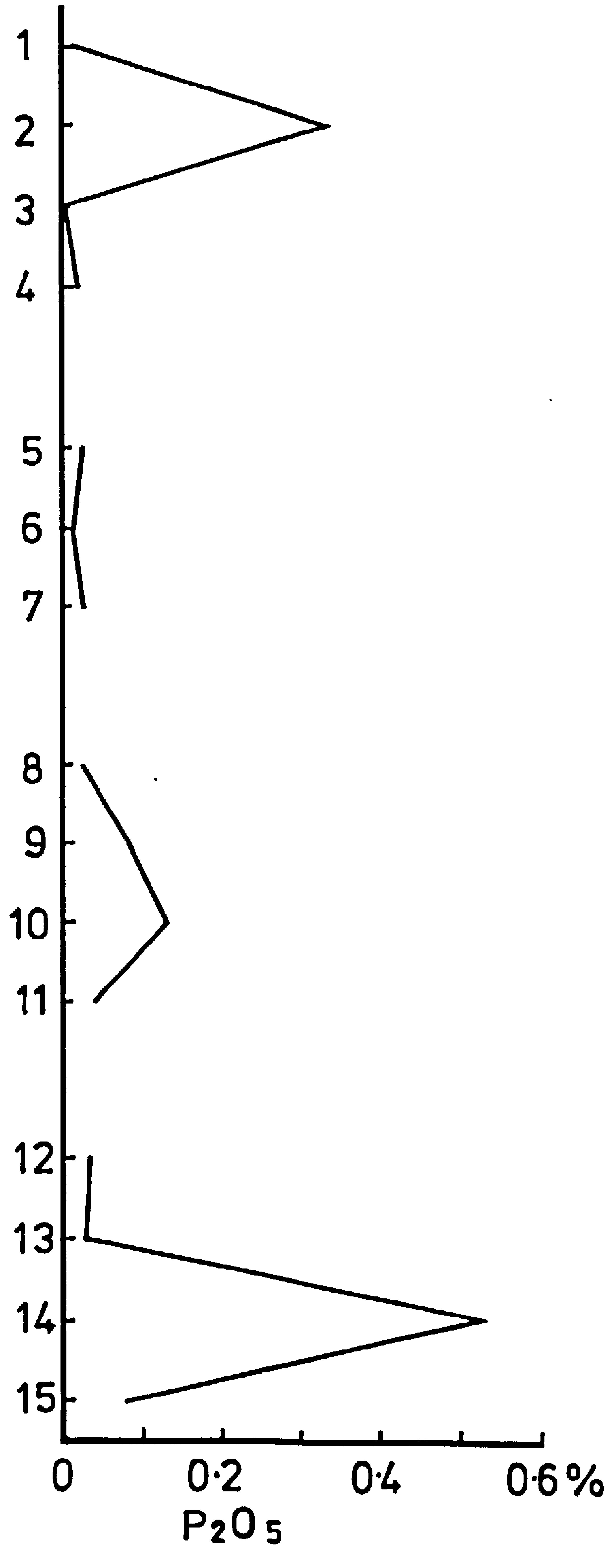


FIGURE 9.1 Cleat Carbonates from selected samples.

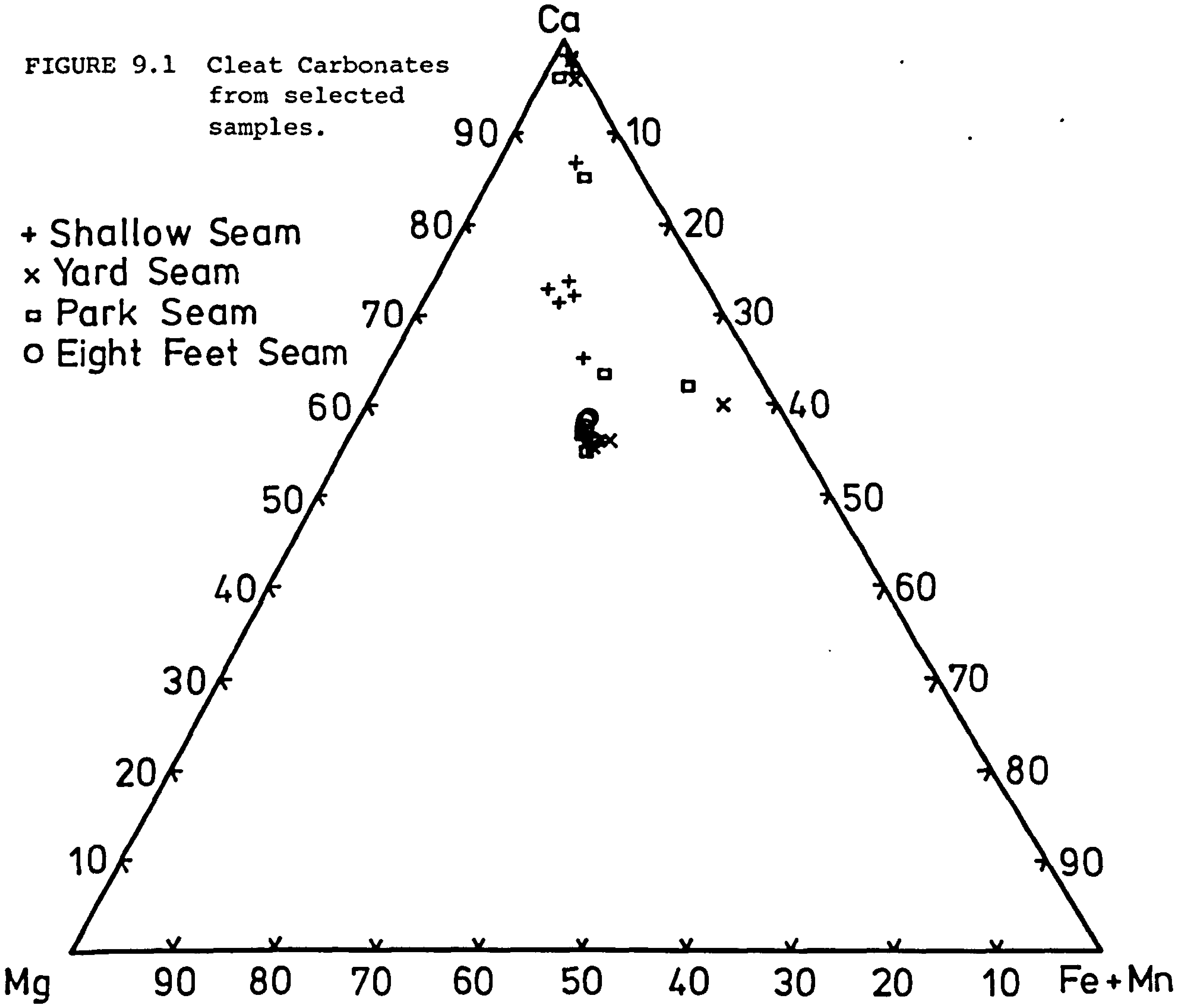


FIGURE 9.2 Carbonate Classification (Watt, 1968).

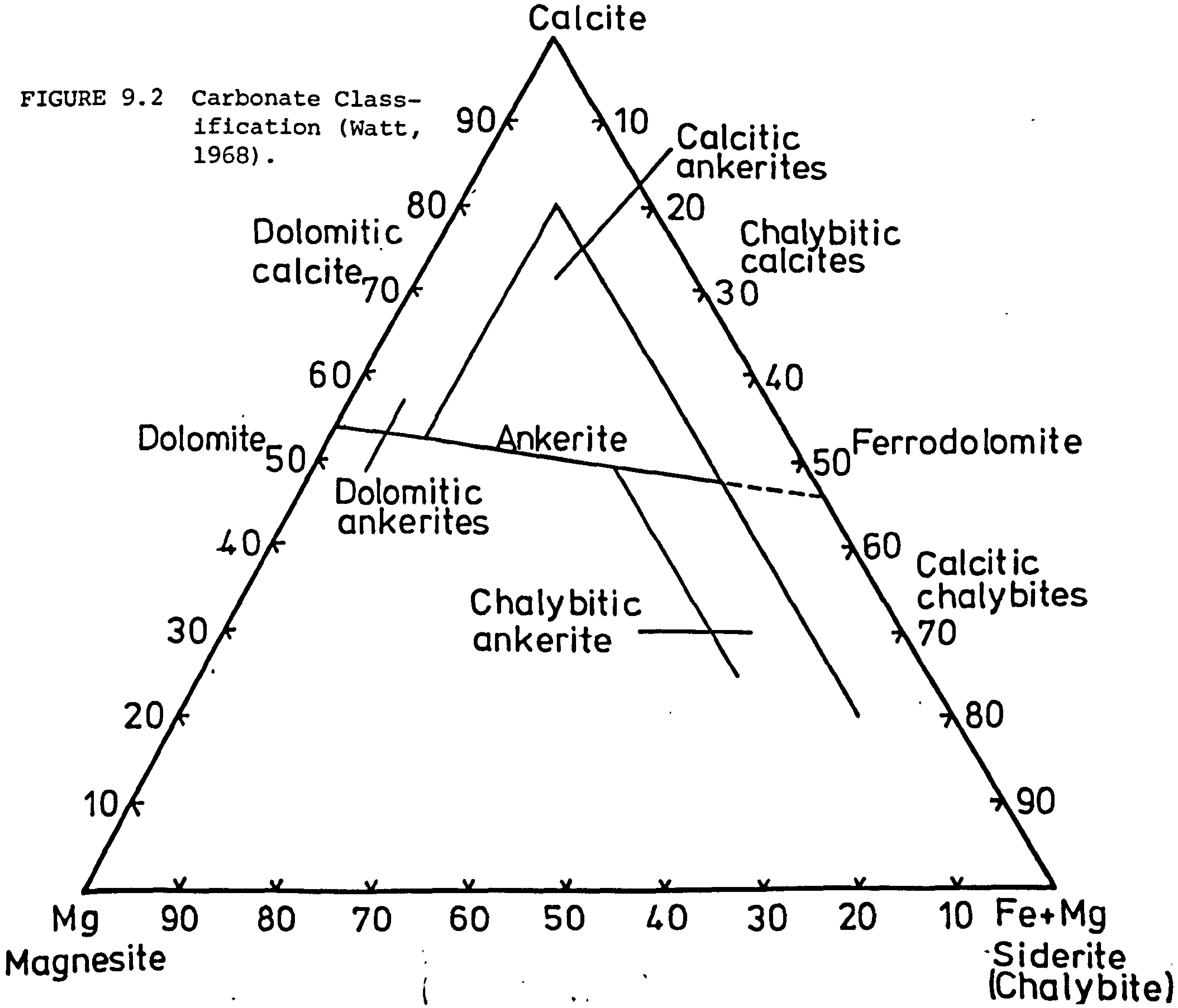


TABLE 9.3 Average compositions of carbonate minerls in British coals (from Pringle and Bradburn, 1958).

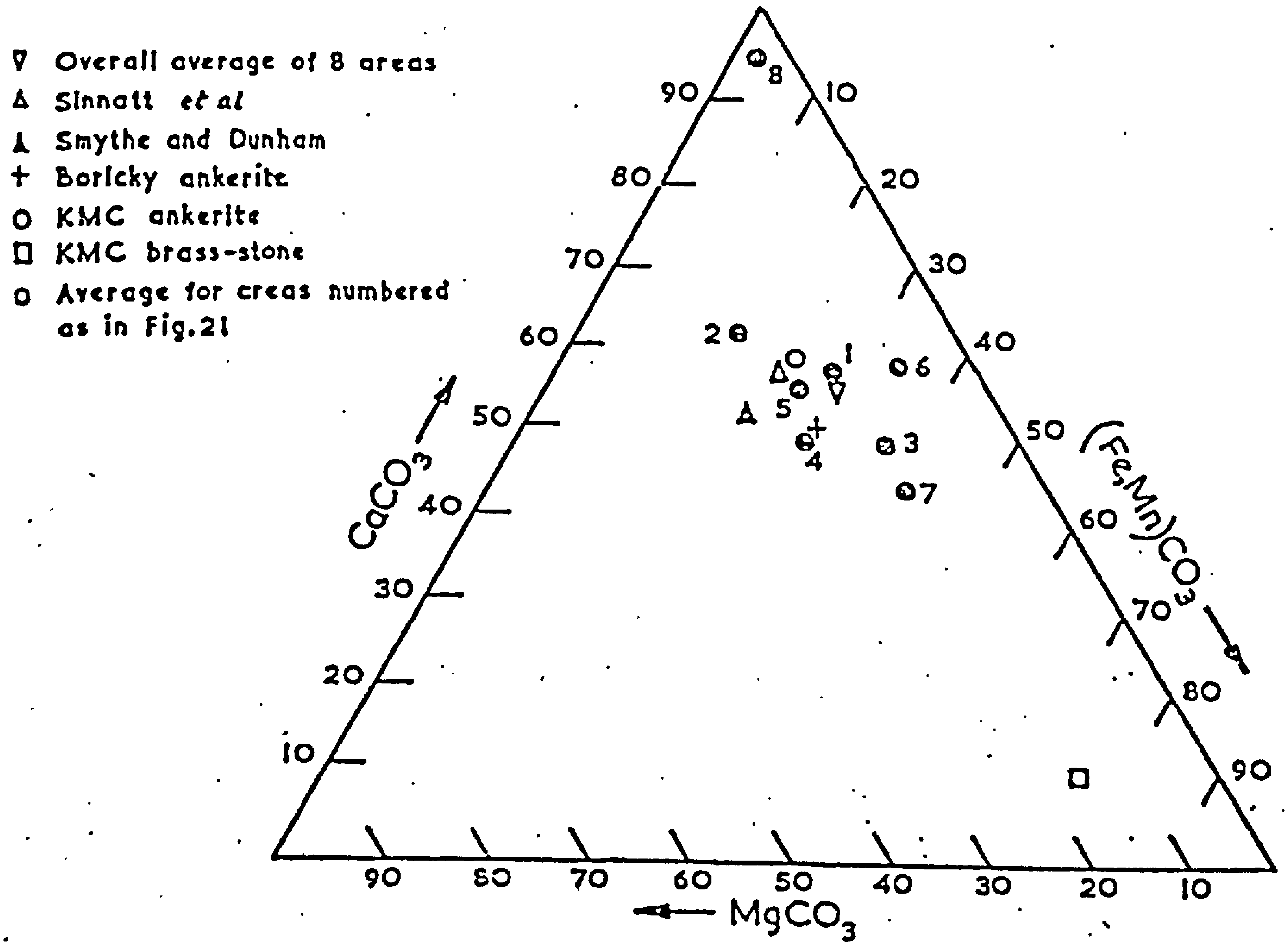
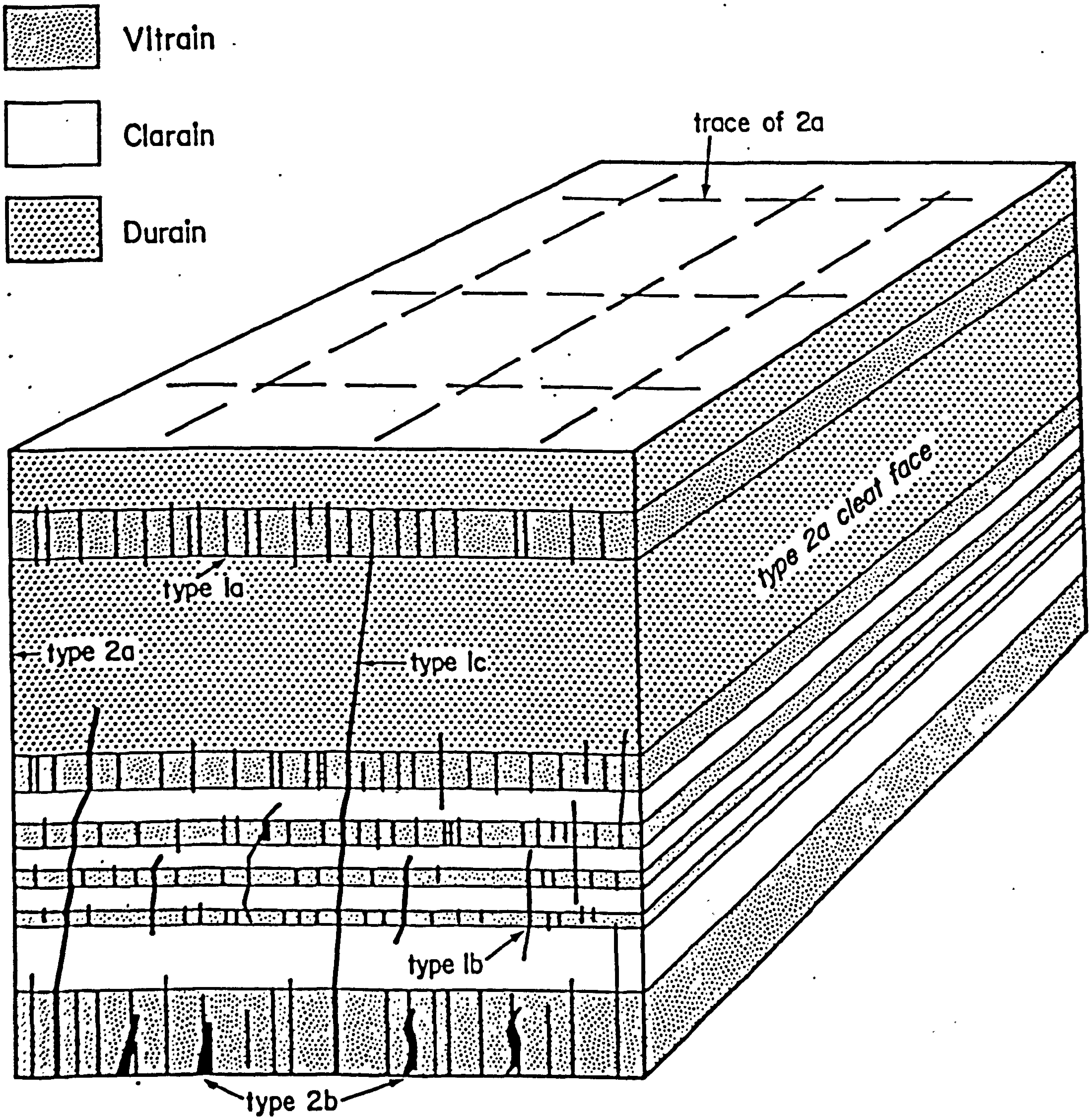


FIGURE 9.4 Classification scheme of coal cleat (Fellows, 1979)



classification scheme of coal cleat (fractures)

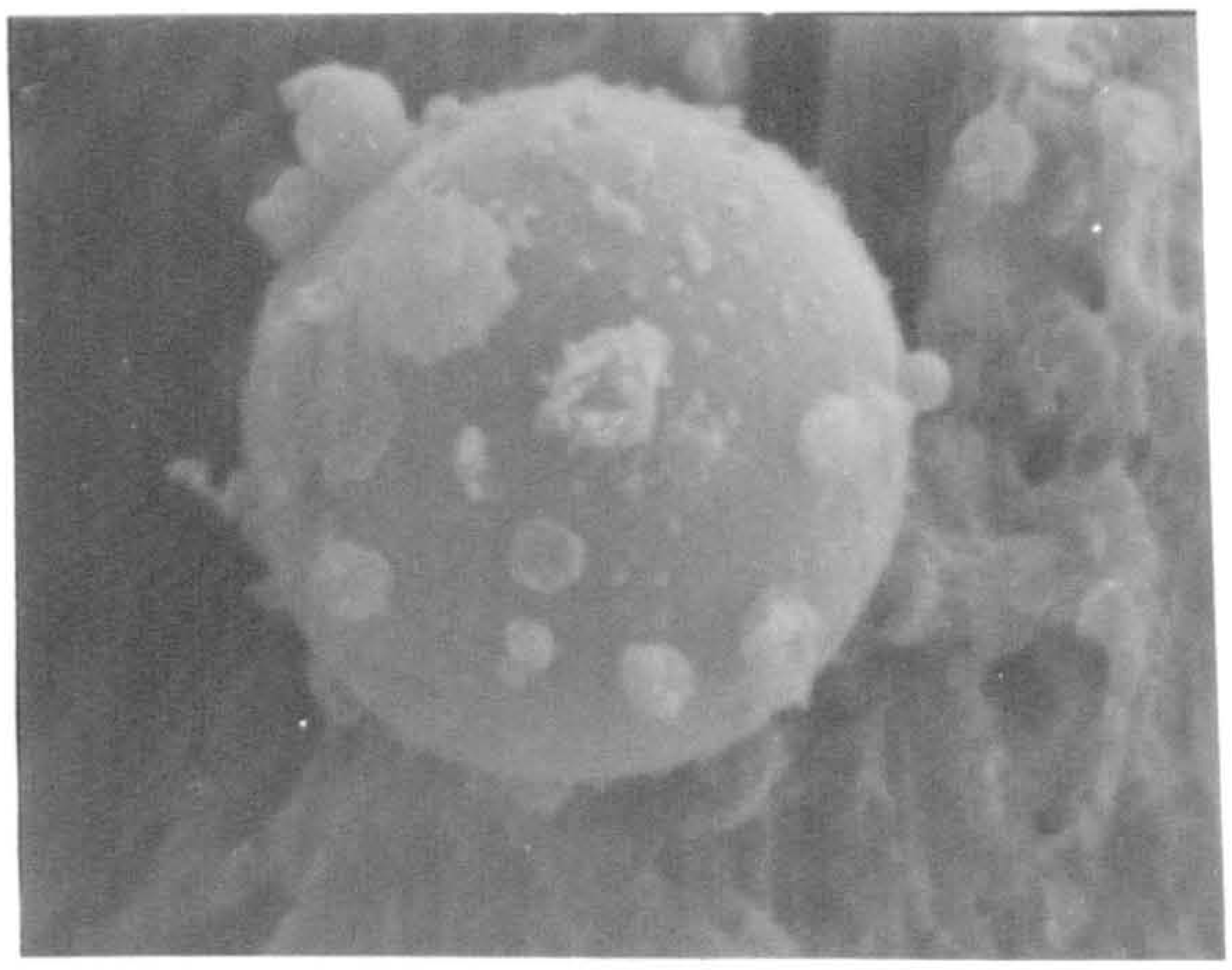


PLATE 5.1 Lead: Bismuth Fusion Sphere produced by L.T.A.

(x5000)

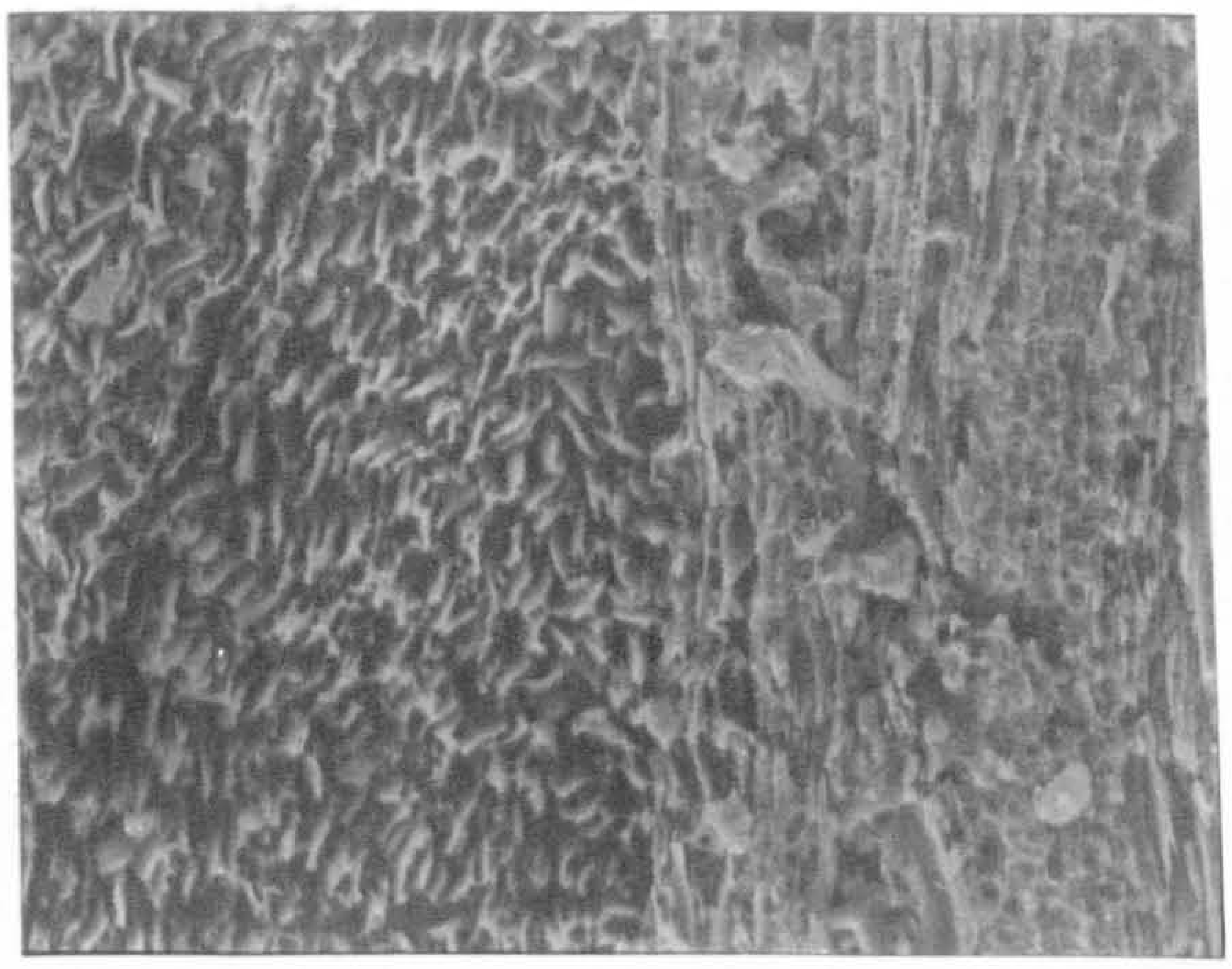


PLATE 5.2 The Effect of L.T.A. on Dull (left) and Bright Coal (right)

(x160)

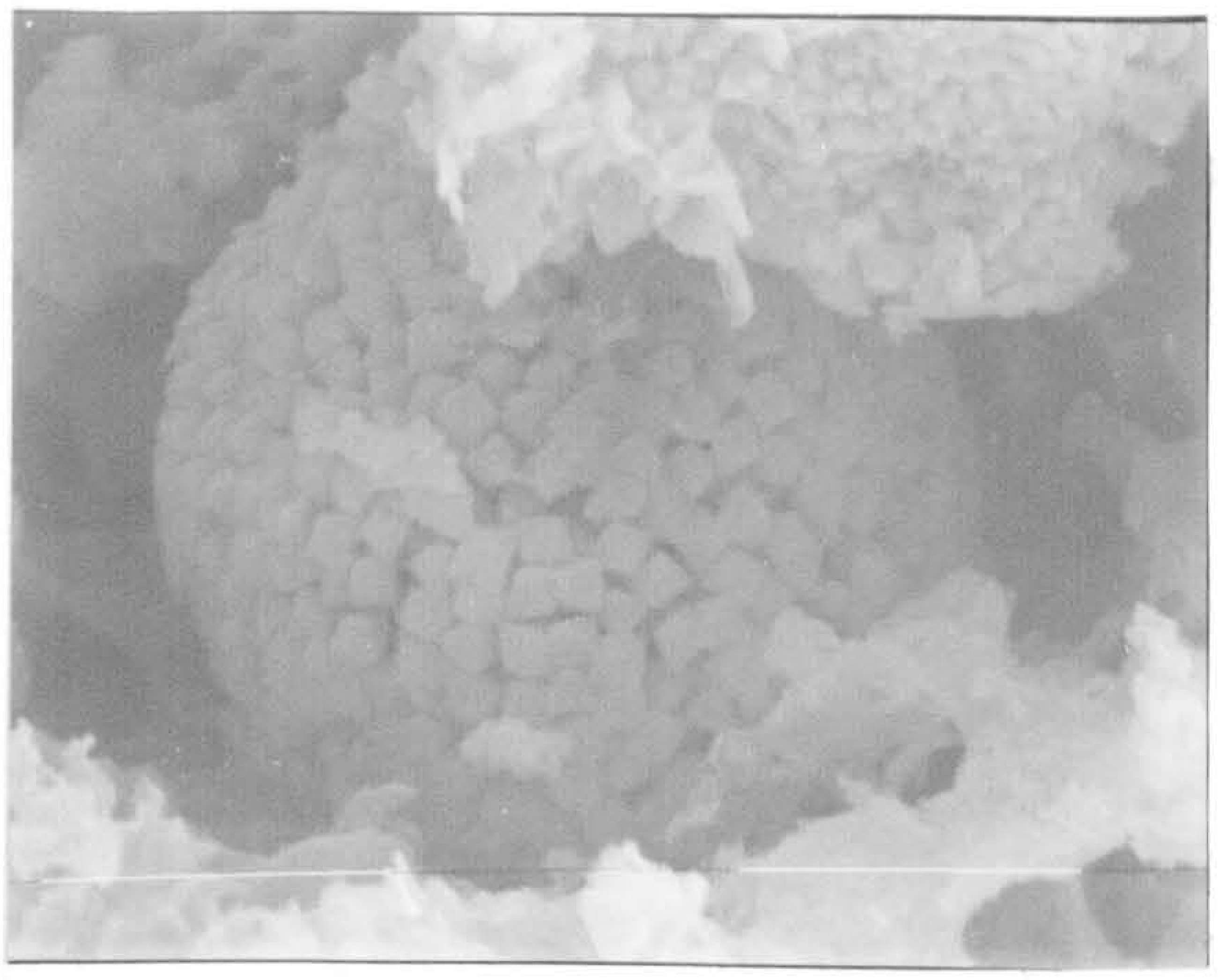


PLATE
8.1 A Pyrite Framboid (scale division 10μm).

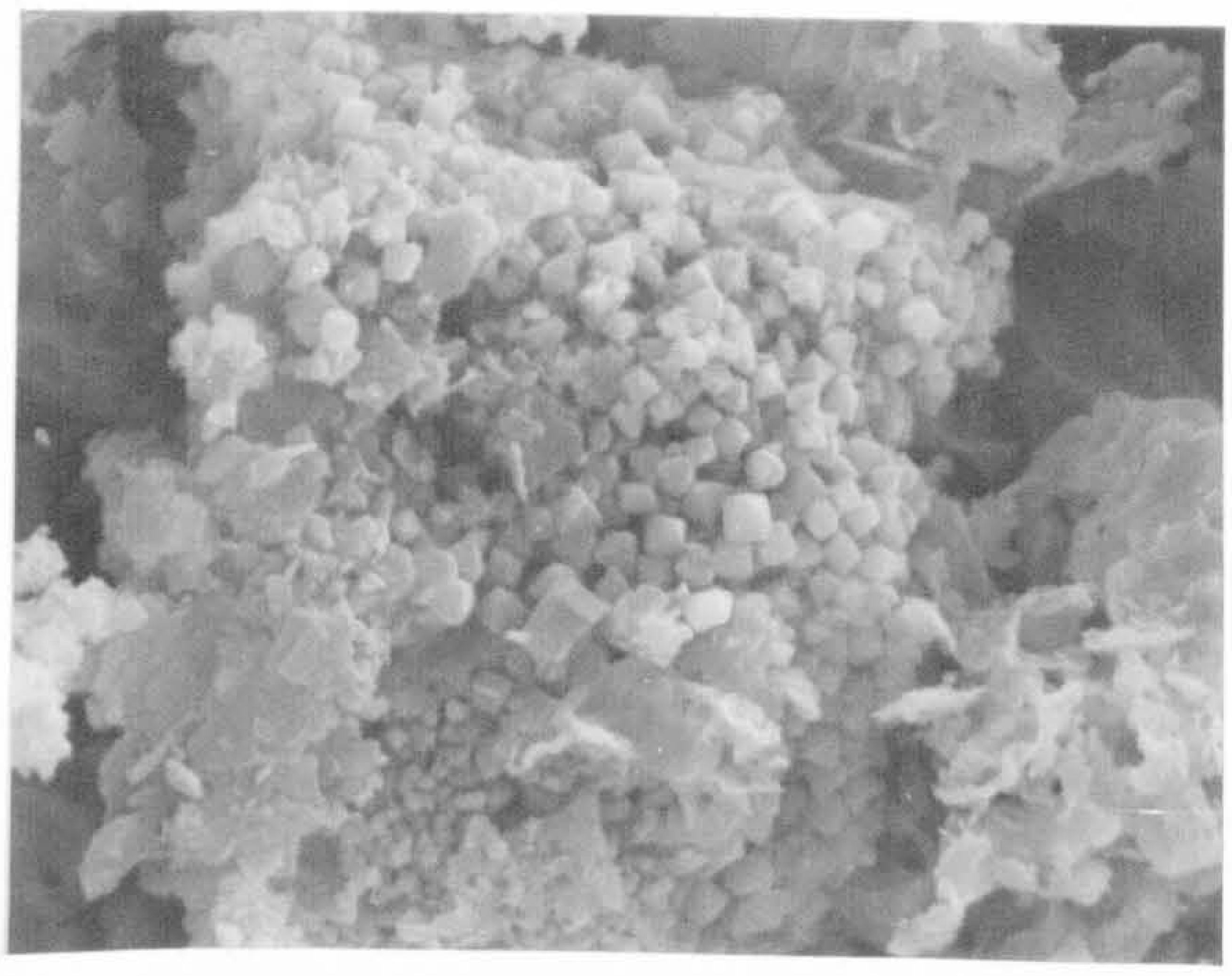


PLATE
8.2 An Irregular Pyrite Framboid.

PLATE
8.3 Close-up of Pyrite Crystals in 8.1.

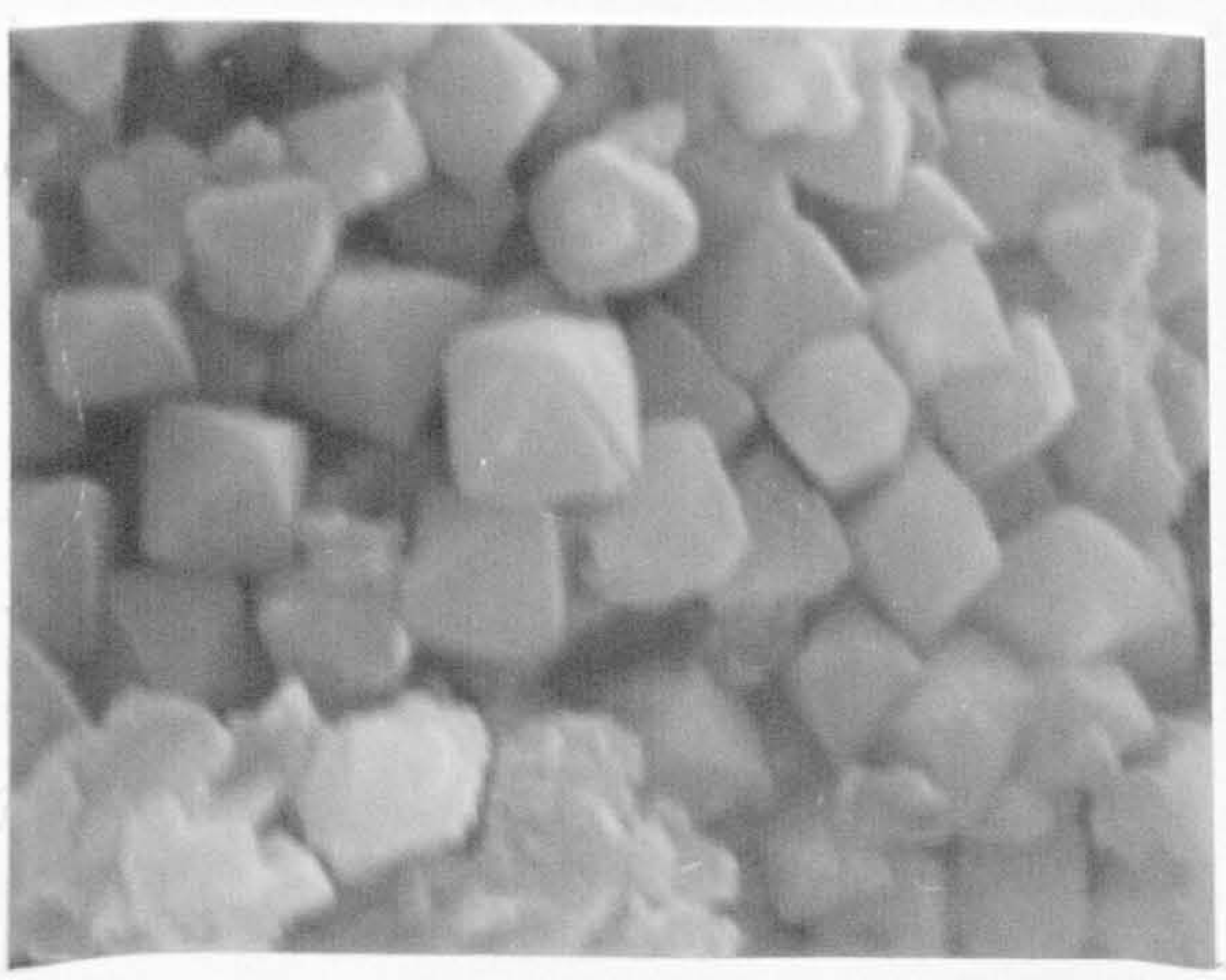


PLATE
8.4 Close-up of Pyrite Crystals in 8.2.

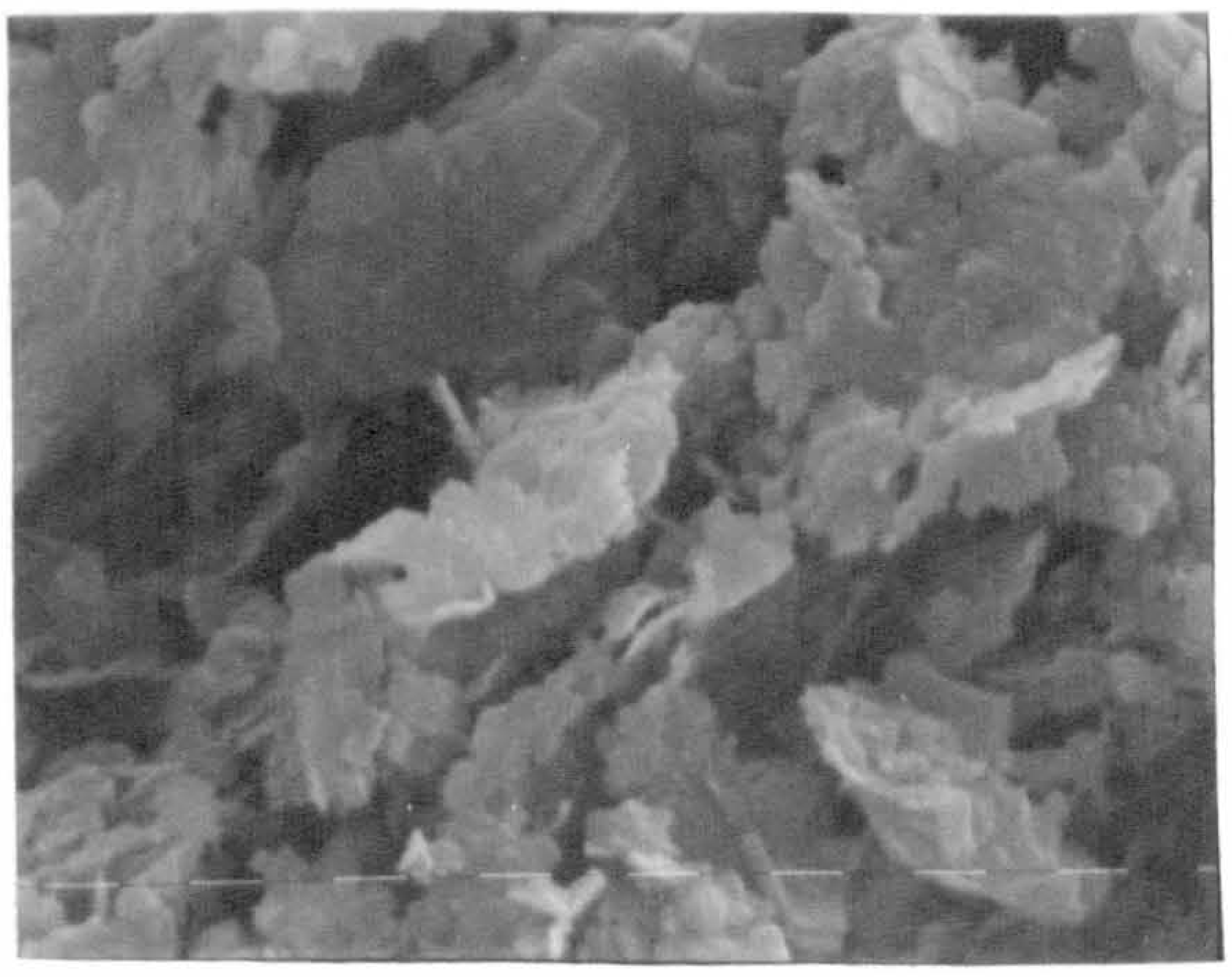


PLATE
8.5 Kaolinite in Coal after L.T.A.

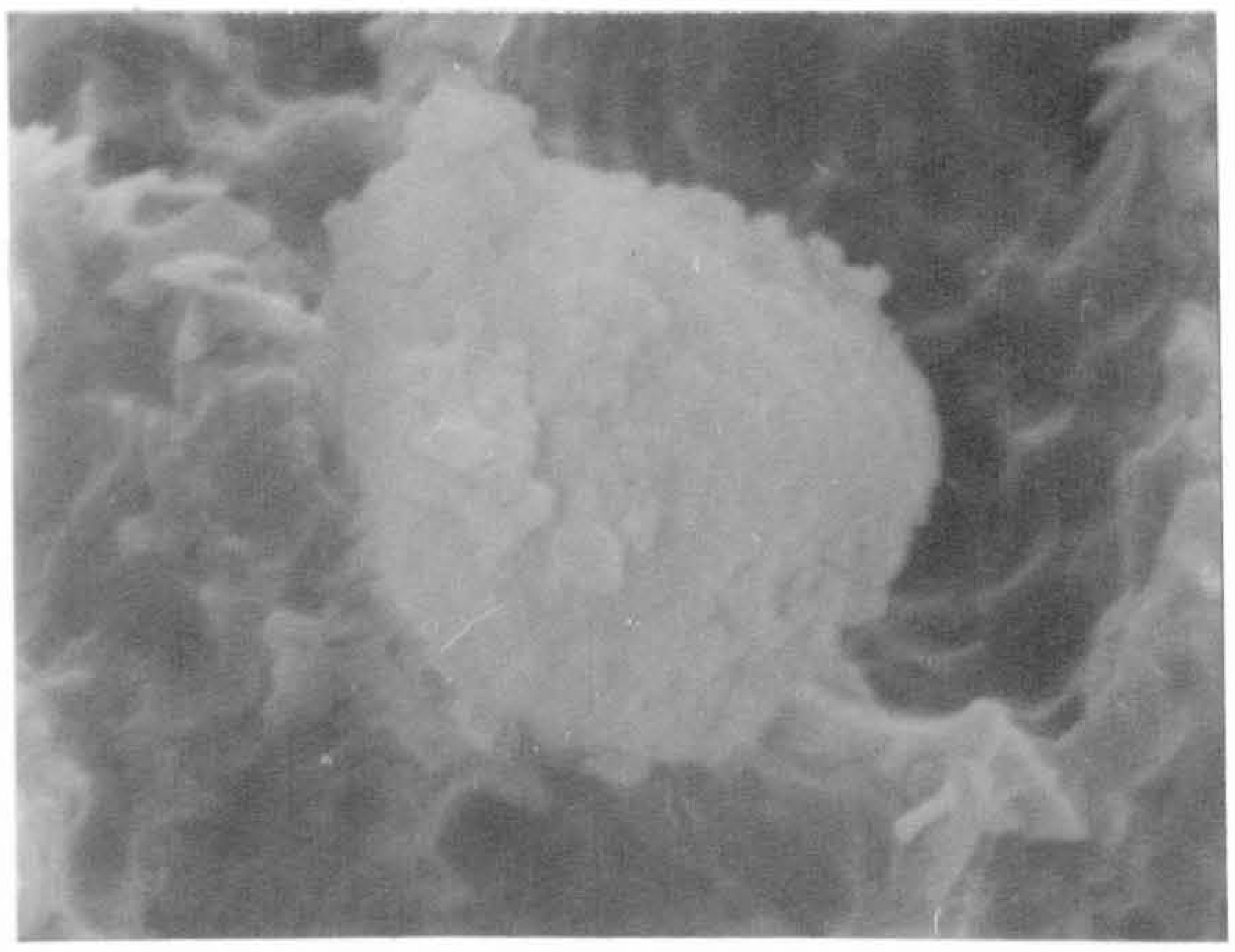


PLATE
8.6 Irregular Quartz Grain.

0 5 µm

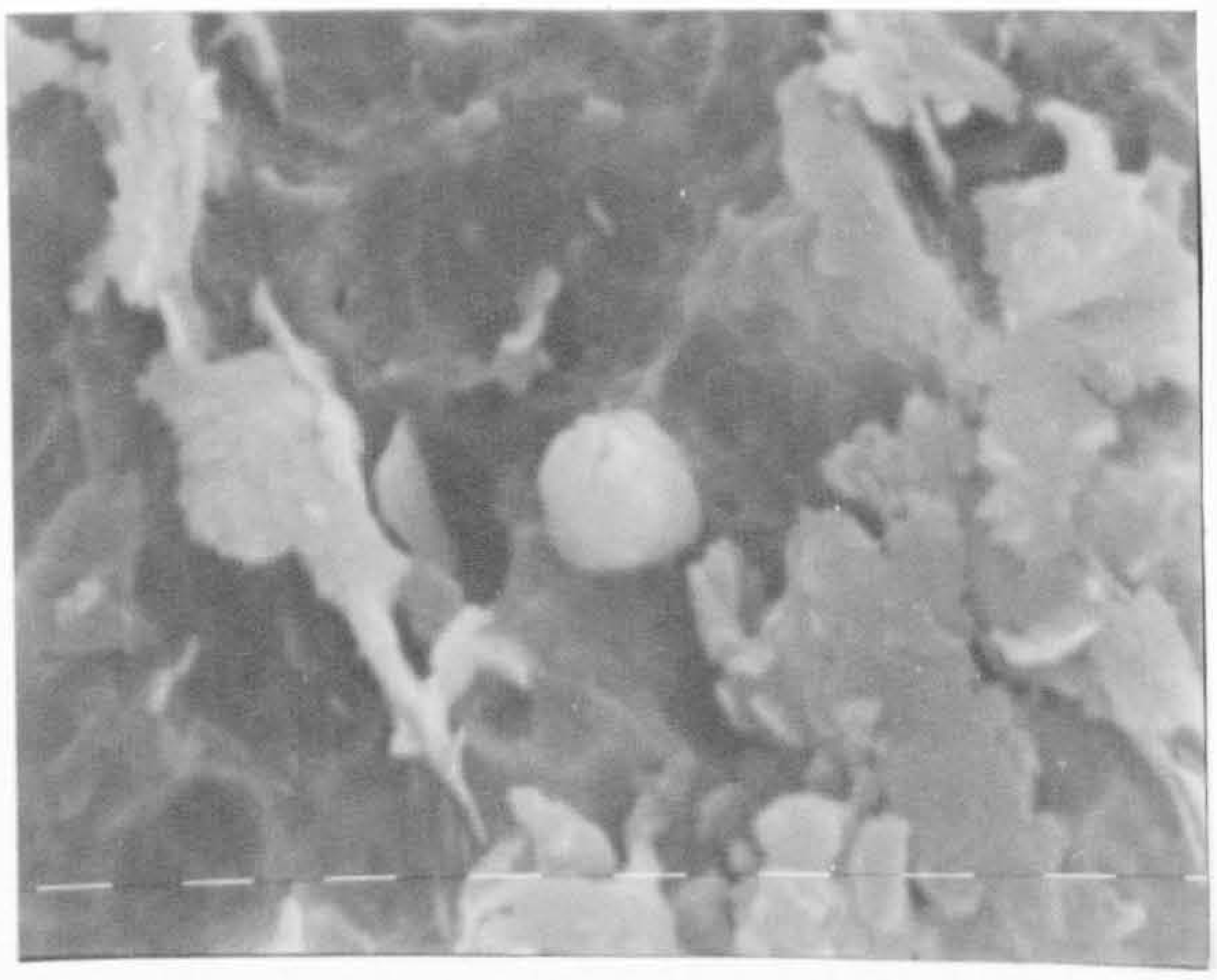


PLATE
8.7 Sub-rounded Quartz Grain.

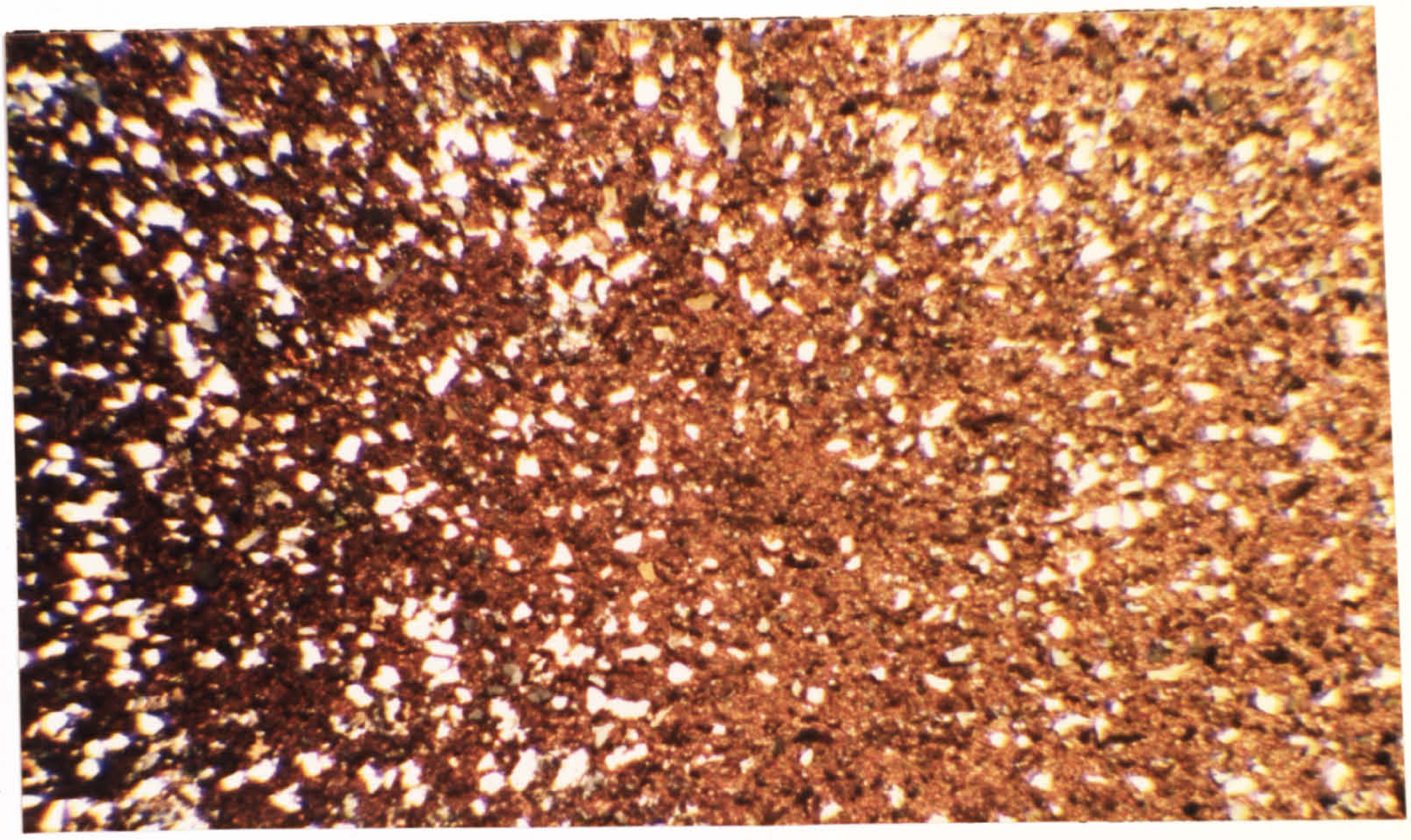


PLATE 8.8 C.P.L. and Reflected Light Section, through a Stigmaria. Note quartz crystals in a pyrite ground mass. (x 30)

PLATE 8.9 Cuspate Diagenetic Quartz in Stigmaria, surrounded by a Pyrite Ground-mass. Note occasional mica lath. (x 75)

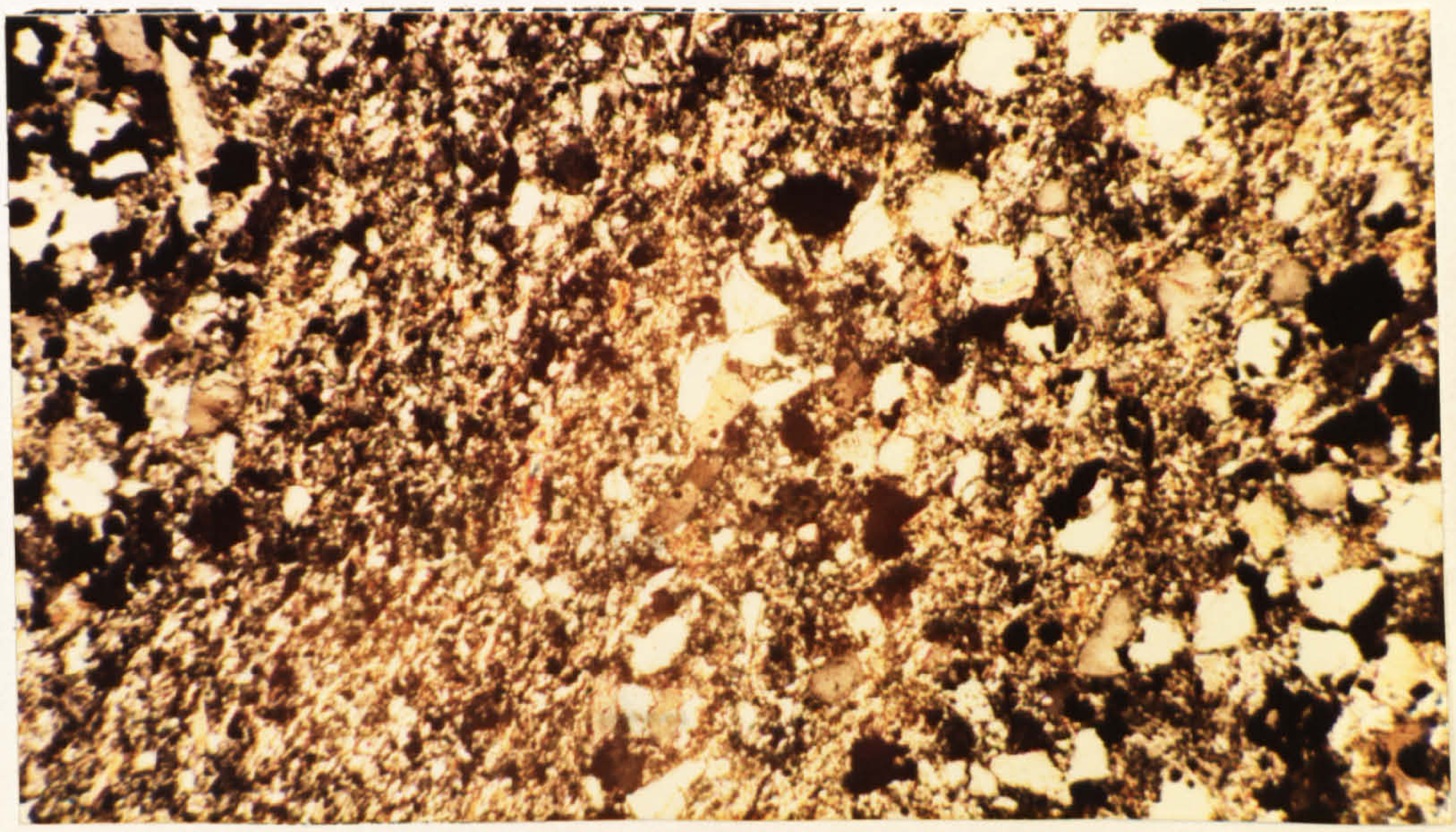


PLATE 8.10 Kaolinite in the Stigmaria Core. Note prefered orientation of Kaolinite and secondary growth in quartz. (x 75)

PLATE 9.1 Pyrite surrounded by Kaolinite in Shallow Seam Cleat (x 700)

PLATE 9.2 Pyrite Ornamentation (x3500).

PLATE 9.3 Subhedral Pyrite in Y7 Cleat (x350).

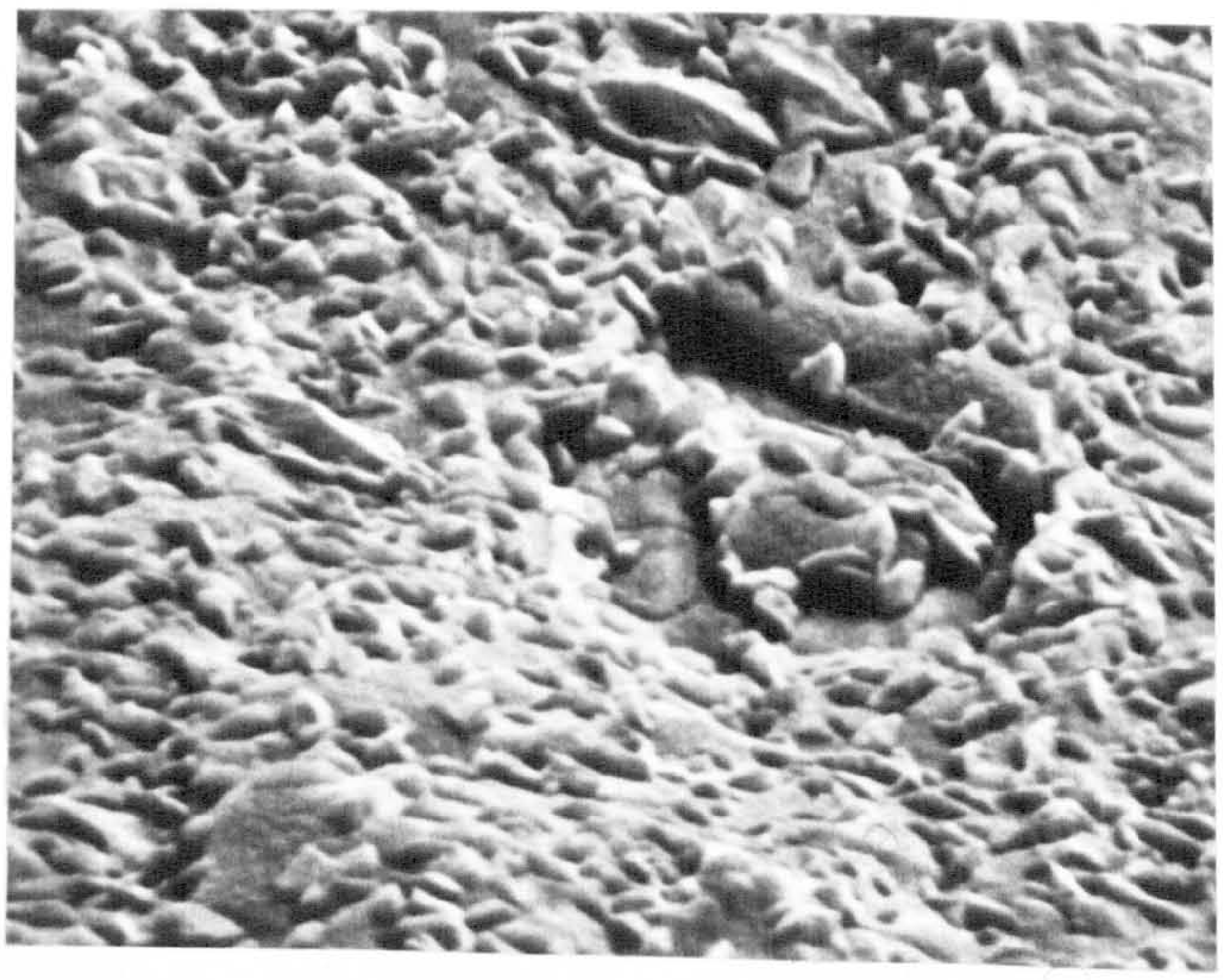


PLATE 9.4 Surface Relief of Pyrite (9.3) showing a Prefered Orientation (x3500).

PLATE 9.5 Surface Relief of Pyrite (x3500).

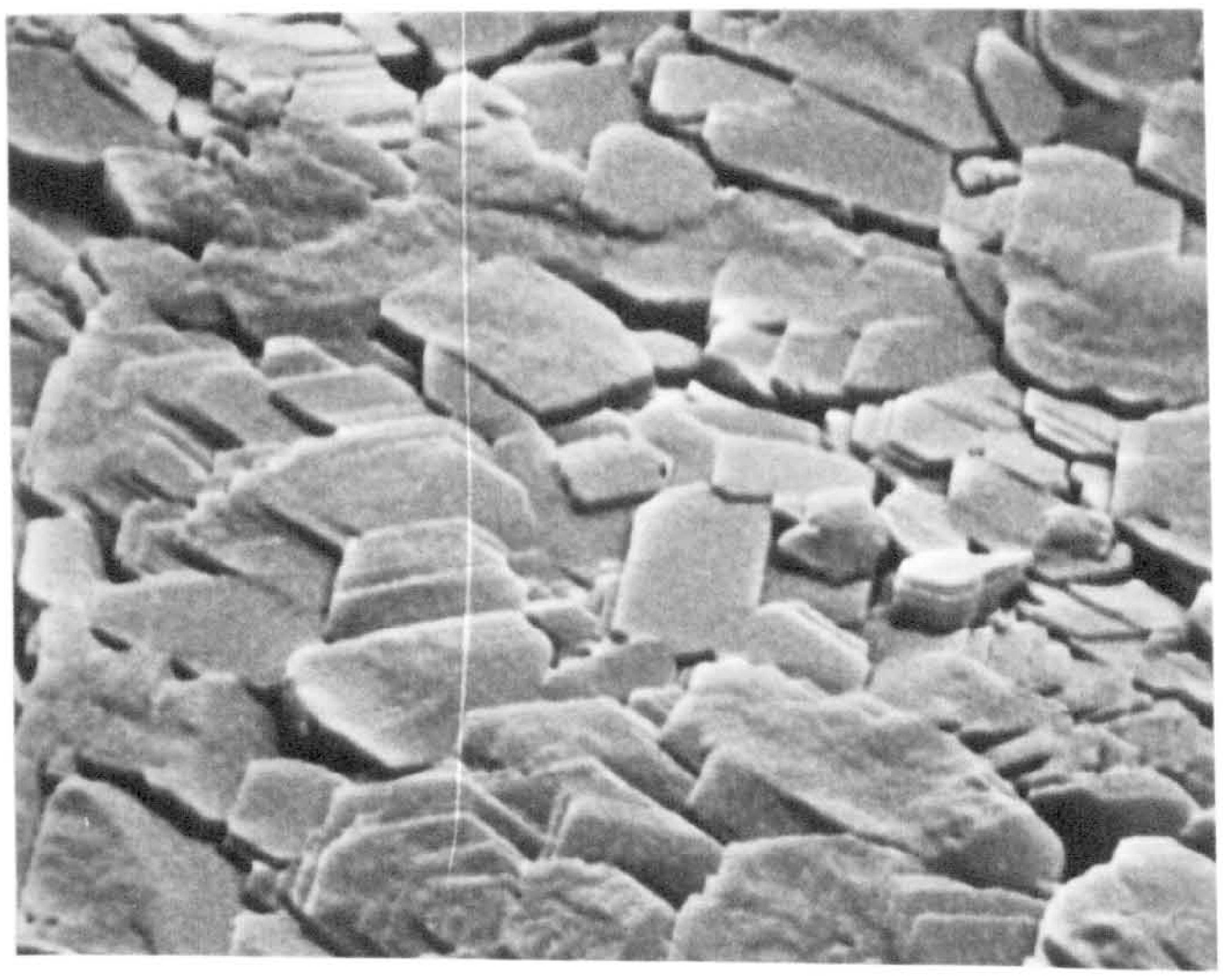


PLATE 9.6 Shallow Seam Cleat Kaolinite (x3600).

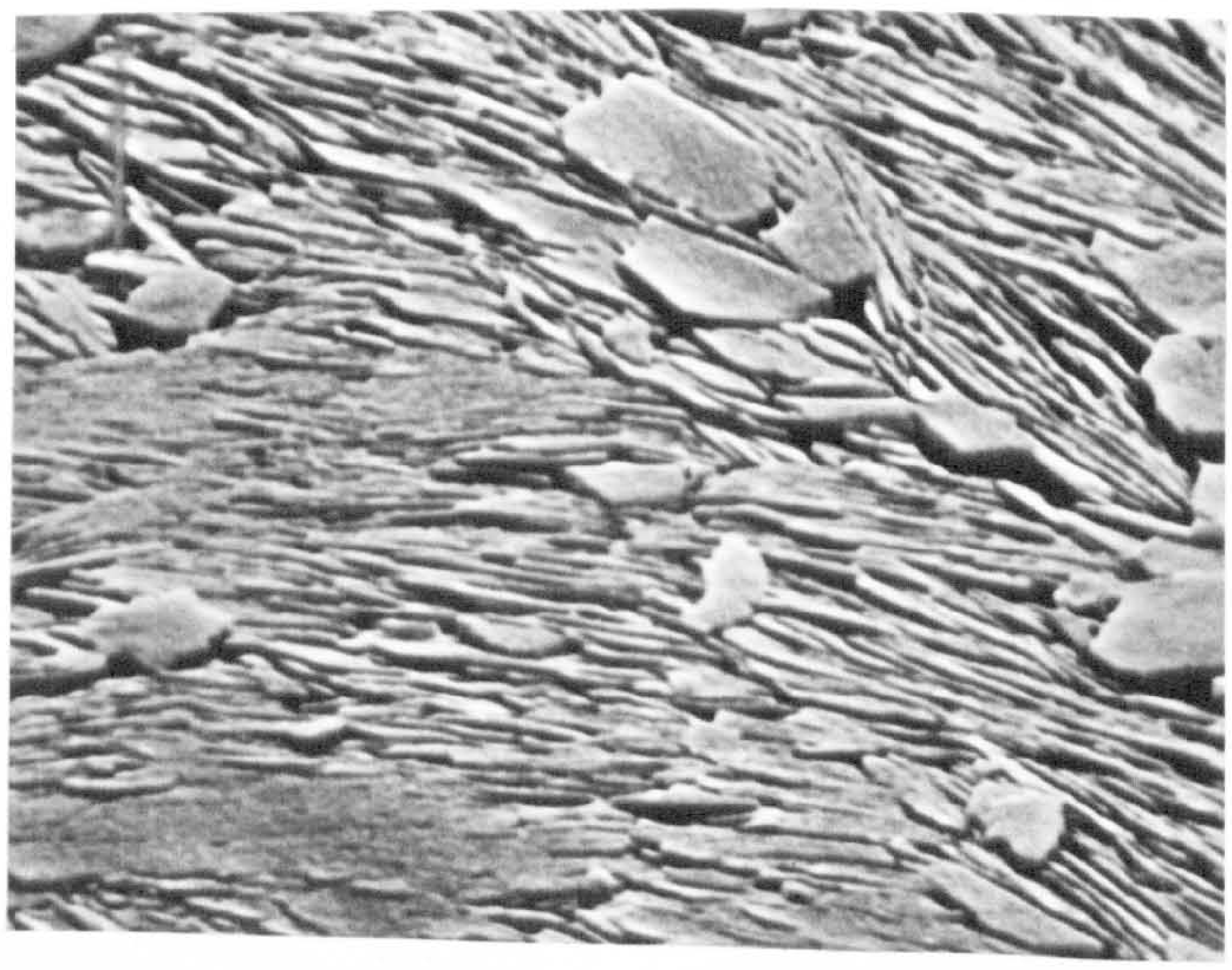


PLATE 9.7 Shallow Seam Cleat Kaolinite (x3800).

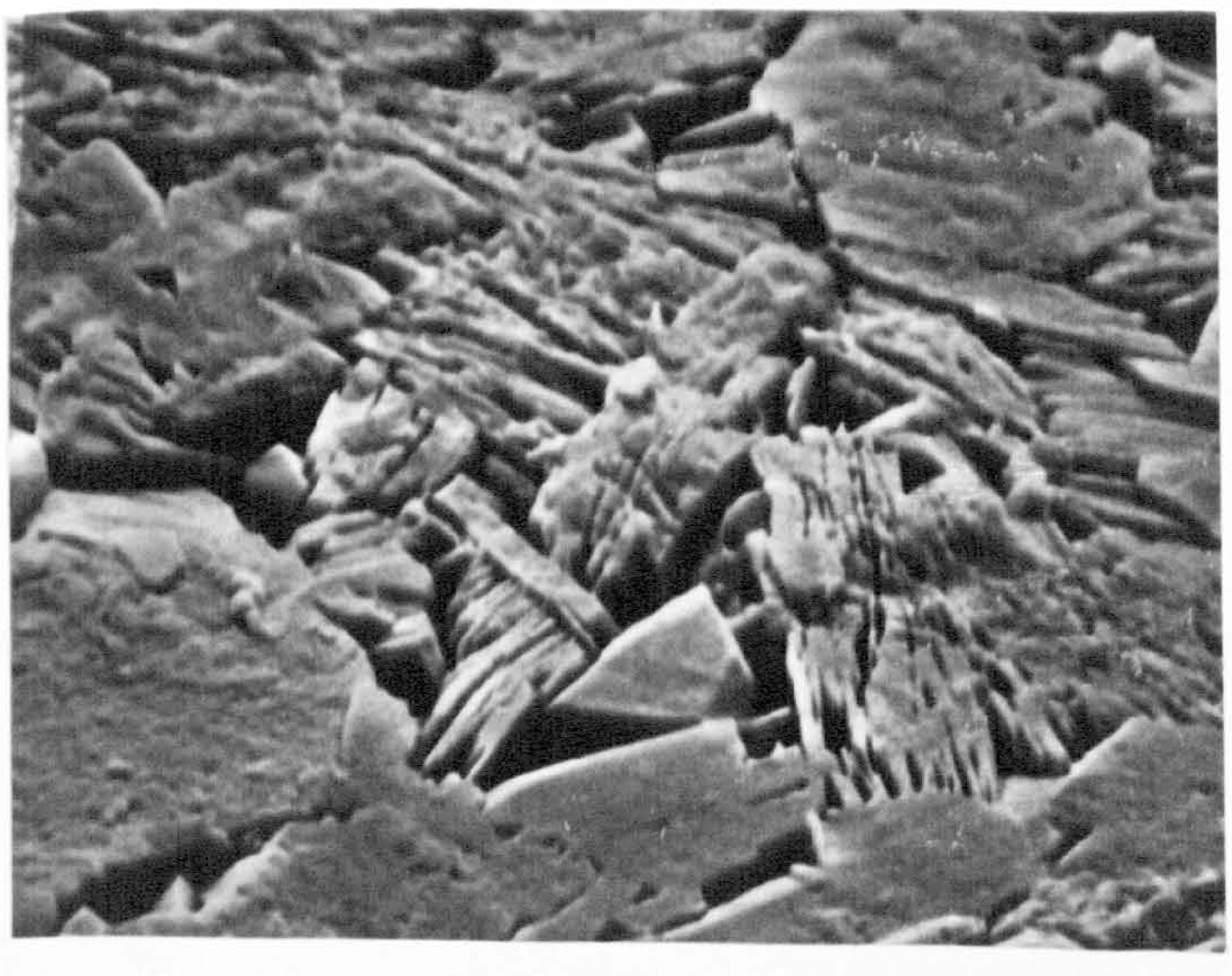


PLATE 9.8 Shallow Seam Cleat Kaolinite showing a high degree of Porosity Between and Within Kaolinite Books (x3600).

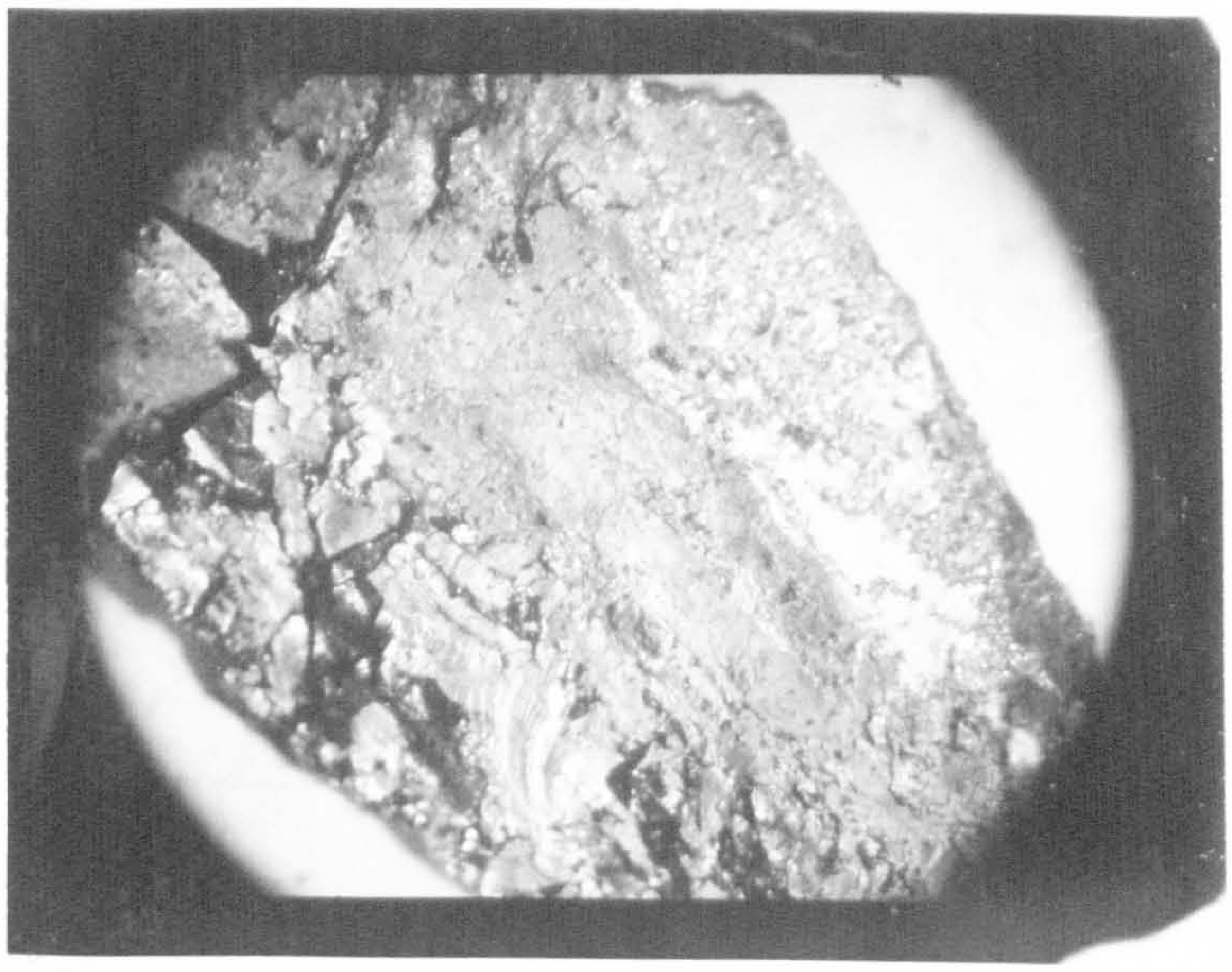


PLATE 9.9 Pyrite and Carbonate in Y7 Cleat showing Differences in Pyrite Surface Form (x15).

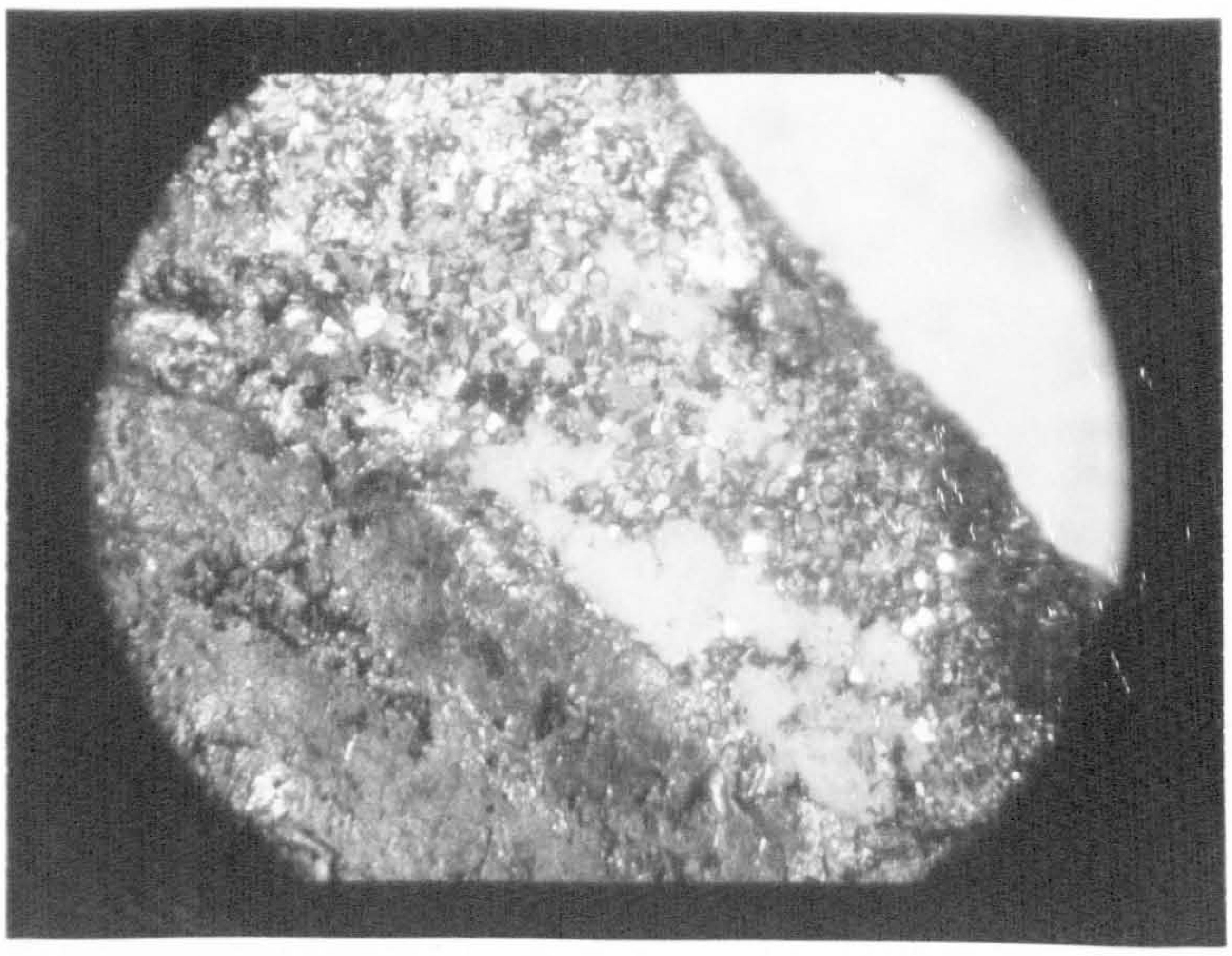


PLATE 9.10 Pyrite and Carbonate Close-up of 9.9 (x25).

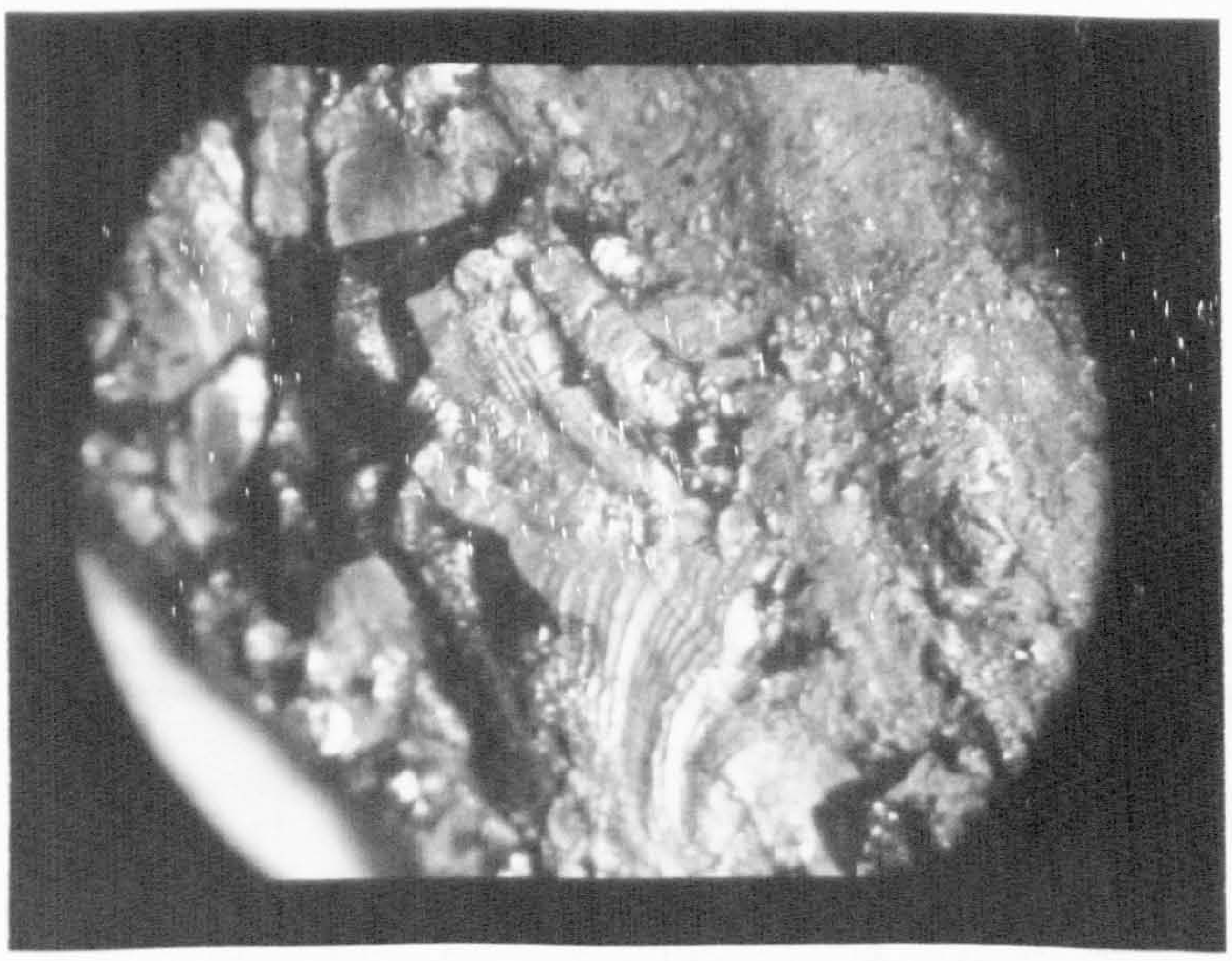


PLATE 9.11 Concentric Pattern in Pyrite Cleat (x 25).

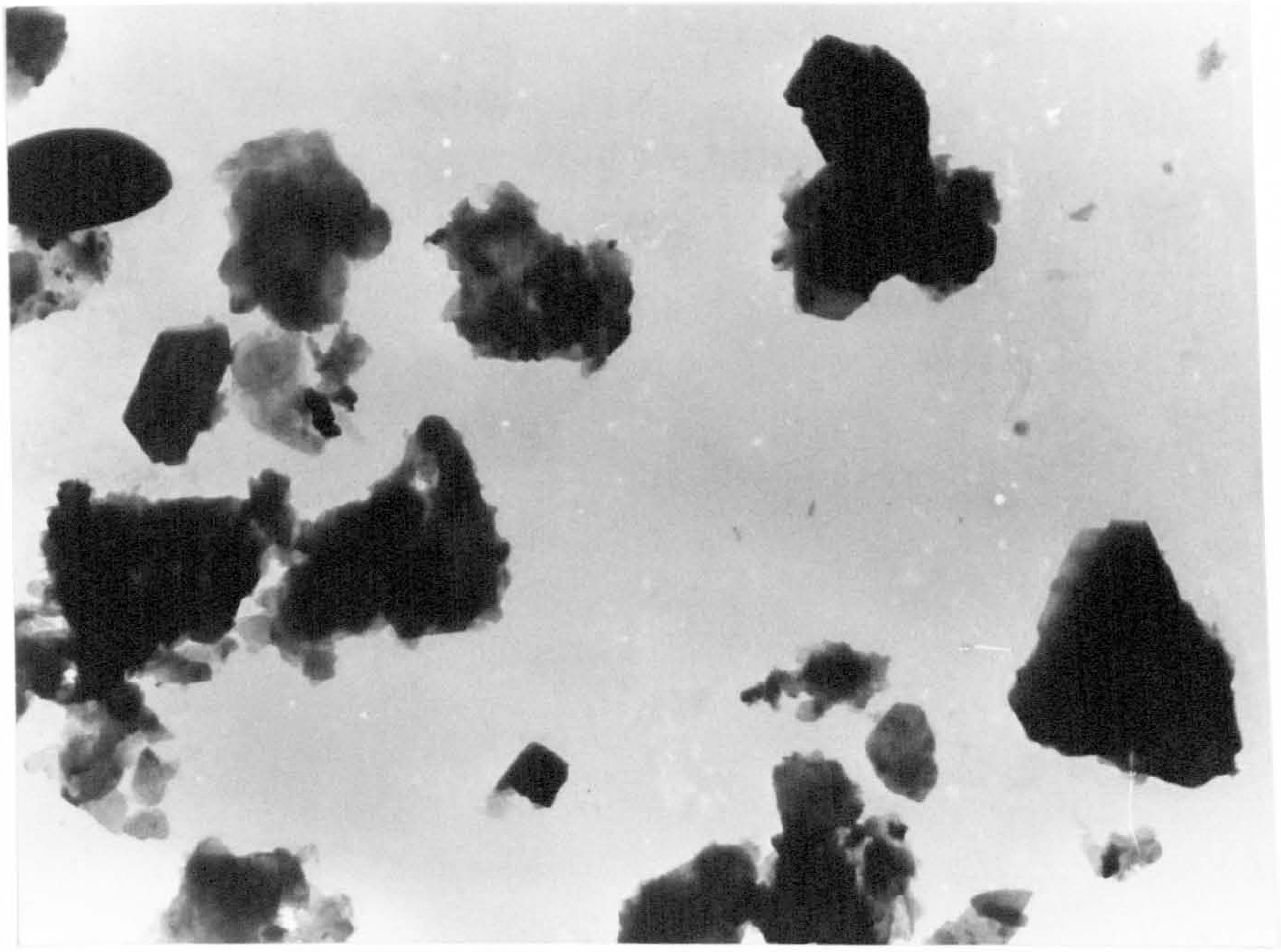


PLATE 9.12 T.E.M. Photomicrographs of Well Crystallised Cleat Kaolinite (x20000).

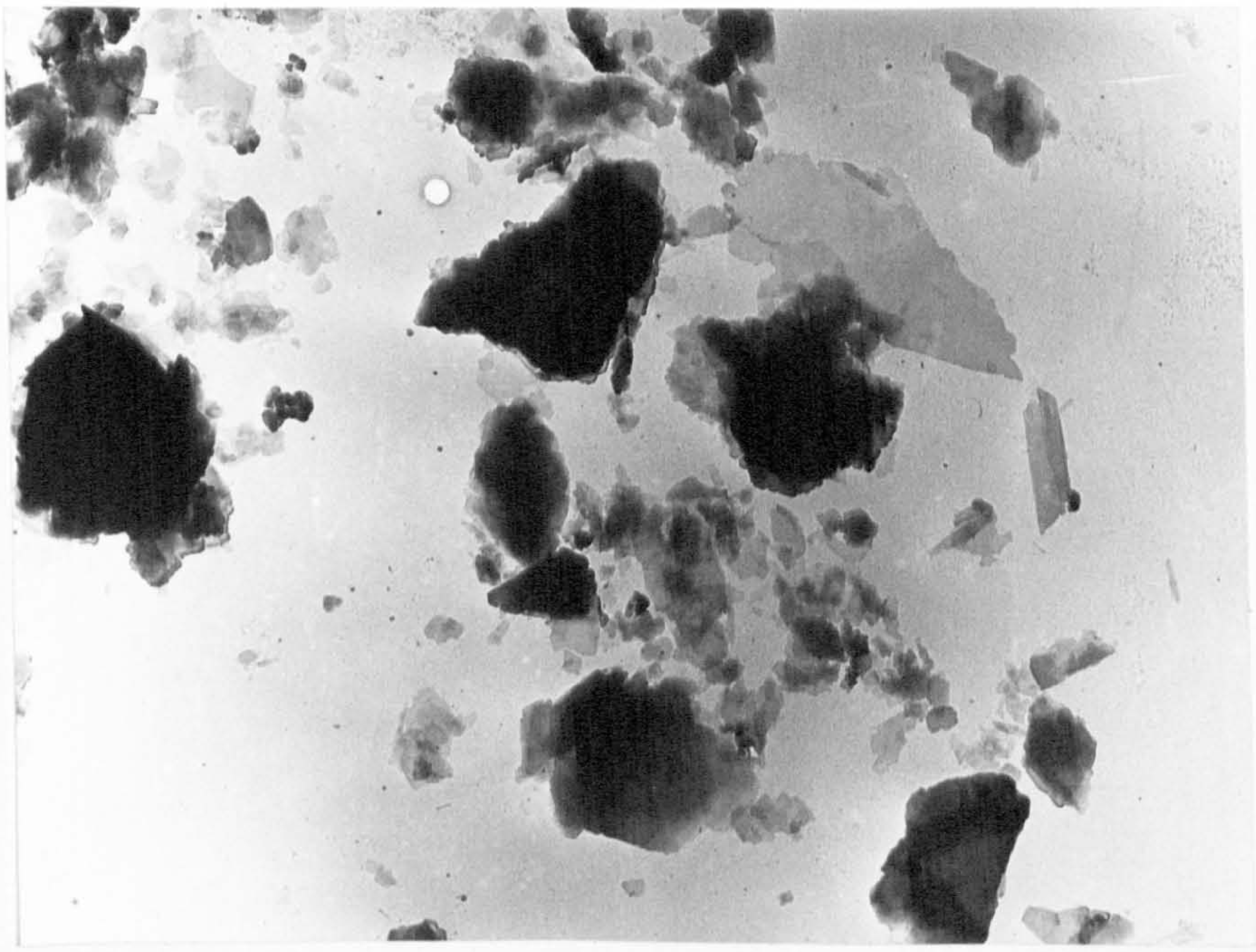


PLATE 9.13 T.E.M. Photomicrograph of Floor Measure (8F1) Clays (x20000).

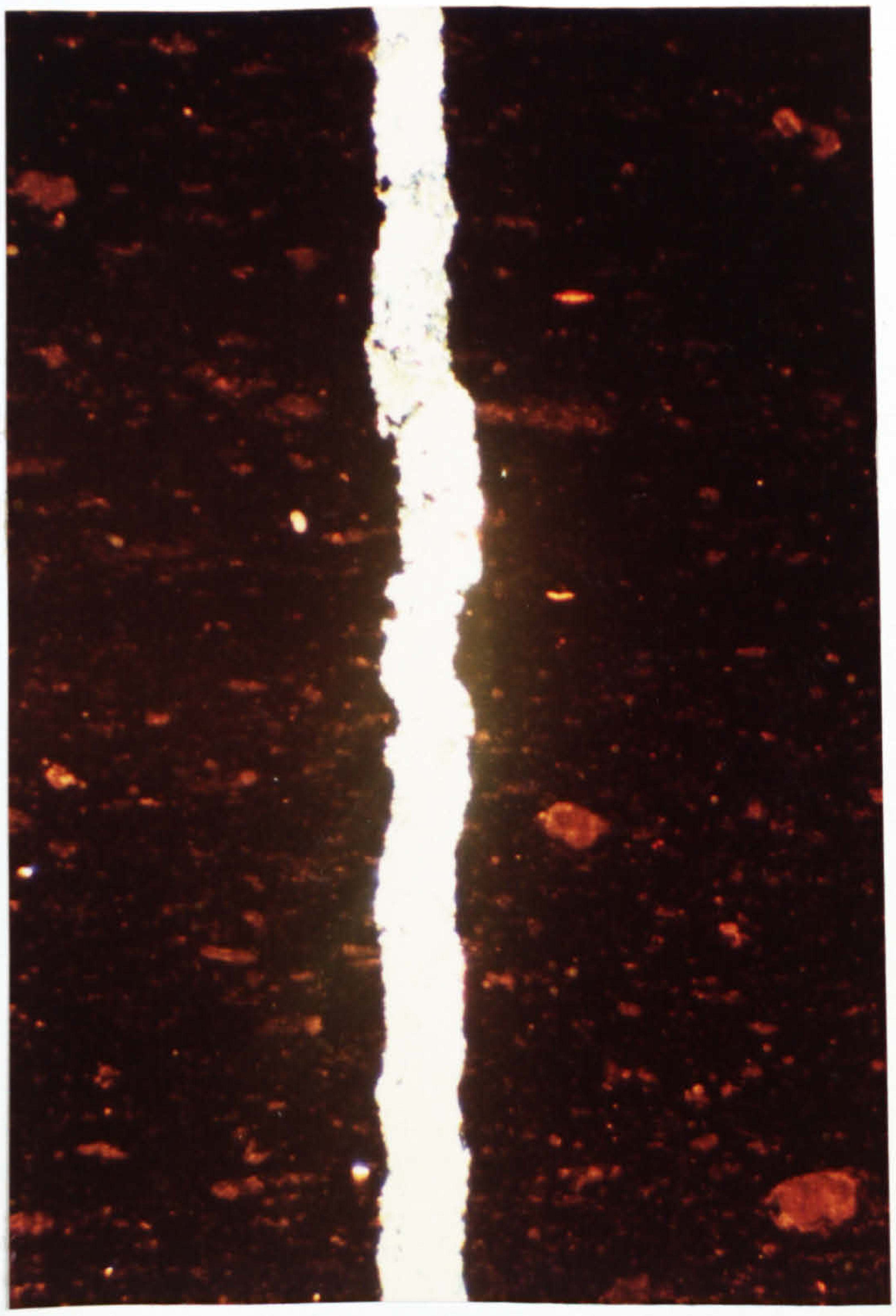


PLATE 9.14 Dilational Cleat in 8R2.

(x30)

PLATE 9.15 Calcite (orange) after Ankerite (turquoise) in 8R2 Cleat.

(x 30)

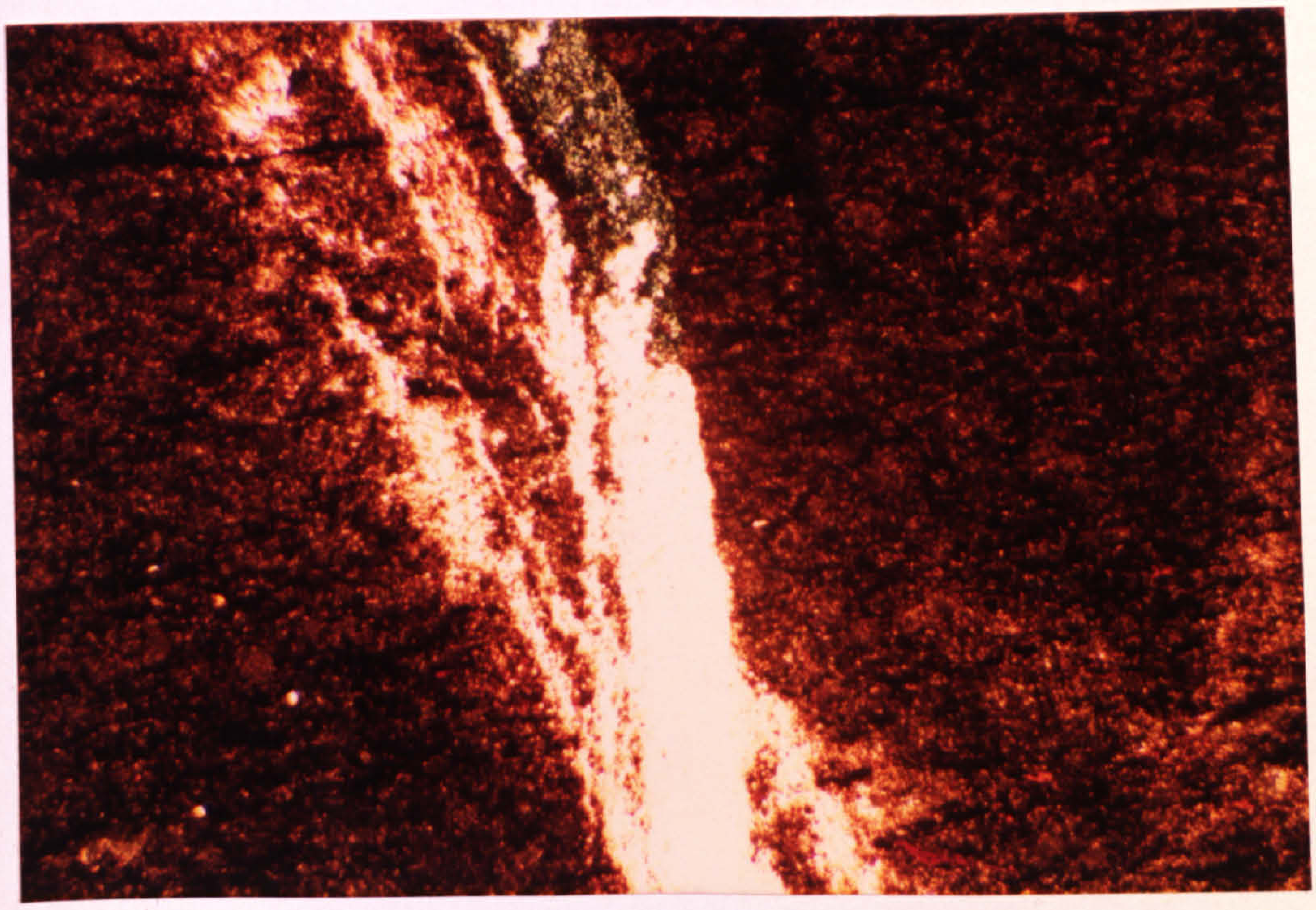


PLATE 9.16 Calcite Cleat Cross-Cutting Ankerite in 8R2.

(x 30)

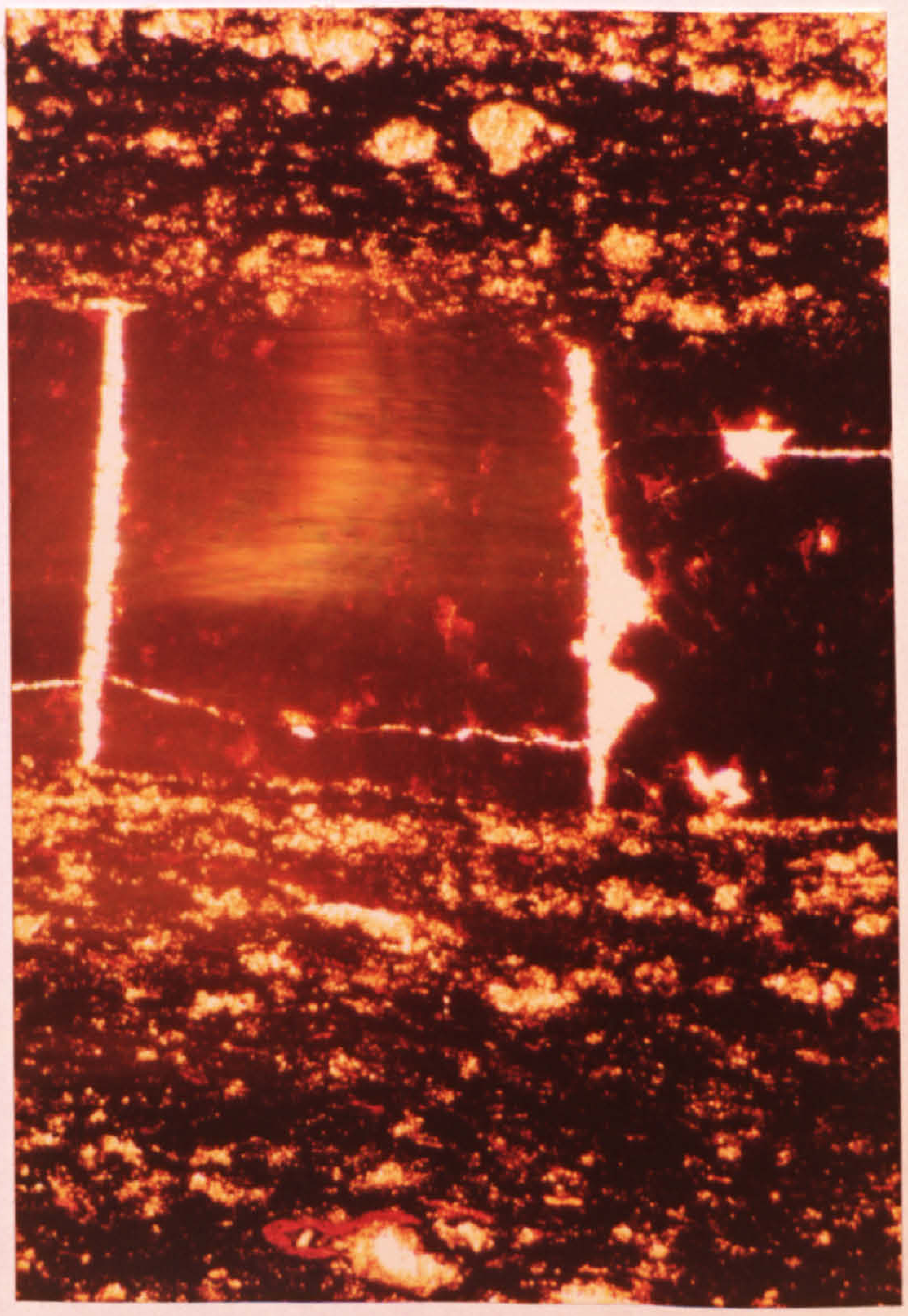


PLATE 9.17 Thin Vitrain Band in 8R2 showing small Carbonate Cleat.

(x 75)

PLATE 9.18 Cleat Displacement by Non-Coally Material.

(x 75)

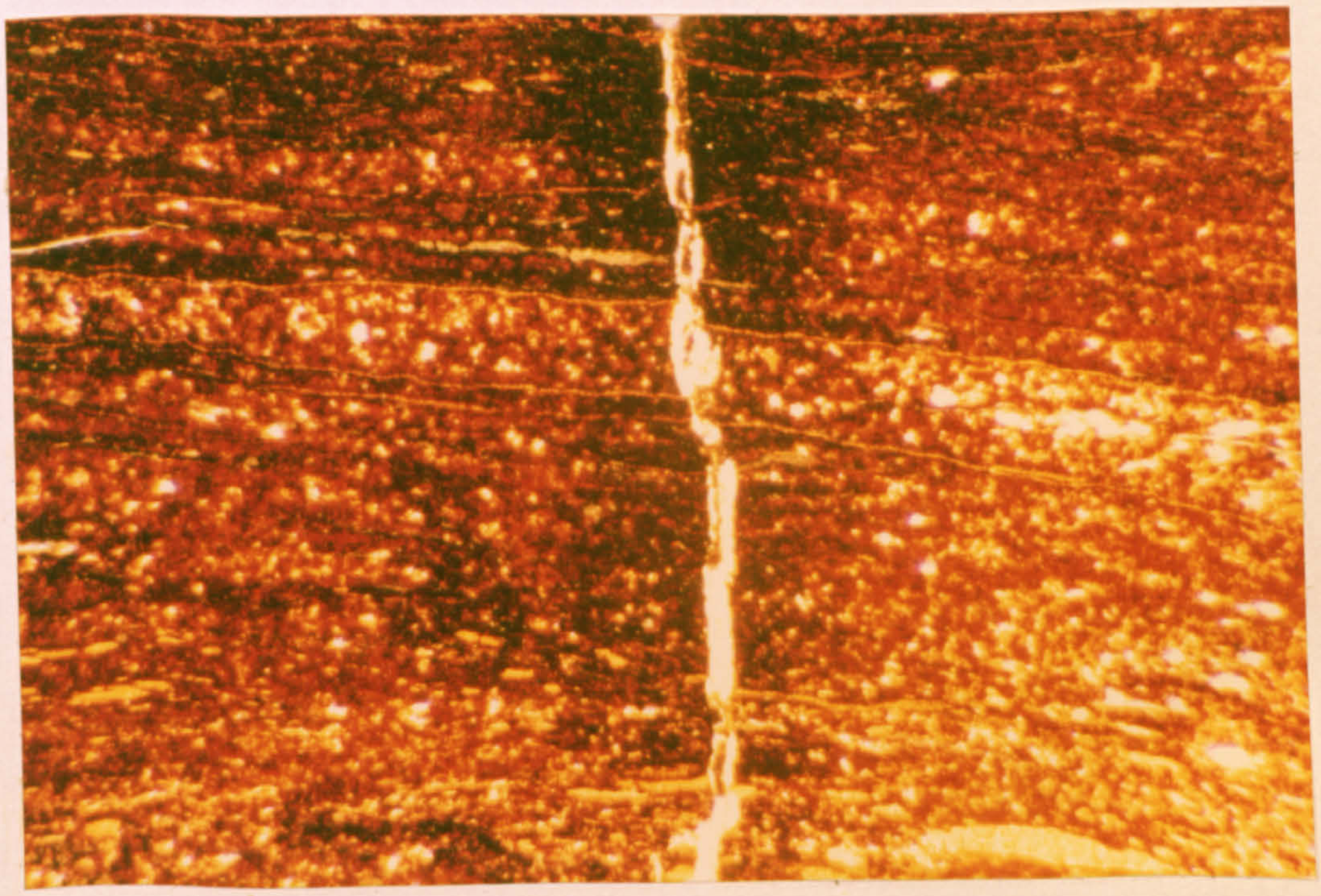


PLATE 9.19 Thin Cleat in 8R2 showing Minor Lateral Movement.

(x 30)

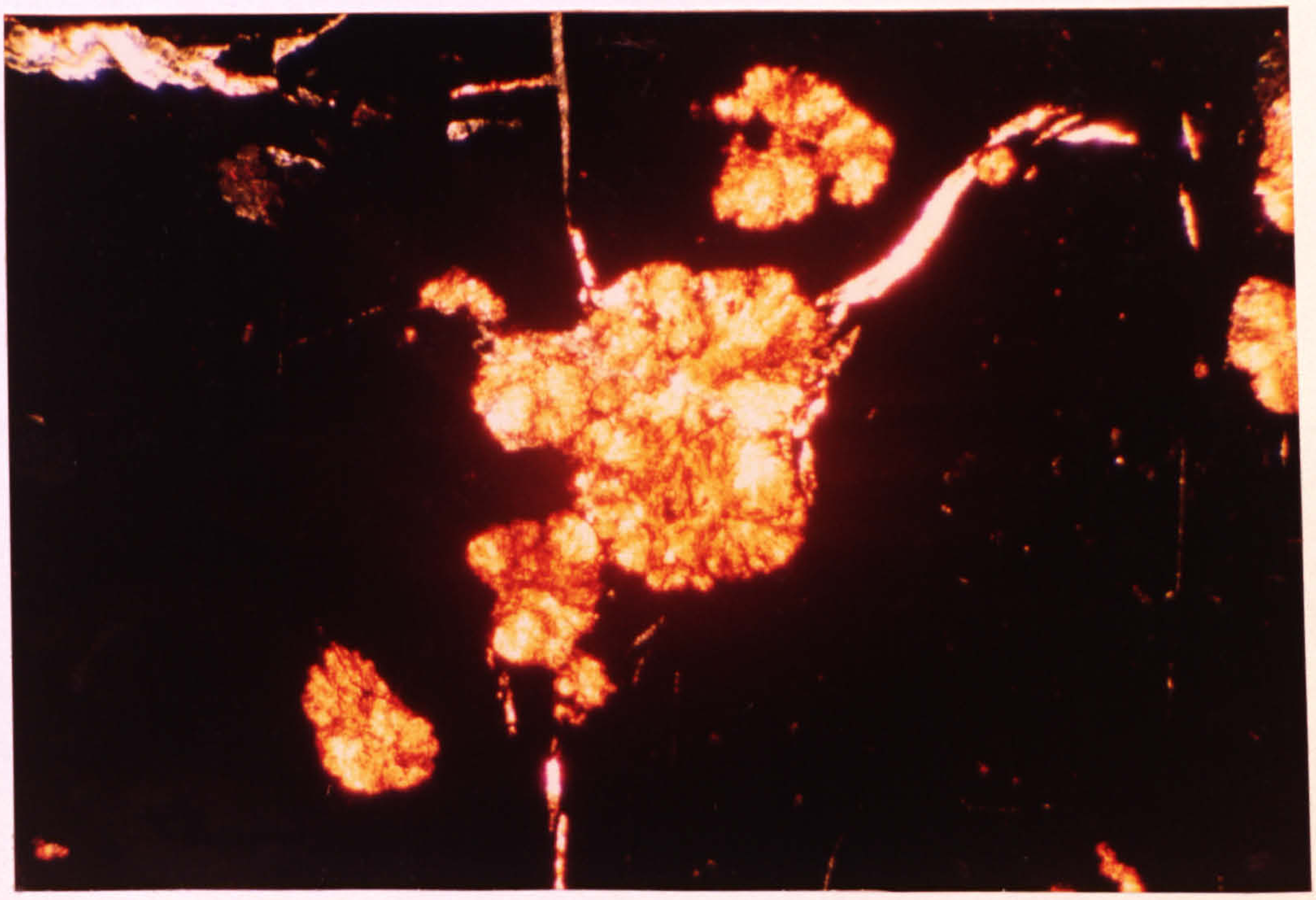


PLATE 9.20 The Relationship between Early Diagenetic Siderite Nodules and Late Carbonate Cleat (2.6).

(x 30)

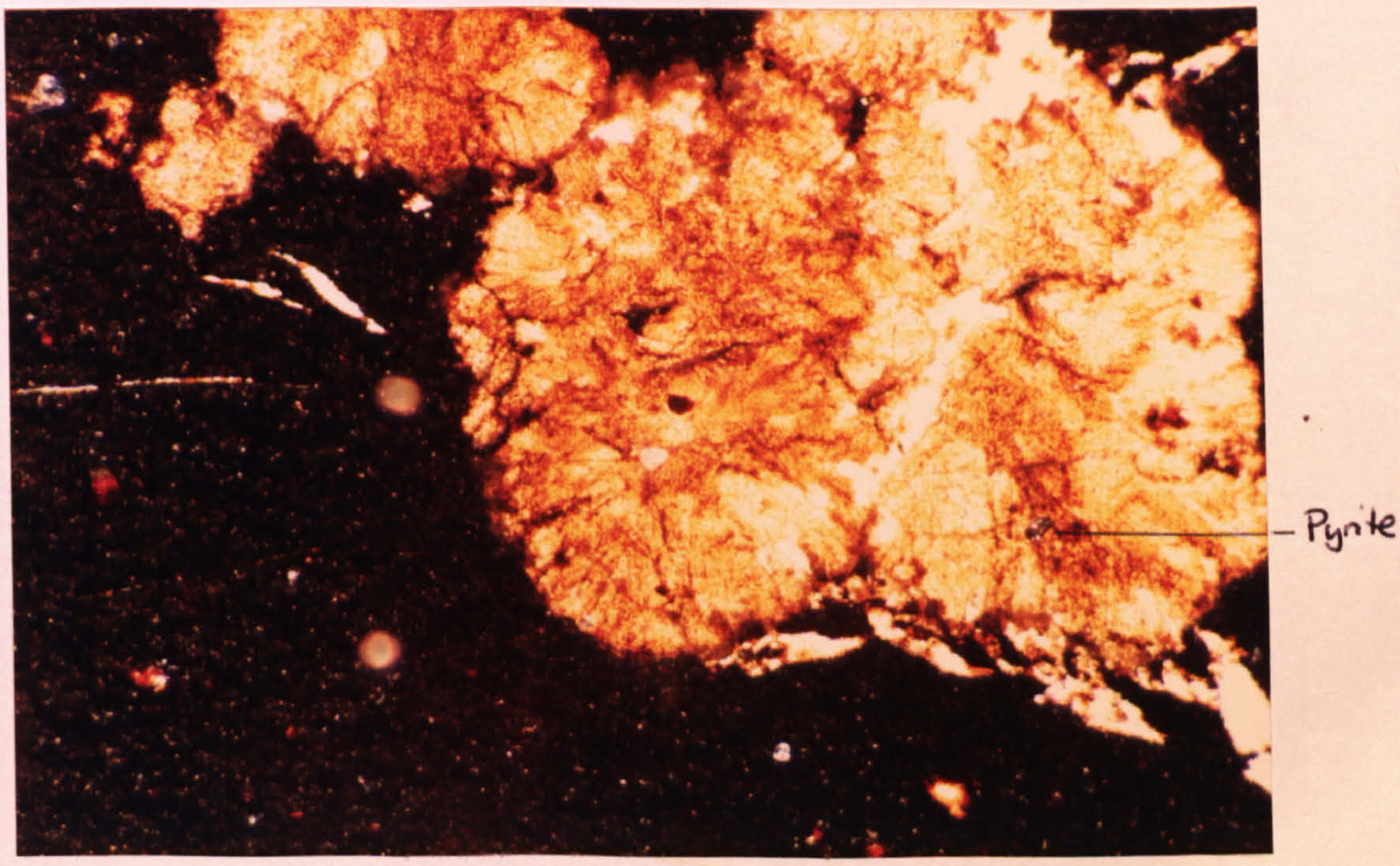


PLATE 9.21 Siderite with a Minor Pyrite Core. Note termination of Carbonate Cleat.

(x 75)

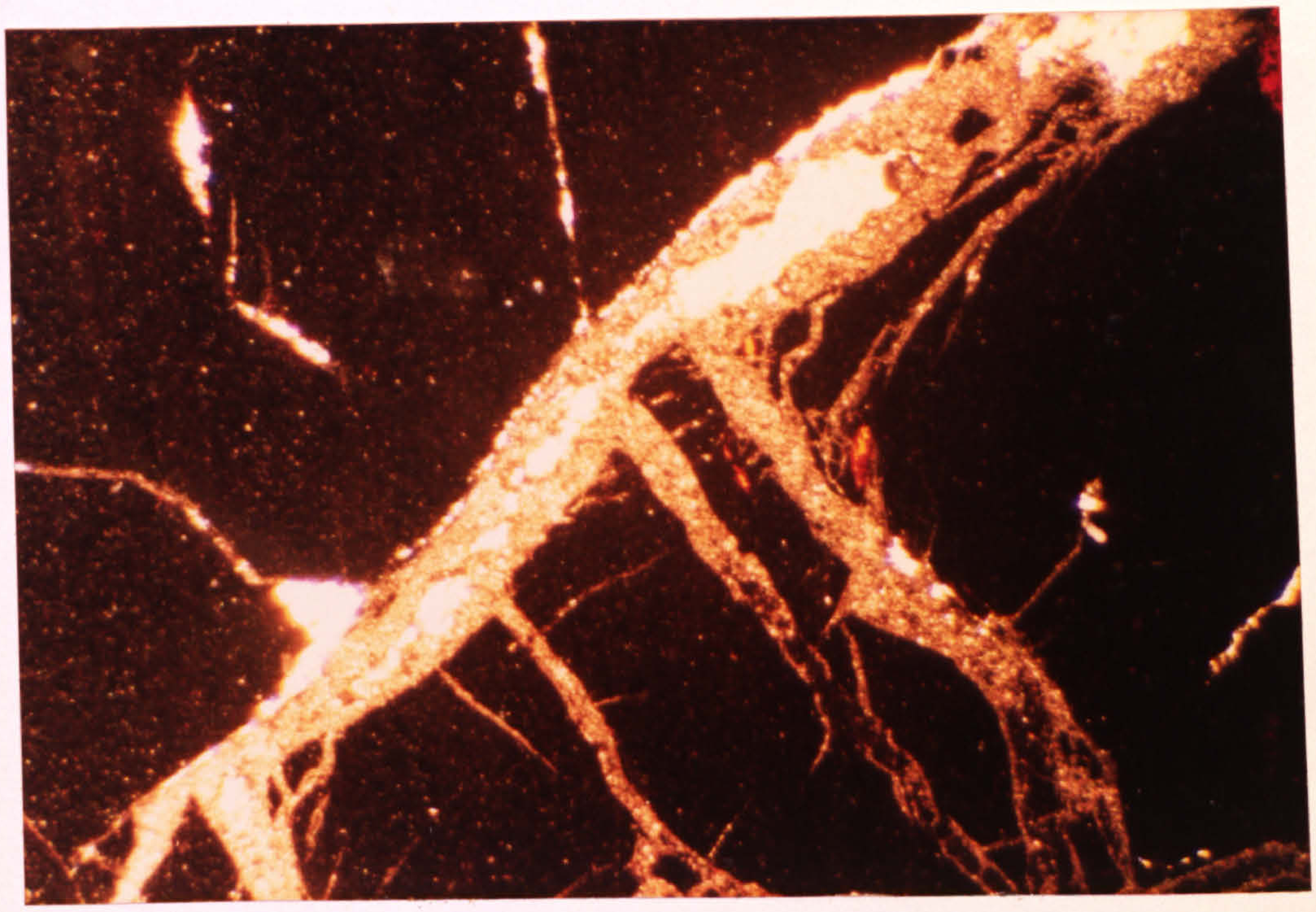


PLATE 9.22 Pyrite Cleat (Y7) showing Rafted Coal and later Carbonate (white) Infilling. (x 30)

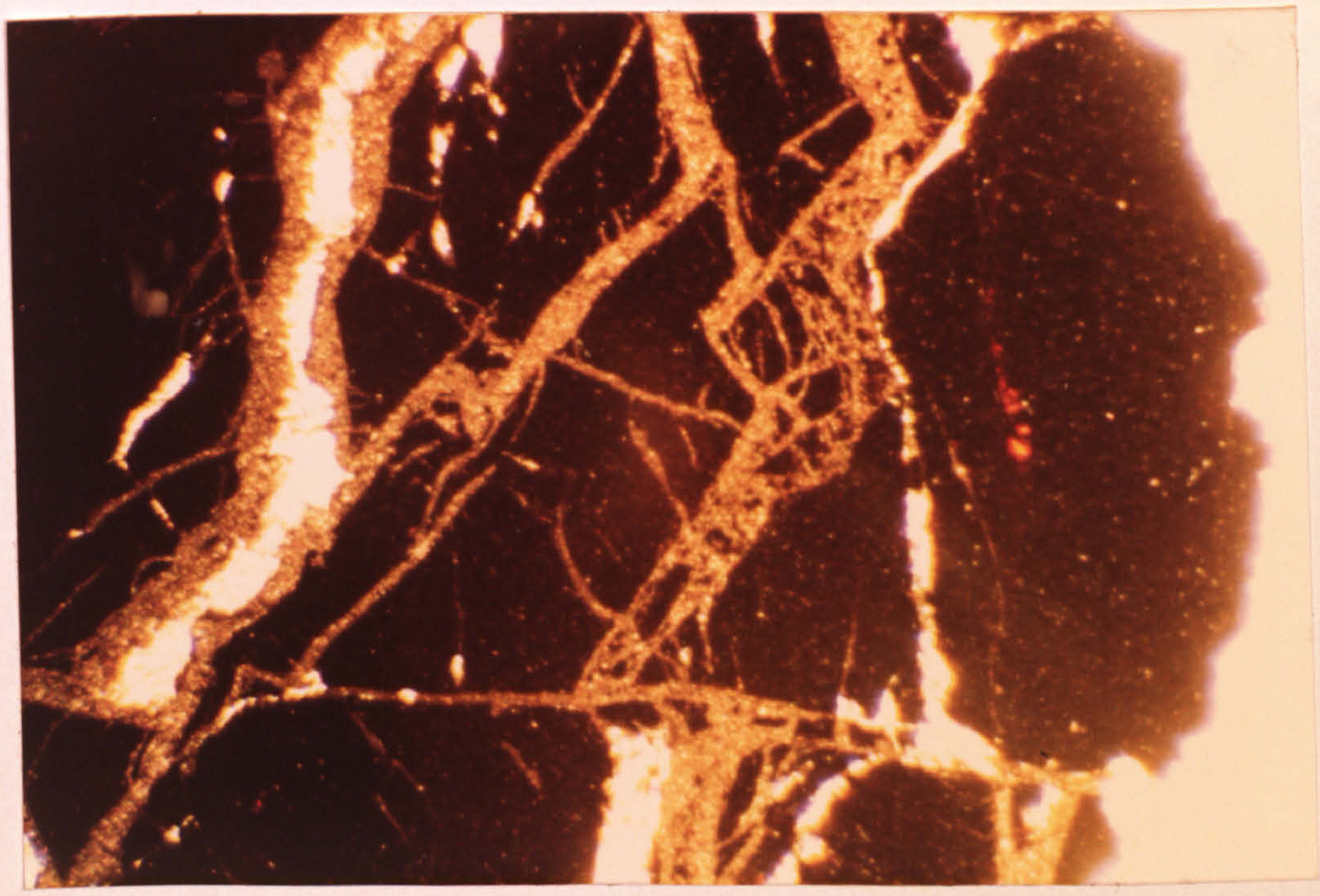


PLATE 9.23 Pyrite Cleat (Y7) showing Angular Fracturing. (x 30)

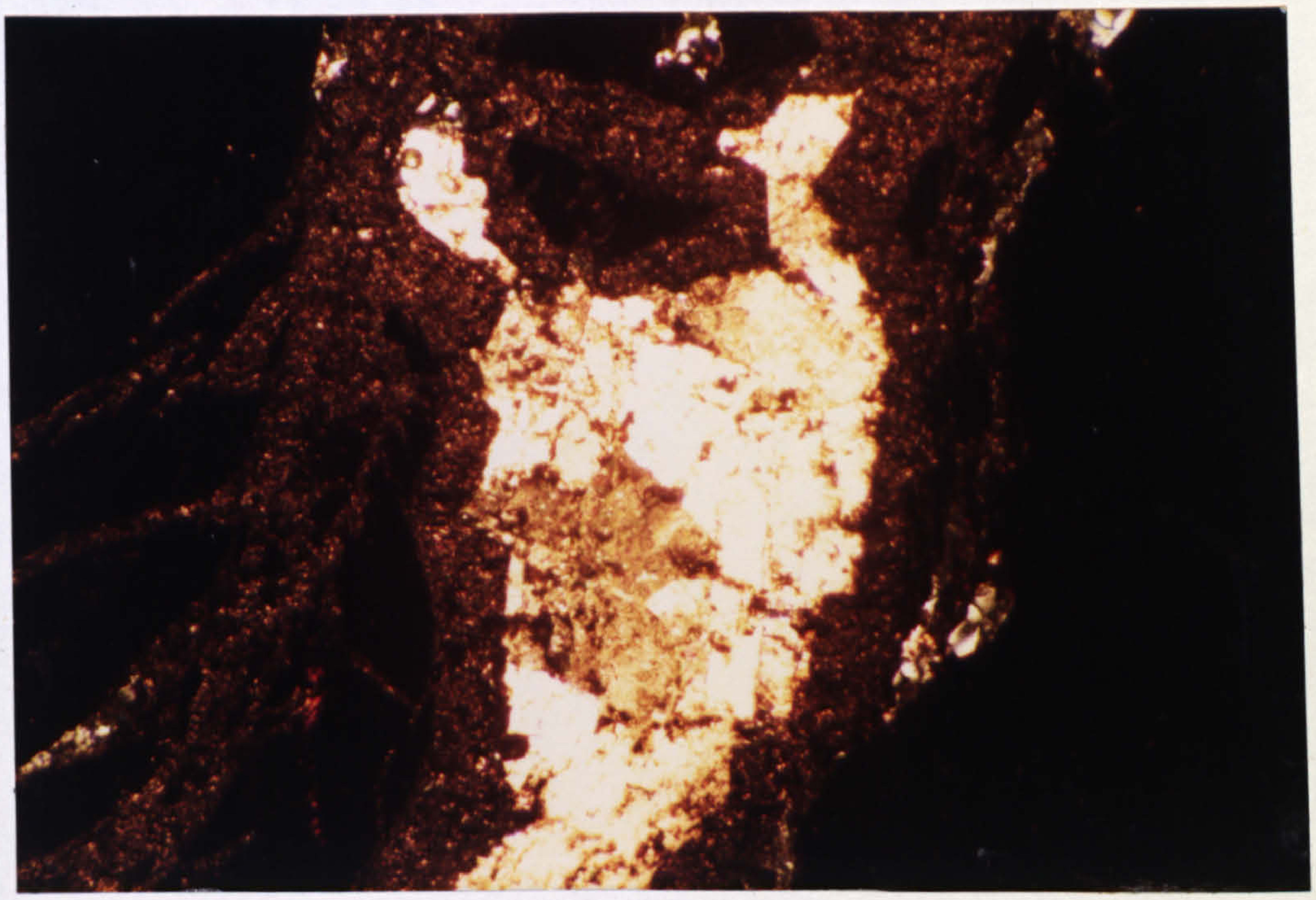


PLATE 9.24 Coarse Crystalline Ankerite in a Pyrite Cleat (Y7).

(x 75)

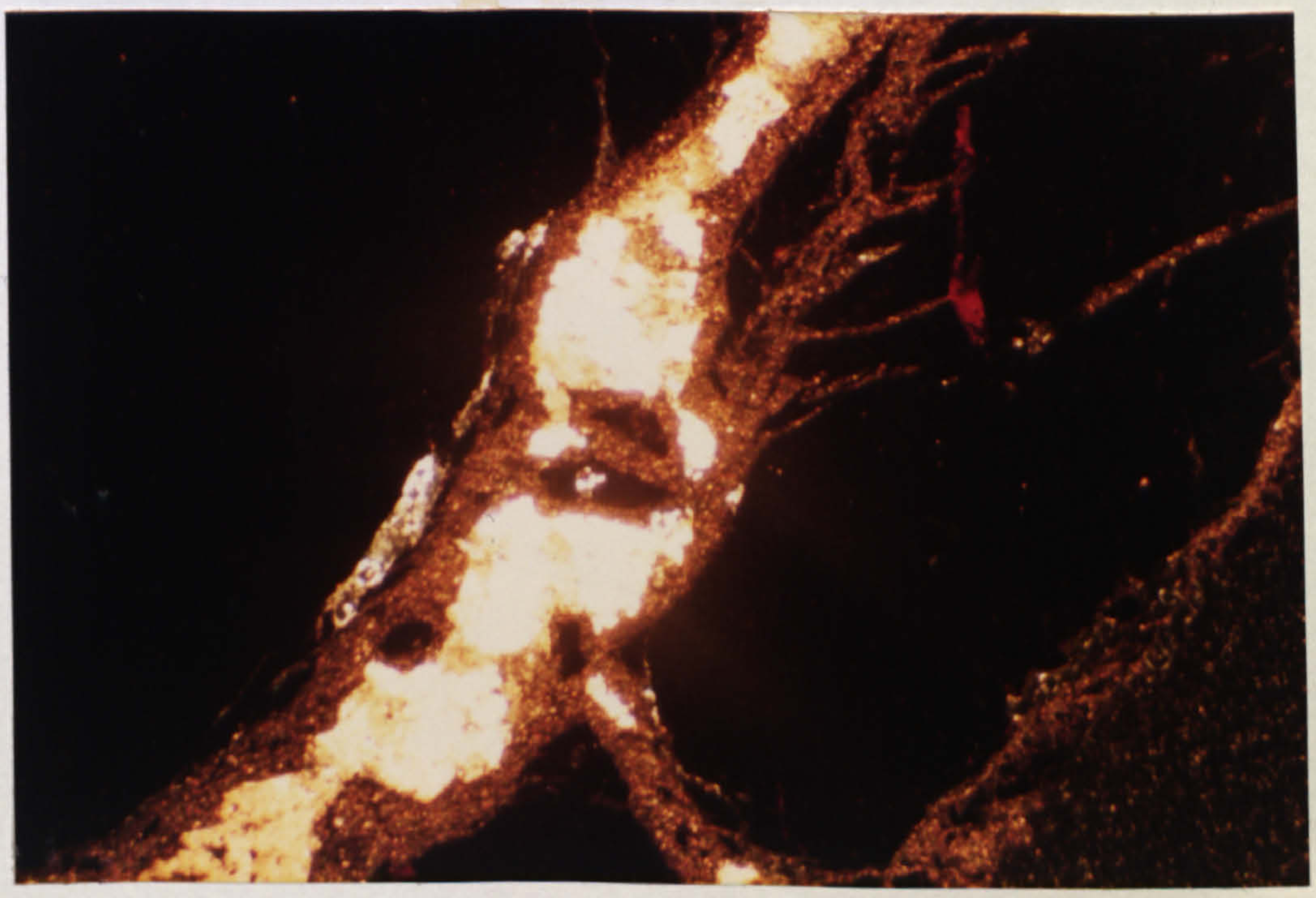


PLATE 9.25 Rafted Coal Fragments showing Multiple Activation during the Sulphide Phase. Note termination of pyrite against a spore.

(x 30)

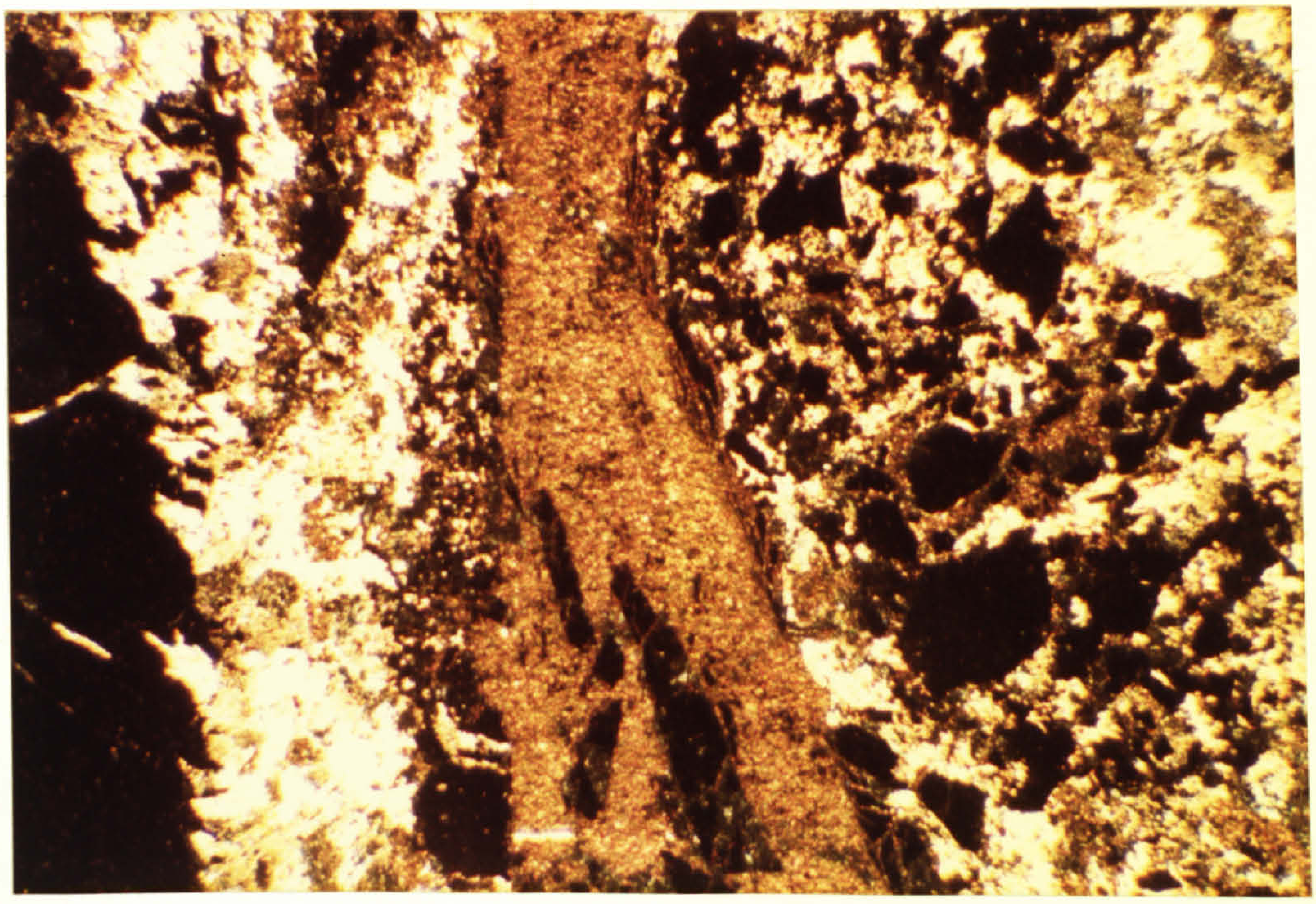


PLATE 9.26 A Pyrite Cleat showing Multiple Rafting of Coal Fragments. (x 75)

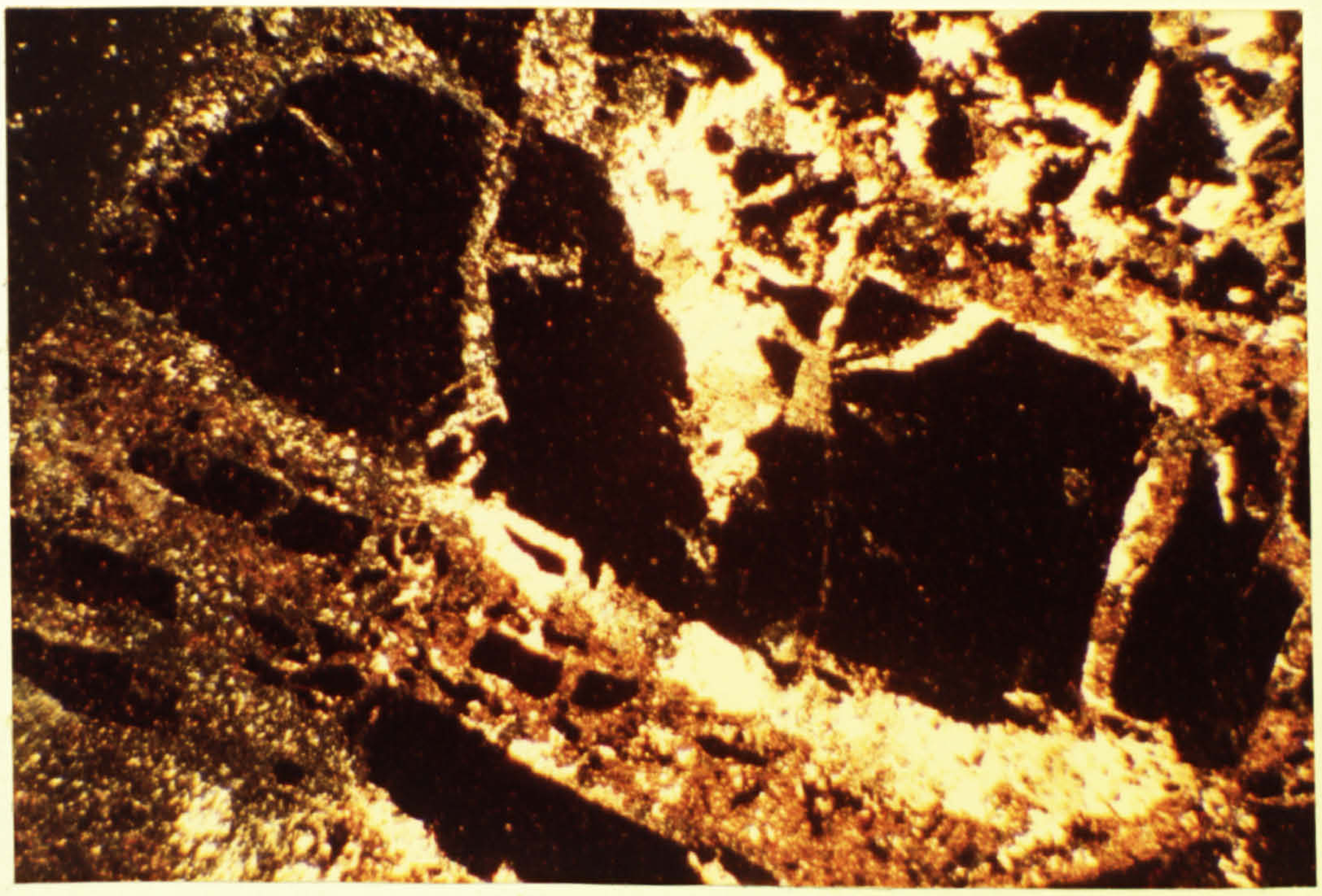


PLATE 9.27 Close-up of Fractured and Rafted Coal. (x 75)

APPENDIX 1

Total Chlorine in Coal Seam Profiles from the South Staffordshire (Cannock) Coalfield

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(In press - Fuel)

Abstract

From a coalfield of noted high chlorine coals, seam profiles were taken from two collieries, Littleton and Lea Hall. Three seam profiles from each colliery were analysed for total chlorine to try and correlate chlorine level with position in the seam. Moisture and ash contents were determined for four of the seams. Total chlorine is highest in the coals, reaching 1%, and low in the mudrocks, down to 0.08% (by weight). Intermediate chlorine values are associated with dirty coals and carbonaceous mudrocks. Water centrifuged from an intraseam dirt band showed that the moisure held the total chlorine content. Similar element ratios were achieved from water centrifuged from coal. These extracts, together with National Coal Board groundwater data suggest that the majority of chlorine in coal has been introduced by chlorine rich groundwaters which evolved during diagenesis. This has been suggested for Illinois and Nottinghamshire coals. There is a very significant positive correlation between coal moisture and total chlorine contents. Total chlorine levels are thus thought to be controlled by groundwater concentration levels and coal porosity, hence the positive relationship between organic carbon and chlorine concentrations. Variations in the carbon content are due to the amount of ash which acts as a dilutant. Total

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chlorine levels vary through the seams but there is not a consistent change with position in the seam. There exists a correlation between coal type and total chlorine content. Bright coals hold significantly more chlorine than dull coals. This relationship is explained by the relative porosities of the coal macerals. Vitrinite, the major component of bright coal, has a greater porosity than either exinite or inertinite. Departures from this relationship with coal type may be explained by mineral matter dilution or the ingress of recent groundwaters over-riding the original coal type chlorine relationship.

Introduction

The presence of large quantities of chlorine in coal has long been known to be detrimental when coal is fired. Chlorides may damage the brickwork of coke ovens and gas retorts by forming a glaze on the refractory linings which crack away from the wall (Chakrabarti and Dasgupta[1]). A problem of greater significance, especially in Britain, is the corrosion of power station superheater tubes. Crossley[2] indicated that such problems may arise if the coal contains more than 0.15% chlorine (by weight).

The distribution of productive Coal Measures within England and Wales means that some 70% of the National Coal Board's production comes from the Eastern Pennines and Midlands coalfields. The properties of these coals makes them most suitable for power station consumption. High chlorine coals (above 0.4% wt.) are confined exclusively to high volatile bituminous coals and coals of this rank are restricted to the Midland, circum-Pennine and East Durham coalfields. Within these coalfields, trends may be seen in the chlorine content of the coals. Total chlorine is seen to increase with depth and hence rises as a given coal seam dips. Vertical sections indicate chlorine to increase with depth until a maximum value is encountered, thereafter the content is high but variable (Daybell[3], Skipsey[4]). On a smaller scale, local variations over-ride the regional trends. Abnormally high chlorine coals are encountered immediately below Permian (saline) strata in South-East Durham (Edmunds[5]) but such occurrences are limited. Skipsey[4] showed that in the Nottinghamshire Coalfield, chlorine increased with depth below the Permian unconformity demonstrating that leaching of the overlying saline strata is not necessarily the origin of the chlorine. Structures may concentrate or dilute the chlorine content. Lower values are to be found in anticlines than in adjacent synclines, as in the Thoresby district of the Nottinghamshire Coalfield (Skipsey[4]). Faulting and old mine workings have also been shown to have effects upon chlorine levels.

Investigation into groundwater chemistry has shown that total dissolved minerals increase with depth. Diagnesis of compacting and buried sediments has a marked effect upon the groundwaters trapped within them. Diagenetic reactions lead to the precipitation of mineral species characteristic of distinctive diagenetic zones (Curtis[6]) and changes in the clay mineralogy (Hower et al.,[7], Foscolos and Powell[8]). Alterations in the detrital mineralogy and the precipitation of new minerals (diagenetic minerals) changes the composition of the groundwaters (Blatt, Middleton and Murray[9]). Deep groundwaters are chlorine rich and the chlorine content increases with depth and becomes the dominant anion (Gluskoter[10]). Gluskoter and Rees[11] concluded that the chlorine level in coal is controlled directly by the composition of the groundwater. Skipsey[4,12] echoed these findings but indicated that above 85-86% carbon content the chlorine holding capacity of coal is dramatically reduced and rarely exceeds 0.2% (by weight). This cut-off point he attributed to structural changes within the coal and hence its moisture holding capacity. The micropore structure of the coal, he argued, could accommodate percolating chloride brines within interconnecting pores. Changes in coal structure were shown by Bond and Hirsch (van Krevelin[13]) to take place at this rank. From being highly porous, alignment of the coal lamellae reduces the porosity of the coal considerably. Such a physical change would explain the association of high chlorine values with high volatile bituminous coals. Seam profiles were studied in the present work, rather than run-of-mine coal, because of the potential relationship between groundwater content and coal type.

Coal Diagenesis

Once vegetable matter or peat has been buried, temperature may convert the organic debris into coal. Early diagenetic changes are essentially biological, a function of bacterial decay. True coalification follows this process and is essentially chemical and physical. The degree of coalification, and hence its rank, is dependent upon temperature and the time over which that temperature is operative. Pressure may retard the chemical changes of coalification. However, pressure does play a role in changing the structural arrangement of the coal and may,therefore, affect the pore space and hence moisutre holding capacity of the coal. The reader is directed to Flaig, concerning biochemical changes, and Teichmüller, M. and R., for the geological aspects of coal metamorphism in "coal and coal-bearing strata" capita (Murchison and Westoll[14]).

The South Staffordshire Coalfield - A Brief Geological History

The isolated coalfields of the Midlands and north of England were once part of a single area of swamp flats. They stretched from the low but stable St. Georges Land and Mercian Highlands - forming the Midland barrier - to the Southern Uplands of Scotland (Rayner[15]).

Coal Measures sedimentation was dominated by these stable basement structures. Progressing further from these positive areas, subsidence became greater, reaching a maximum in the area now occupied by Manchester. This differential subsidence rate had a marked influence upon the deposits that accumulated. The total Coal Measures succession is approximately 180 m in the Dudley area of the South Staffordshire Coalfield, reaching 490 m. in the Cannock Chase region. Further north, in the North Staffordshire Coalfield, 670 m of Coal Measures strata is encountered. When traced into the basin the coal component of the succession is reduced,and the thick seams of the Dudley area split and form several thinner seams to the north. Uplift of the Hercynian Orogeny folded the succession, followed by further sedimentation and erosion, giving us the present configuration of coalfields.

The South Staffordshire Coalfield - Structure

The exposed coalfield is spindle-shaped in outcrop, 40 km north to south from Rugeley to the Lickey Hills. The eastern and western boundaries are largely fault defined, being some 16 km apart in the central section. The Cannock Coalfield is the northern part of this region. Structurally, the coalfield is a north-south trending anticline. The Coal Measures rocks lie unconformably on a largely pre-Carboniferous basement which is brought to the surface in a few small anticlines. Samples were taken from the concealed extensions of the Cannock Coalfield in the north (Fig. 1) at Littleton Colliery (north-west of Cannock) and Lea Hall Colliery (Rugeley).

Sample Collection

The seams sampled were the Yard, Shallow and Deep Seams at Lea Hall and the Eight Feet, Park and Shallow Seams at Littleton. The general stratigraphy is given in Fig. 2. Samples were collected from the Yard, Eight Feet and Park at 20 cm intervals through the seams and into the floor and roof where possible, except where notable changes in coal lithology necessitated sampling at a lesser interval. The Shallow Seam was sampled at a 25 cm interval, and the roof at 20 cm intervals. Samples from the Shallow Seam at Littleton and the Deep at Lea Hall were collected to represent each 10 cm of the seams except where distinct lithological changes occurred at intervals of less than 10 cm when sampling was restricted to each lithology. Intra-seam dirt bands were also sampled. In all cases at least 1 kg. sample was taken. All samples, with the exception of Y8 and Y9 (Yard Seam), where taken from freshly exposed faces. These two Yard samples were taken from an old roof section. Because of the fissile nature of the roof measures, the top 30 cm of the seam are not mined, but are left as a roof support. Its characteristics are, therefore, somewhat different to the remainder of the seam.

Methods

In the laboratory 50 gm samples were hand ground in an agate mortar and pestle to less than 72 mesh size. Samples from the Lea Hall Shallow and Yard Seams and Littleton Eight Feet and Park Seams were tema milled. Total chlorine determination followed the general method of B.S.S. 1016 part 8[16], with one exception. Rather than using nitrobenzene to coat the Ag Cl precipitate and hence prevent its interference in the titration, the precipitation was filtered off prior to titration. These two methods are stated by Kolthoff et al[17] to produce results of comparable accuracy.

As a measure of the precision of the method, four samples from the Lea Hall Deep seam were analysed in duplicate. The following results were obtained:

Sample Number	Aliquot 1	Aliquot 2
Roof	0.54	0.56
8	0.99	0.98
12	1.08	1.07
15	1.06	1.05

The three coal samples show that at Cl contents of 1%, the results are reproducible to ± 0.01%.

Na, K, Ca and Mg were determined by atomic absorption spectrometry and the moisture content by oven drying at 105°C. Ash content was determined by low temperature (plasma) ashing.

Discussion of Results

The values obtained for the three Littleton Seams are shown in Fig. 3 and those for Lea Hall in Fig. 4. The Yard and Shallow from Lea Hall and Eight Feet and Park of Littleton were analysed on a moisture free basis whereas the Deep of Lea Hall and Shallow of Littleton were analysed as received. The coal types are given on Figs. 3 and 4 and are based on visual examination of the samples and are thus accurate only at the sub-class/lithotype level. This does, however, indicate the predominance of the maceral groups, vitrinite, inertinite and exinite.

It is accepted that visual classification of coals into lithotype groups may be very subjective in transitional cases. In particular, the boundary between dull banded and bright banded coals may be very vague. Maceral counts would give more accurate results but this is a time consuming procedure. It is felt that the method adopted is acceptable in the majority of cases but that errors may arise in border line cases.

One of the most notable features of Figs. 3 and 4 is that, with few exceptions, the chlorine contents of the mudrocks are well below those found in the adjacent coals. Fig. 5 is a plot of Cl vs. Organic matter content (determined by difference after plasma ashing) for samples from the Lea Hall Yard and Shallow and Littleton Eight Feet and Park seams. Examination of the graph shows that the majority of the samples fall into two broad groups, the coals, having ash contents of 2-28% and chlorine contents of 0.5-1.0% (approximately), and the mudrocks having ash contents of 90-99% and chlorine contents of 0.08 to 0.26%. The seven samples which fall outside these two groups represent inferior coals and carbonaceous mudrocks. There is a positive correlation for all the data between the contents of Cl and organic matter.

The values shown in Fig. 5 indicate that for non-carbonaceous mudrocks, an average Cl content is 0.1 to 0.15%. Further work has shown that the Cl present in the mudrocks examined is easily removable and hence not bound to the clay minerals. It seems that the Cl is present as salts associated with the moisture held within pores. Evidence for this is offered by water centrifuged from an obviously damp mudrock, Ydb 1, an intraseam dirt from the Yard Seam. Porewater was extracted using the centrifuge method described by Edmunds and Bath[18]. The water was analysed for major cations using atomic absorption spectroscopy and for chlorine using Mohr's titration. The sample volume was too small for the determination of other anions. The results are given in Table 1. The Cl content shows that the water accounts for all the chlorine present in the mudrock. Table 2 shows an analysis of water centrifuged from a run-of-mine Shallow Seam (Lea Hall) sample. The element ratios are similar to those found in Ydb 1 but concentrations are lower by a factor of 10. It is not intended to place too much emphasis on the latter results as it is not known to what extent this sample is representative of the coal moisture as a whole considering the very small pore sizes in coal. The water was extracted by Mr. E. Hall, Water Research Centre, using a higher speed centrifuge than was available in our laboratories. Even so only a very small fraction of the total moisture was extracted. It may be said that the mudrocks and the coals do contain chloride rich solutions which may thus contribute a considerable fraction to all the chlorine held in a mudrock or coal. Supplementary evidence is afforded by the roof sample from the Lea Hall Deep seam, which is a fairly pure quartz sandstone with a high moisture content. Its total chlorine content is 0.54% which cannot be associated with the quartz and as the Cl is water soluble, the porewater is probably responsible. National Coal Board groundwater analyses show that water associated with the coal seams is rich in chlorine. Values for the Yard, Shallow and Deep seams at Lea Hall and Eight Feet at Littleton are given in Table 3. In general, there is little information in the literature concerning deep groundwater composition for the area under study. In the East Midlands, Downing and Howitt[19] give comprehensive details of groundwaters associated with Coal Measures (and other)strata. This work too, as with other information over wide ranging areas, indicates chlorine rich deep groundwaters.

The groundwaters are thus chlorine rich, as would be predicted, and chlorine is present in the water extracted from two of the present samples. If the inherent water in the samples does contain a significant fraction of the total chlorine it follows that the relationship between chlorine and organic matter content (Fig. 5) is indirect and a relationship should exist between chlorine and moisture content. This data is shown plotted on Figure 6 for the Yard and Shallow seams from Lea Hall Colliery and the Eight Feet and Park seams from Littleton

Colliery. There is a significant positive relationship (r = +0.51, 99.9% significance level) between the chlorine and moisture contents for the coals alone. The reduced major axis regression equation is shown plotted in Fig. 6. Inclusion of the mudrocks would increase the significance of the correlation (r = +0.85, 99.9% significance level). It is therefore concluded that a signficiant fraction of the chlorine is present in the water contained in the coal. Although we do not have porosity measurements it is a reasonable assumption that because the rocks occur below the water table and are saturated, that the moisture content relates directly to porosity. This relationship has been demonstrated for Illinois coals and also the variation in porosity with coal type and rank (Thomas and Damberger[20]).

One sample which is of note and does not fit into the general scheme is YR1 (Fig. 5). It has a high ash content (84%) and a Cl content of 0.80%. This sample is from the roof of the Lea Hall Yard seam and part of an old section like the aforementioned Y8 and Y9. When these samples were collected it was noted that evaporation of groundwaters had led to the precipitation of salts on the fractures of this sample and to some extent on Y8 and Y9. It is evident therefore, that the Cl contents of these samples should not be considered with the other values as they are enhanced due to evaporation.

Examination of Figs. 3 and 4 show that there is no consistent relationship between Cl content and position in the seam. Thus the Littleton Shallow Seam shows lower Cl contents towards the top of the seam, the Park has 'random' variations and the Eight Feet is slightly higher at the base of the seam. From Lea Hall, the Yard seam total chlorine decreases downseam, the Shallow exhibits a maximum in the centre of the seam and the Deep seam has highest values at the top. It is evident that any relationship between seam position and Cl content is not causative but a reflection of more fundamental variations.

Examination of Fig. 3 reveals a possible fundamental determinant of coal Cl values. In the Eight Feet Seam, three of the lowest four Cl values are from dull coals whilst the other is a dull banded coal. It appears that the Cl content may be related to coal lithology. It is possible to test statistically whether there is a significant difference between the means of the dull and bright coals. Dull coals, with a predominance of inertinite and/or exinite have a mean Cl content of 0.607 with a standard deviation of 0.058, while the bright coals, in which vitrinite predominates, have a mean of 0.675 and standard deviation of 0.035. Bright coals, therefore, have higher average Cl contents. Calculation of the standard error of the two means show that the difference is significant at the 95% level. It appears, therefore, that coals with high vitrinite contents will have correspondingly high Cl contents. The Shallow Seam from Littleton confirms this finding. The bright and bright banded coals ($n = 23$) contain Cl contents in the range of 0.35 to 0.45% with only one sample showing a lower value. The four dull and dull banded samples from the seam show Cl contents of 0.26 to 0.35%. It is evident therefore, that for these two seams variations in coal type is largely responsible for the variations in Cl content.

Support for the conclusion that vitrinite is the major Cl containing maceral group in coal comes from the work of Saunders[21]. Using optical microscopy, scanning electron microscopy and X-ray microanalysis techniques, on Lea Hall and Hem Heath seam samples, Saunders showed that vitrinite usually contained 3-4 times the Cl held in exinite and inertinote. This may be explained by the greater porosity of vitrinite (Thomas and Damberger[20]).

In the Littleton Park Seam, the relationship between total Cl and coal type is not so clearly seen. Indeed two of the three lowest Cl contents shown by coal samples are in bright or bright banded coals. However, ash contents range up to 20% and decrease the Cl holding capacity of the coal (Fig. 5). If the Cl contents are re-expressed on a dry mineral matter free basis (d.m.m.f.) four out of five lowest Cl contents are in dull or dull banded coals (Fig. 3). The variation with coal type is however, still not quite so marked as with the Eight Feet and Shallow Seams.

The Lea Hall Shallow Seam has no dull banded coals, and only one dull coal. The latter has a lower chlorine content than the remaining bright and bright banded coals (Fig. 4). When expressed on a dry mineral matter free basis four of the five highest chlorine contents are in bright coals. Therefore, with one exception, the bright banded coals have Cl contents which fall between those of the bright and dull coals. The same relationships between coal type and chlorine content are therefore demonstrated by the Shallow Seam.

In the Lea Hall Deep Seam, there is again, only one dull coal sample and this has a lower Cl content than the other coal samples. There are two dull banded samples in this seam but they contain Cl contents higher than most of the bright banded samples of which the remainder of the seam is composed. The roof of the Deep Seam is a sandstone and as the dull banded coals are at the top of the seam it would appear that their higher than normal Cl contents are due to ingress of Cl-rich brine from the sandstone. Examination of Fig. 4 shows that the Cl content decreases through the top of the seam with increasing distance from the sandstone suggesting very recent additions of Cl from brines at the top of the Deep seam. In the Yard Seam from Lea Hall (Fig. 4) the picture is complicated by the samples from the top of the seam, which have high Cl contents attributed to evaporation of groundwater in a non-fresh section, and also by samples from the base of the seam where the ash content rises to 55%, with a corresponding decrease in Cl. The relationship between Cl content and coal type may therefore be overshadowed due to other factors. These may vary from seam to seam and in this work comparisons have been limited to the variation within one seam profile. Previous work has demonstrated a variation in Cl content with depth and coal rank (Daybell[3], Skipsey[4]). In the present work five of the six seams do conform to the depth relationship, the exception being the Littleton Shallow Seam. Thus the Cl content of a given lithotype will vary depending on the composition of the solutions in contact with the seam throughout its history.

Conclusions

Samples obtained from three seams at both Lea Hall and Littleton Collieries, in the Cannock Coalfield, show that variations in chlorine content within coal seams are determined by changes in moisture content. This in turn is determined by changes in ash content and coal lithology. Mudrocks associated with high-chlorine seams (> 0.4% Cl) contain low Cl contents (approx. 0.15%). A positive correlation has been shown to exist between chlorine and organic matter content, indicating that organic matter has a higher capacity for holding chlorine than does non-organic matter ('ash'), which acts as a dilutant. As well as having much lower chlorine contents, mudrocks release their chlorine more readily than coals. It is suggested that this is due to a fundamental difference in pore size and accessibility, coals having a greater total porosity (see moisture contents, Fig. 6), but these pores being individually smaller and less accessible than those in mudrocks.

Samples from the Eight Feet and Shallow Seams at Littleton show that bright and bright banded coals contain higher chlorine contents than dull and dull banded coals. This reflects the importance of vitrinite in being the major chlorine holding coal maceral group. Samples from the other Littleton seam (Park) show the interaction of ash content and coal lithology in determining chlorine contents, chlorine contents being highest in bright and low ash coals. The three seams from Lea Hall unfortunately contain very few dull or dull banded samples and so lend little support to the relationship between coal type and chlorine content. It has been shown that chlorine contents tend to vary randomly with position in seam, this variation being a reflection of changes in coal type or ash content through the seam.

It is suggested that the origin of chlorine is diagenetically altered groundwaters and such chloride rich brines are associated with and in some instances can be removed from coal and associated mudrocks. The presence of chloride rich groundwaters has been shown by the analysis of coalfield mine waters (Table 3) and of waters extracted from coal and associated mudrocks (Tables 1 and 2). Indirect evidence for the presence of chloride rich groundwaters is given by the positive relationship between chlorine and moisture content (Fig. 6) and the high chlorine concentration found in the analysis of a roof sandstone.

Skipsey[12] proposed that the chlorine content of British Coalfields was fixed during coalification. The rank and associated microstructural changes which govern the coal's ability to hold chlorine are, therefore pre-Triassic and a result of the Hercynian Orogeny. Evidence has been produced to show that subsequent alterations of chlorine content may be brought about by the passage of chloride rich brines through the coals and associated strata. Alternatively, it is conceivable that leaching and, therefore, decrease in chlorine content may occur with the passage of a chloride poor groundwater. These later alterations, for which the more permeable mudrocks and sandstones possibly act as aquifers, may tend to obscure original relationships of coal type and total chlorine content.

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TABLE 1

Ydb 1 Analysis of Centrifuged Moisture

(p.p.m.)

Cl^-	Na^+	K^+	Ca^{++}	Mg^{++}
23,000	14,375	340	1,610	300

Moisture content = 5.80% = 0.13% Cl in whole rock

Total Chlorine analyses = 0.14%

TABLE 2

Shallow Seam Coal - Centrifuged Moisture

(p.p.m.)

Cl^-	Na^+	K^+	Ca^{++}	Mg^{++}
2,300	1,305	20	330	50

TABLE 3

N.C.B. Mine Water Analyses

	Lea Hall				Littleton Eight Feet
	Yard	Shallow	Deep		
Cl^- (ppm)	52,500	15,370	24,850	17,570	34,000
Na^+	-	8,480	13,760	9,737	
K^+	-	-	-	123	
Ca^{++}	-	905	1,410	1,210	
Mg^{++}	-	275	410	333	

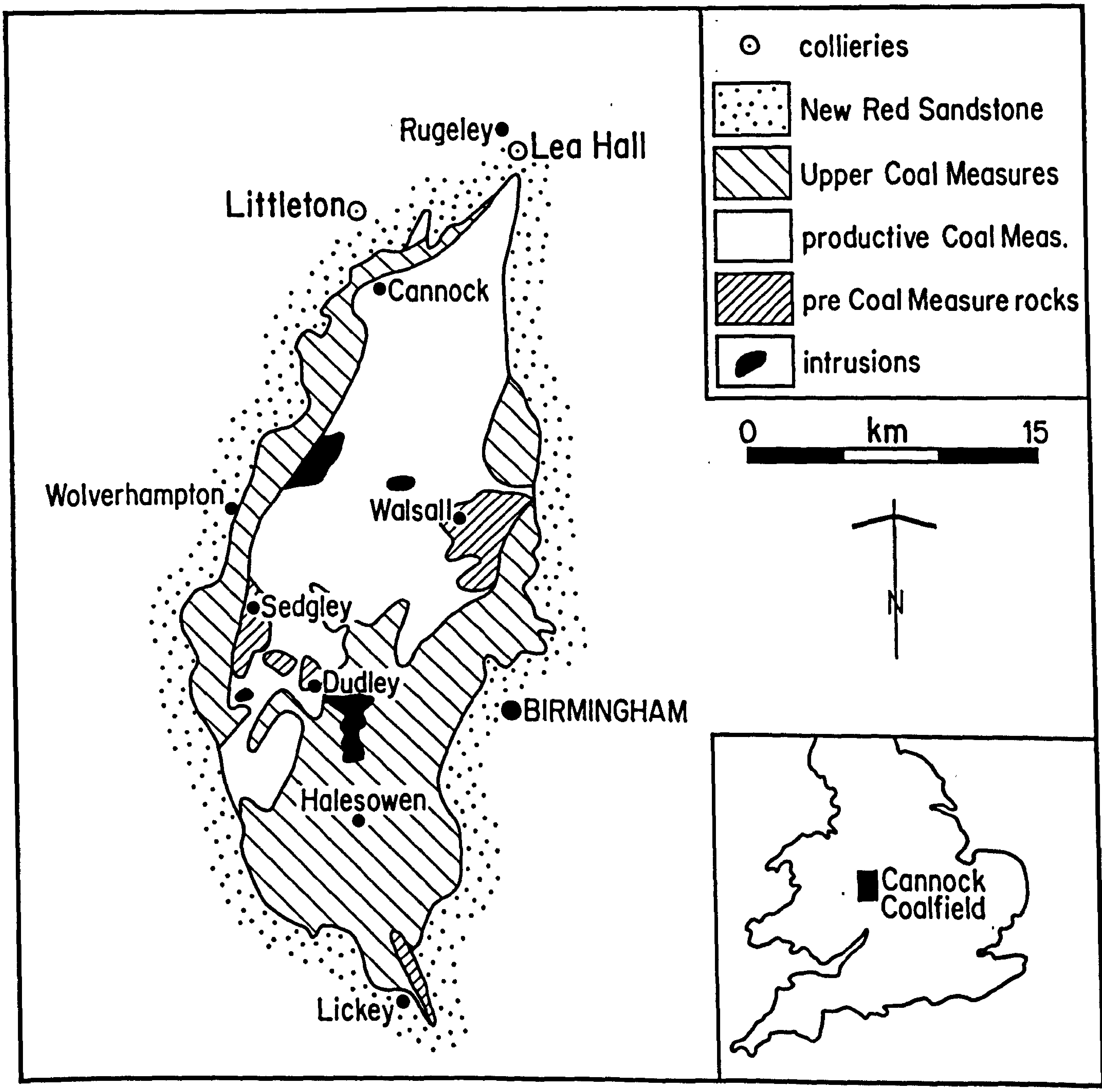


Figure 1: Location of the Cannock Coalfield and Littleton and Lea Hall Collieries.

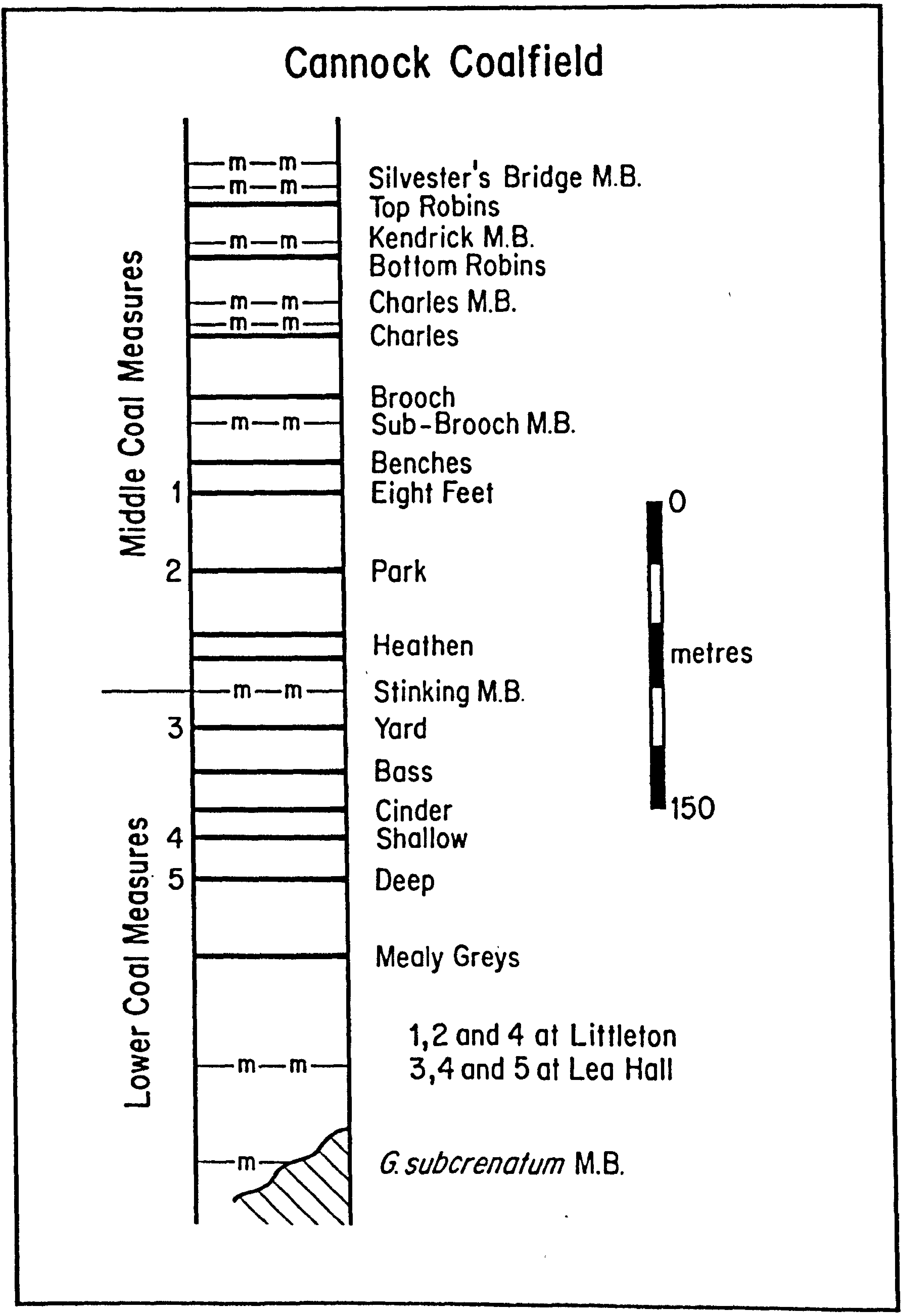


Figure 2: General stratigraphic sequence in the Cannock Coalfield and the seams sampled.

Fig. 3a EIGHT FEET SEAM, LITTLETON

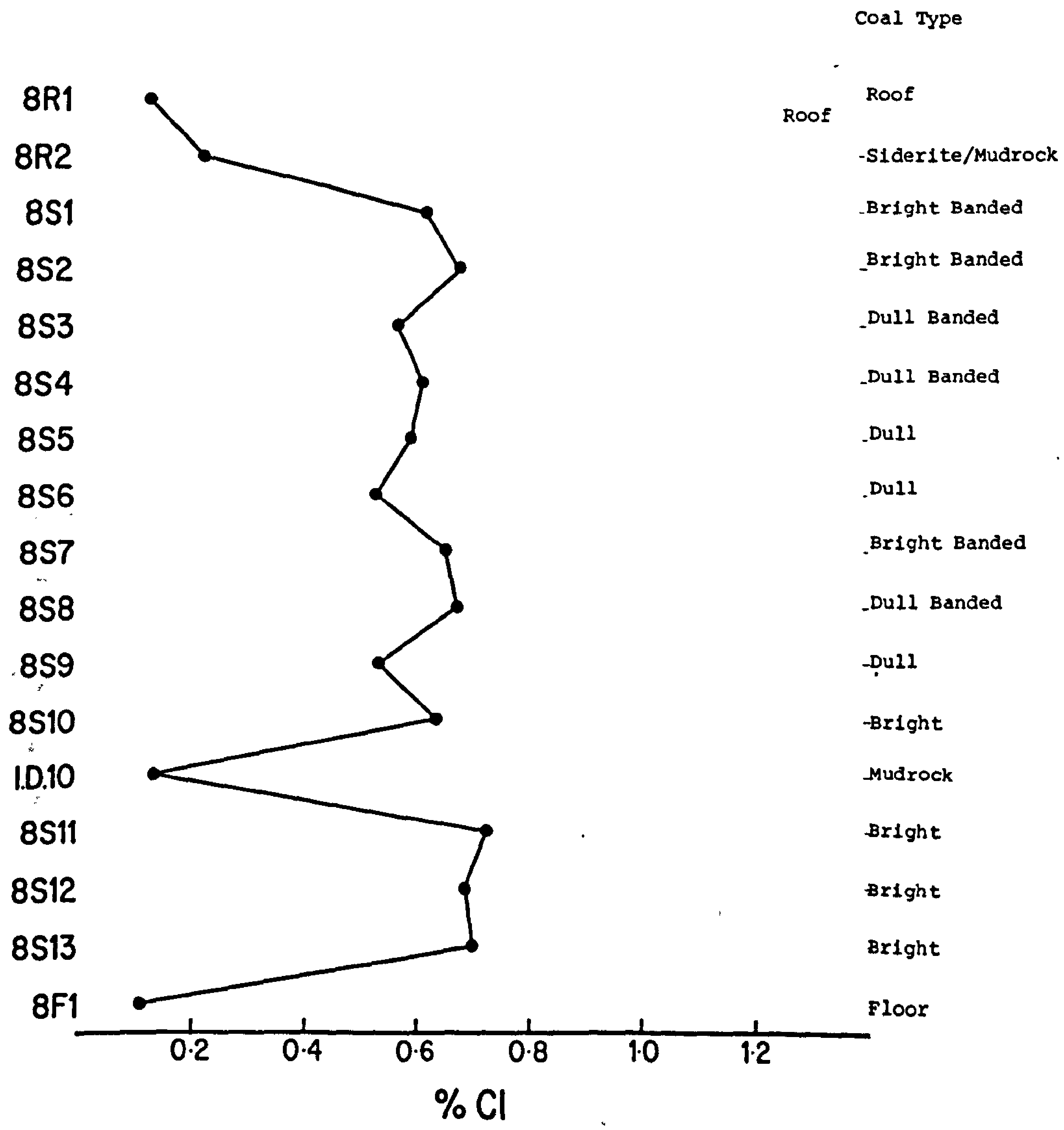
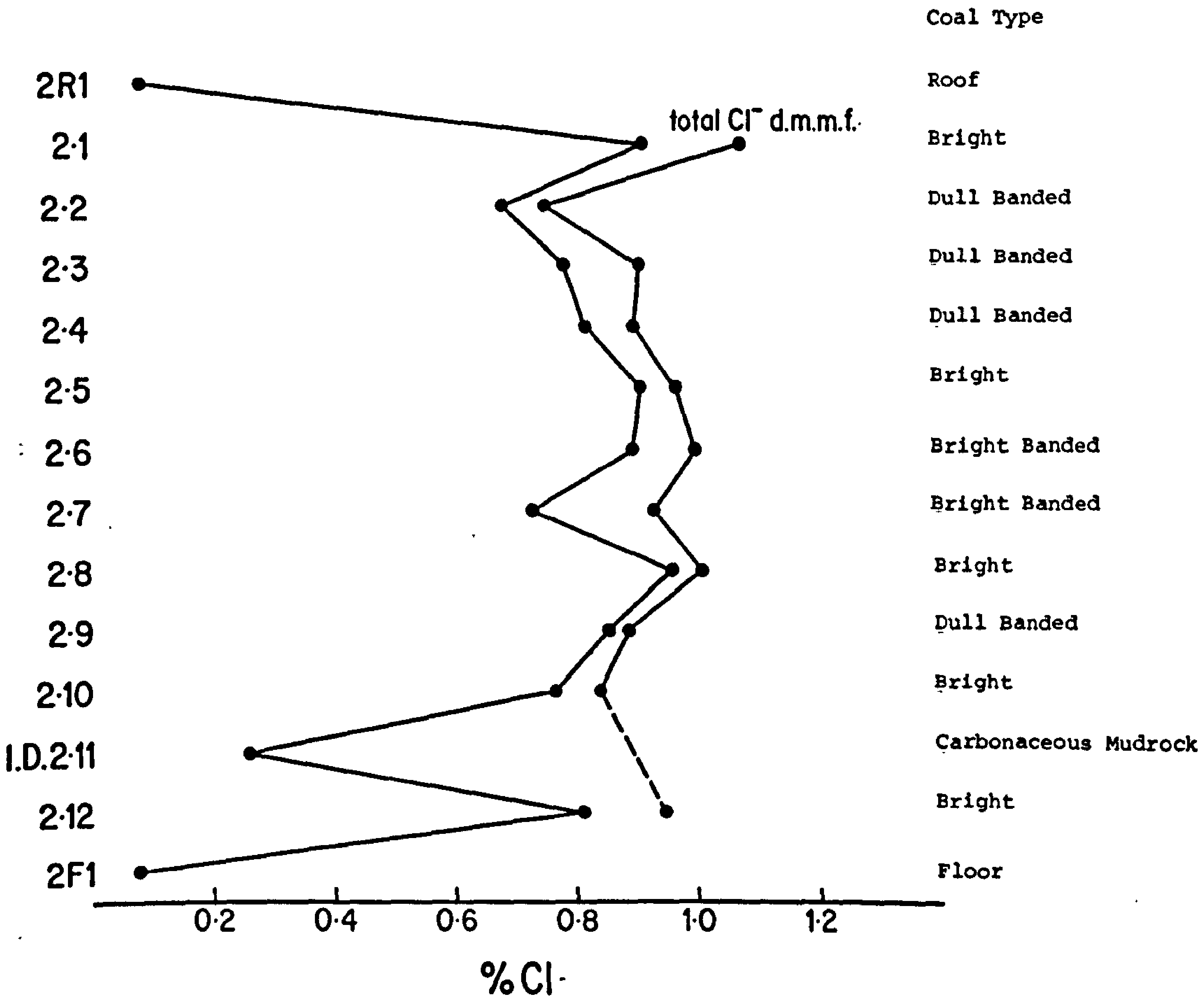


Figure 3: Littleton Colliery

(a) Eight Feet Seam. Total chlorine, whole rock.

Fig. 3b PARK SEAM, LITTLETON



d.m.m.f. = dry mineral matter free basis

Figure 3: Littleton Colliery

(b) Park Seam. Total chlorine, whole rock and dry mineral matter free.

Fig. 3c SHALLOW SEAM, LITTLETON

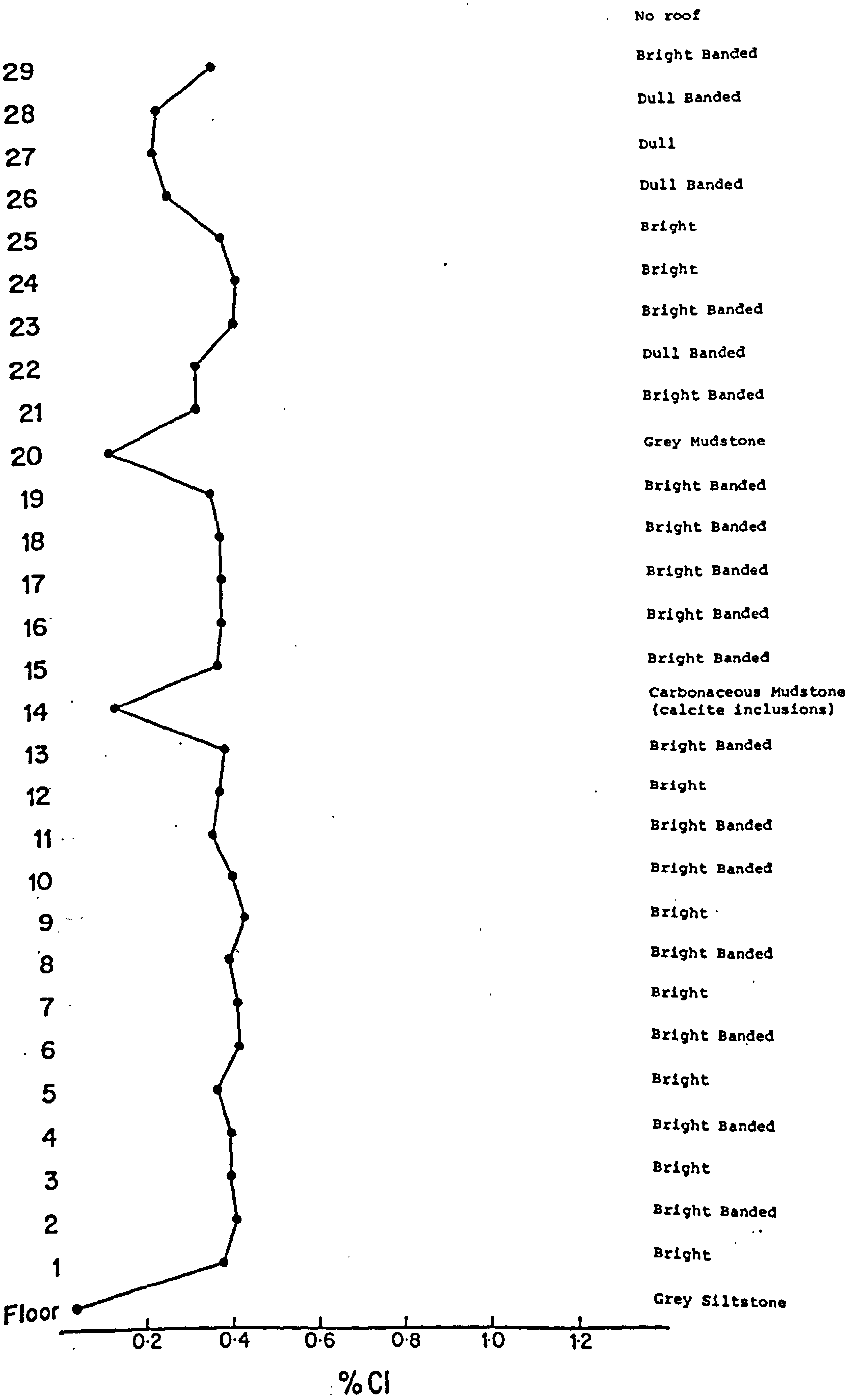


Figure 3: Littleton Colliery

(c) Shallow Seam. Total chlorine, whole rock.

Fig. 4a YARD SEAM, LEA HALL

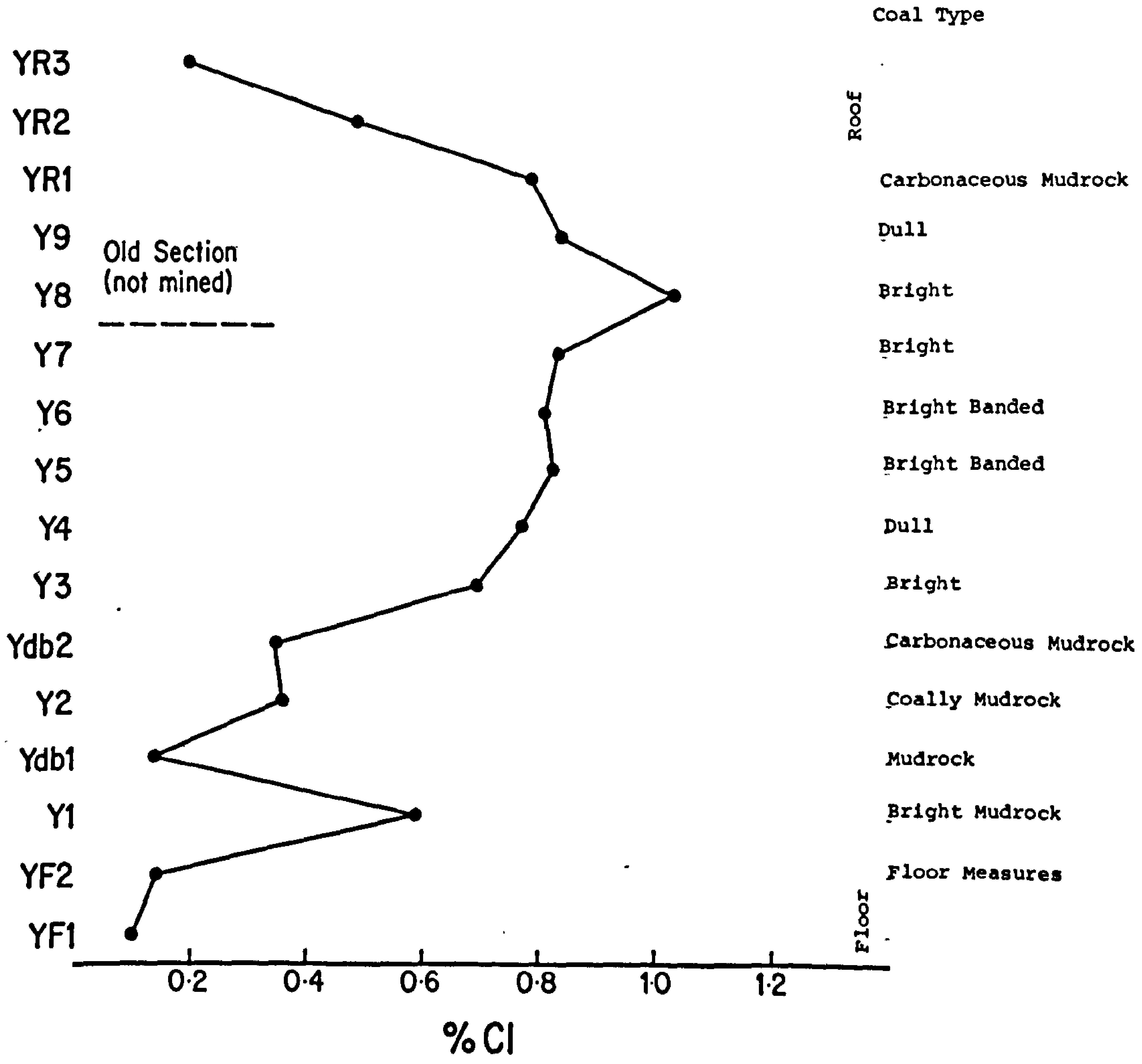


Figure 4: Lea Hall Colliery

(a) Yard Seam. Total chlorine, whole rock.

Fig. 4b SHALLOW SEAM, LEA HALL

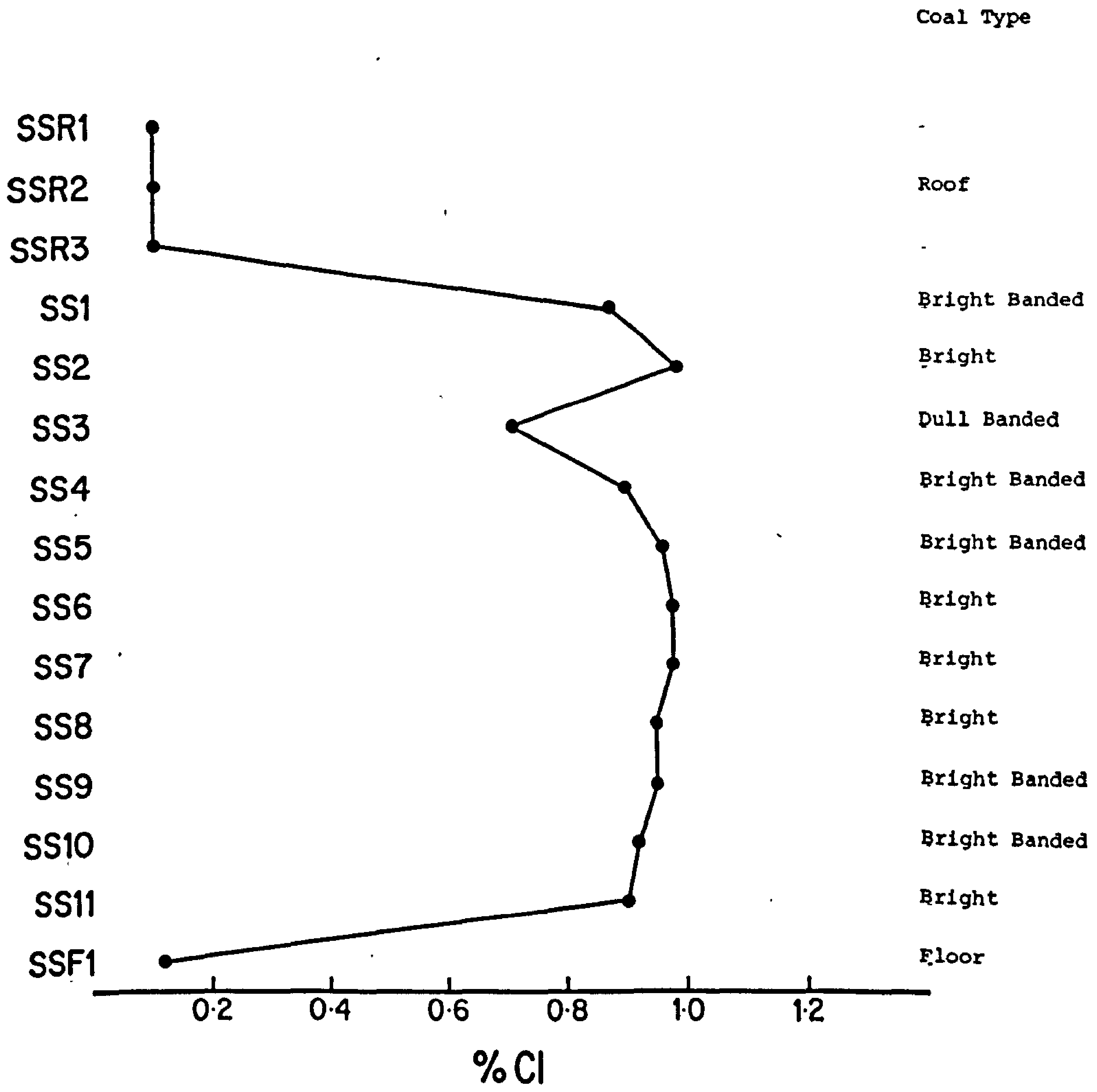


Figure 4: Lea Hall Colliery.

(b) Shallow Seam. Total chlorine, whole rock.

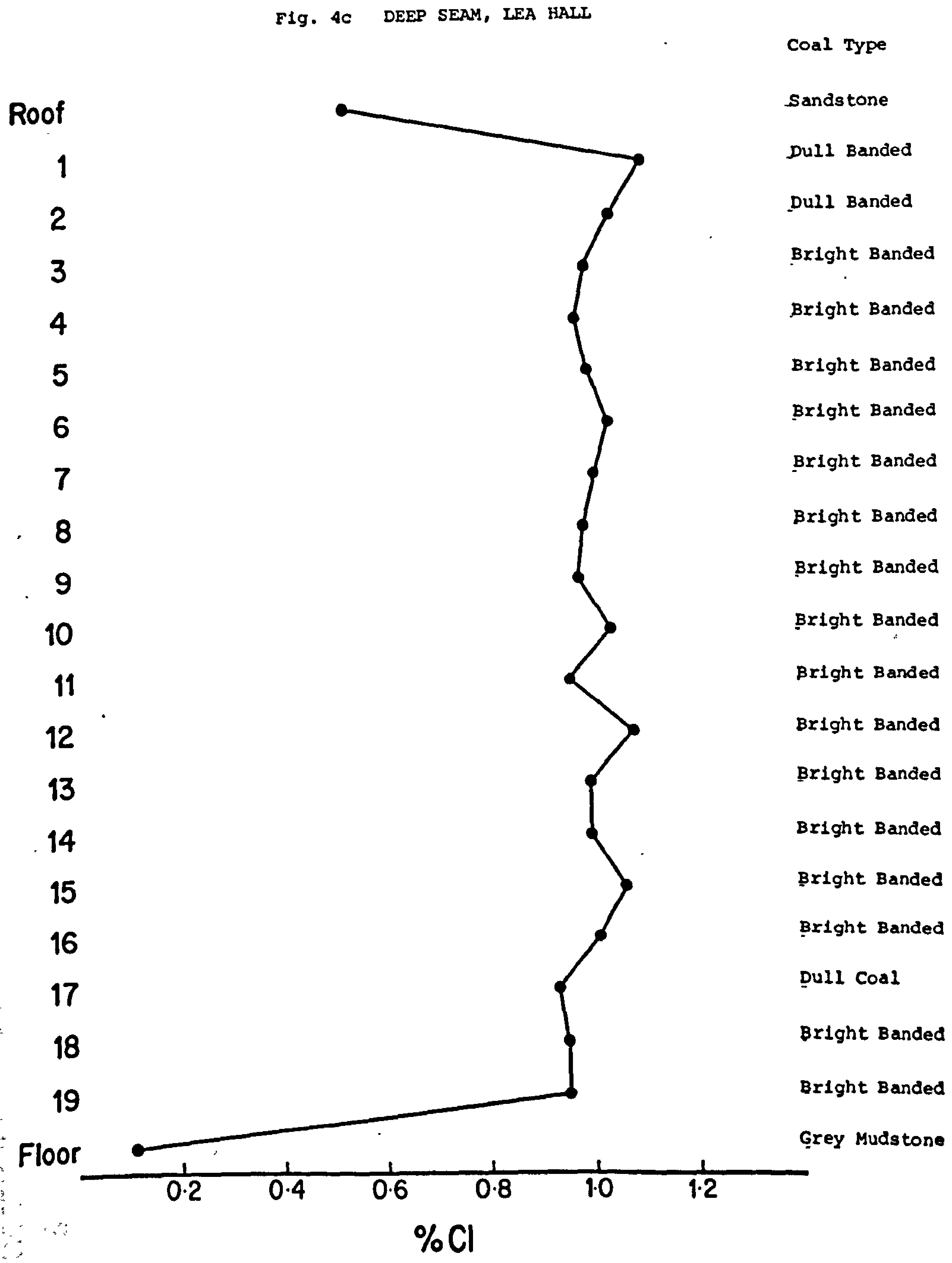


Figure 4: Lea Hall Colliery

(c) Deep Seam. Total chlorine, whole rock.

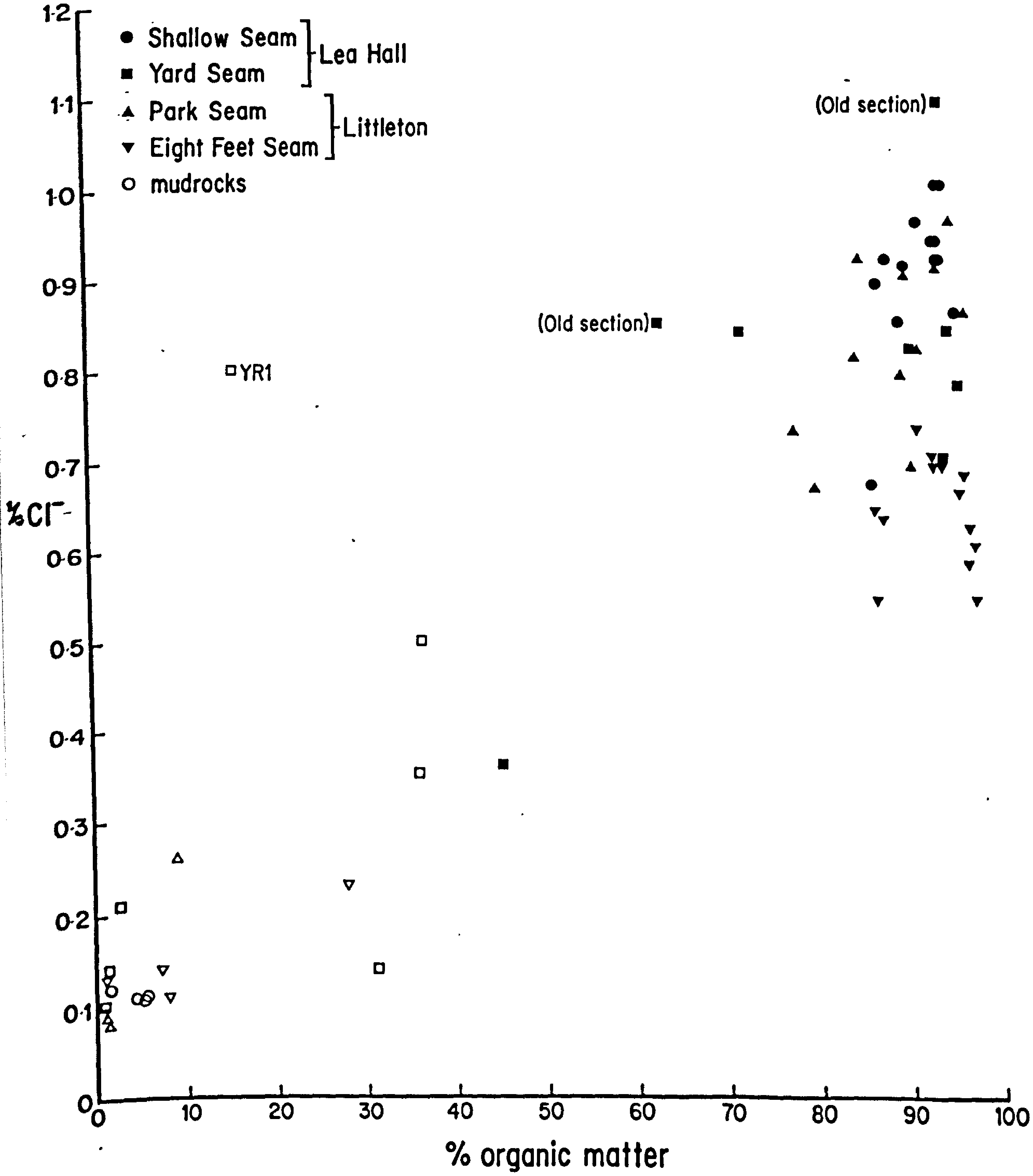


Figure 5: Plot of percentage chlorine, whole rock against percentage organic content.

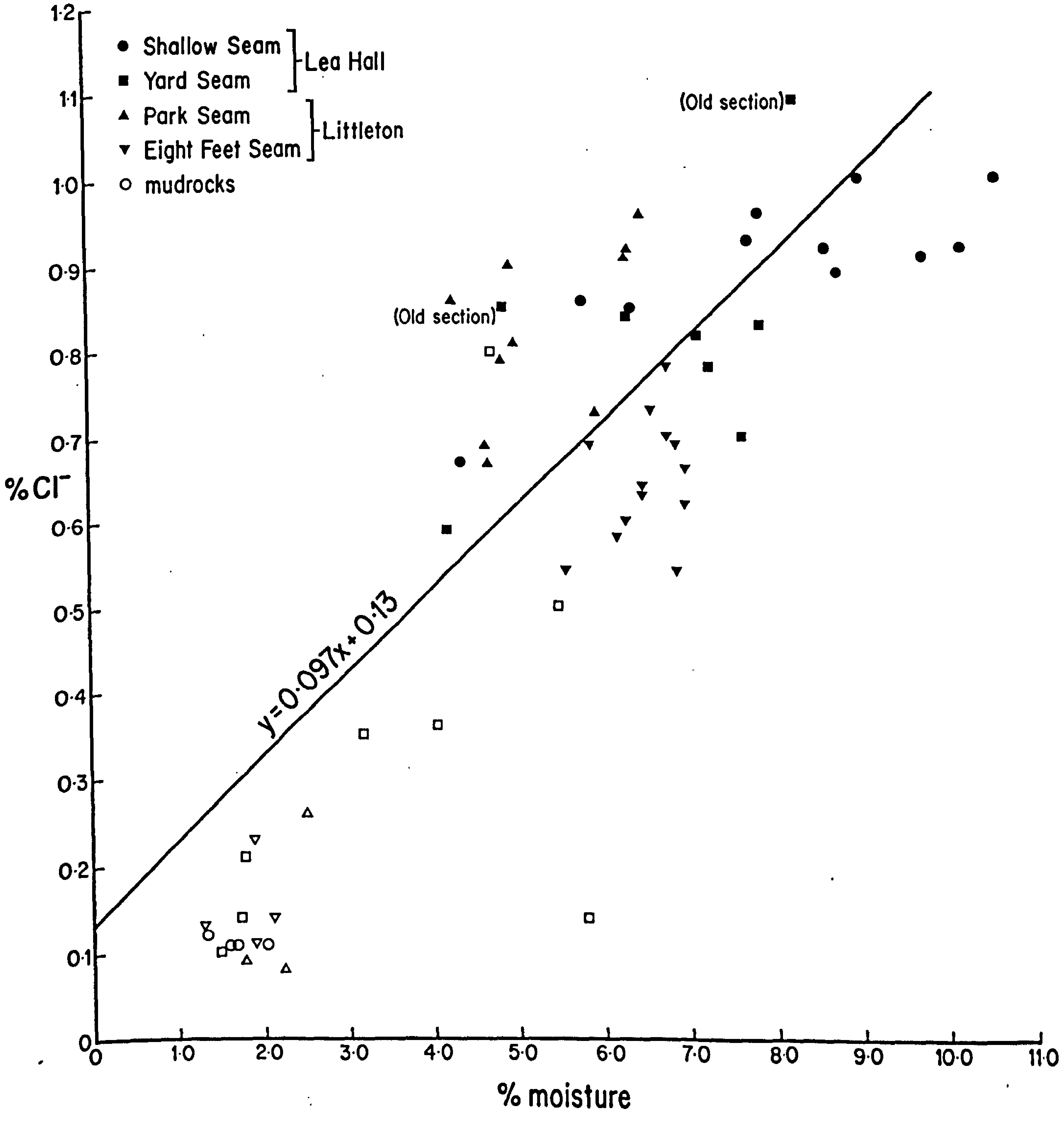


Figure 6: Plot of percentage chlorine, whole rock, against percentage moisture. Reduced major axis regression equation shown.

APPENDIX 2

Water-Soluble Chlorine and Associated Major Cations from the Coal and Mudrocks of the Cannock and North Staffordshire Coalfields

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ABSTRACT: Samples of high Cl coals from Lea Hall, Littleton (Cannock) and Hem Heath (North Staffordshire Coalfield) together with their immediate roof, floor and intraseam dirt bands were analysed for major water-soluble ions in order to predict their Cl leachability. In organic poor mudrocks the total Cl is a NaCl groundwater solution which is 100% water-soluble. In the coals the absolute water-soluble Cl levels are higher but even with ultrafine (tema) grinding 100% extraction cannot be achieved. The relationship of the water-soluble Cl to Na in the coarse fractions and Ca in tema ground samples suggest different mechanisms of Cl holding and release. There is a relationship of higher water-soluble Cl with dull coal over bright coal, which may be explained by the greater size of dull coal pores and greater accessibility of these pores to the groundwaters. The groundwater Cl is Na associated and leached with relative ease from coarse grained samples and accounts for approximately one-third total Cl. Tema grinding shows a close correlation of water-soluble Cl^-, Ca^{2+}, HCO_3^- and pH. This Cl^- is thought to be combined with the organic matter and released by ion-exchange, OH^- for Cl^- and the acidity created balanced by carbonate solution. Fine grinding is essential to create a maximum surface area for exchange reactions to take place. If the groundwater

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Cl concentrations are high enough, as in the Yard-Ragman Seam, they may over-ride the total Cl coal type relationship seen in the Cannock Coalfield. If the water-soluble Cl is leached from the Yard-Ragman Seam, the 'normal' relationship of highest total Cl in bright coal, lowest in dull coal, holds true.

Introduction

The presence of chlorine in coals at high levels (> 0.4% wt.) is known to cause problems in coal fired steam boilers. This problem is particularly acute in the Pennine and North-East England coalfields where chlorine values may reach 1%. High chlorine and alkali metal contents cause boiler tube fouling, the formation of fireside deposits and the corrosion of superheater and reheater tubes. The literature concerning fireside deposits and boiler corrosion is reviewed in Gluskoter and Ruch[1]. The form of chlorine and its origins are of geological interest. However, such knowledge is of great economic importance to the prediction of future coal-chlorine levels and from a knowledge of its form, a prediction of its leachability may be assessed. A correlation between total chlorine and coal type has been demonstrated elsewhere (Caswell, Holmes and Spears[2]). In the present paper, the leaching characteristics of the coals from three collieries in noted high chlorine areas have been studied in sections taken through seven coal seams. Experiments have been conducted on varying size fractions to determine the relationships between coal type, mudrocks, chlorine leachability and the associated major cations. The composition of the leachates will give an indication of the form of the chlorine and how it is distributed within the coal and associated strata. Literature on the form of chlorine is conflicting but may be divided into two major schools of thought. The first considers all the chlorine to be an inorganic chloride of sodium and potassium and in some cases of calcium and more rarely magnesium and iron (De Waele[3]; Sexton and Davidson[4]; Crossley[5]; Whittingham[6]; Crumley et al[7]; Gluskoter and Rees[8]). Alternatively, some portion of the total chlorine/in is combination with the organic matter (Brame and King[9]; Edgcombe[10]; Daybell and Pringle[11]; Daybell[12]; Gluskoter and Ruch[1]). The former are essentially water-soluble if Na balanced and relatively easily leached. The latter may only be removed, in addition tothe chlorides, by ultrafine grinding and reflux (Edgcombe[10]) so long as the carbonate content is sufficiently high (Daybell and Pringle[11]). Nelson[13] suggested that chlorine may be held in water-insoluble chlorine bearing minerals such as chlorapatite and sylvine. The form of the chlorine and its leachability varies between coalfields (Daybell[12]) and shown here to vary between collieries of the same coalfield and within a seam. Summaries are to be found in Kear and Menzies[14], Watt[15], Gluskoter and Ruch[1], and Saunders[16].

Sample Collection

Samples were collected from the Cannock and North Staffordshire Coalfields. The location of the collieries is given in Figure 1, and the geological succession through the Coal Measures in Figure 2. Staff of the National Coal Board kindly collected seam profiles from the Yard-Ragman (Hem Heath, North Staffordshire), (Figure 4), Deep (Lea Hall, Cannock) (Figure 6), and Shallow seams (Littleton, Cannock) (Figure 7). Samples were taken to represent each 10 cm of the seams except where distinct lithological changes meant the sampling of major coal types. Floor and roof samples were taken where possible and intraseam dirts if they occurred. Further seam profiles were taken from the Yard (Figure 8) and Shallow (Figure 9) seams at Lea Hall and the Eight Feet (Figure 10), and the Park (Figure 11) at Littleton Colliery. The Shallow Seam was sampled at a 25 cm interval and the remainder at 20 cm intervals. Roof and floor measures were sampled at a 20 cm interval in all four seams and intraseam dirts if present. It should be noted that the roof of the Yard Seam is not mined and part of the seam was not fresh. Samples Y8, Y9 and associated mudrocks could therefore have been subjected to evaporation and modification of the water-soluble ions.

Methods

Total chlorine was determined using the general method of B.S.S. part 8[17], with one exception. Rather than using nitrobenzene to precipitate the Ag Cl, the solutions were boiled and filtered before titration. Repeat analyses show the method to be reproducible to ± 0.01% at chlorine contents of 1% (Caswell, Holmes and Spears[2]).

The water-soluble ions were determined shortly after sampling on an 'as received' basis. Total chlorine was determined later, on oven dried samples. To make results comparable, the total chlorine curves were re-expressed on an 'as received' basis using the oven dried (105°C) total moisture chlorine values. Moisture contents for the tema ground samples are included so that comparisons can be made (Table 1).

The methods used to determine water-soluble elements varied depending on the experiment but for the tema ground (vibrating disc) samples the procedure was based on that of Spears[18]. The size fraction used, volume of distilled water and method of separation otherwise varied. Where leaching rates were being investigated in the relatively coarse fraction (30-72 mesh B.S.S.) and several aliquots of suspension were removed at set time intervals, a large sample size was used (40 g of coal in 400 ml of water). The samples were stirred mechanically for 8 hours and left to stand overnight. Aliquots were removed by syringe pipette and the leachate separated from the fine grained coal using a Whatman glass microfibre filter paper under suction.

For the less than 72 mesh B.S.S. samples, approximately 500 g was crushed to < 1 cm and 50 g of this was hand ground in an agate mortar and pestle and then sieved. Ultrasonic disaggregation of the sample in water was used when 15 minutes was shown to achieve similar results to 7 hours mechanical stirring. 2g samples in 50 ml of water were used.

To test the fine grained leachability of chlorine in water at ambient temperature, samples previously crushed to <1 cm were further crushed for a minimum period in a tema mill. Sub-samples were used to determine moisture content by heating in an oven at 105°C for 8 hours. The samples were cooled in a dessicator and the weight loss expressed as the moisture percentage. Water-soluble elements were determined using 0.5 g of sample in a centrifuge tube with 30 ml of water. The suspension was centrifuged and the top 20 ml of the leachate pipetted off. Occasionally very fine material would not settle. This was a problem mainly encountered with the intraseam dirt bands. These samples were filtered through fine paper and run with a similarly prepared blank. The Eight Feet 150-200 mesh B.S.S. samples were treated in the same manner and analysed only for Cl.

The leachates were analysed for Na, K, Mg and Ca using atomic absorption spectrophotometry. Cl was determined for the Eight Feet 30-72 mesh B.S.S. using colourimetric analyses, but all other Cl analyses were made by Mohr's titration. pH was determined immediately prior to pipetting off the leachate. Bicarbonate analysis followed the method of Vogel[19] and sulphate, that of Fritz and Yamamura[20].

Exchangeable cations were determined using 0.05N Ba NO_3 then following the method of Spears[21].

Leaching Characteristics

Leachability is inversely proportional to grain size as seen in the chlorine profiles of the Eight Feet Seam (Figure 3). There is, however, a considerable between sample variation. In mudrocks with no organic matter, the total Cl is water-soluble and is held in the pore moisture. As organic matter increases, the total and water-soluble Cl also increases. However, as a relative percentage of the total Cl, the water-soluble Cl falls. The relationship between organic matter, coal type and total Cl is covered in Caswell, Holmes and Spears[2].

Tema grinding for a minimum period (to reduce possible chemical side effects) shows no difference at the 95% significance level with leachates from samples ground in a mechanical agate for 3 hours. 100% Cl extraction was still not achieved and varied between 41% (8S9) and 88% (8S1). Similar variations were found elsewhere between 21% in the Park Seam (2.12) and 89% in the Shallow Seam (SS9), the extremes in between,and within,seam variation. Edgcombe[10] related that 100% Cl extraction could be achieved on fine samples under reflux. However, this is only the case if sufficient carbonate is present (Daybell and Pringle[11]).

When plotted on log-log paper, % of total water-soluble Cl versus time, a 0.5 gradient indicates a purely diffusional release (Crank[22]) If the pores are holding moisture and some proportion of the Cl is in this moisture (Caswell, Holmes and Spears[2]) then leaching will be diffusional if the pores are accessible. If the Cl is in another form and must be dissolved or exchanged, then the rate will be reduced. Bettelheim and Hann[23] showed that for these two end members the first 50% extraction is a root function of the leaching time. They found markedly different leaching characteristics between the Cannock (Lea Hall Shallow Seam) and North Staffordshire coalfields (Hem Heath Winghay Seam).

Diffusions rates were calculated on two coals from the Eight Feet Seam 30-72 mesh B.S.S. coals showing extremes in leaching behaviour, 8S5 (dull) and 8S12 (bright). Major differences exist between the mineralogy (Lin et al.[24]), physical and chemical properties of the maceral groups. Over a leaching period of 3 to 100 minutes the Cl gradient for the dull coal was 0.16 and 0.40 for the bright coal. Na rates were comparable, being 0.21 and 0.36 respectively. 50% Cl extraction (based on tema ground coal for total water-soluble Cl) was reached in the dull coal after 3.75 minutes and in the bright coal after 57 minutes. The very low gradient in the dull coal is therefore explained by very rapid leaching before the first sample interval. Although a purely diffusional Cl release is not attained in either sample there is obviously a fundamental difference in the Cl holding mechanism in different coal types. Tema grinding vastly increases the leaching rates but other factors play important roles in Cl release as will be seen later.

The <72 mesh B.S.S. profile for the Yard-Ragman (Figure 4) shows a variable water-soluble Cl distribution. Extremes in leachability vary between 10.7% (bright coal, 21) and 63.2% (dull coal, 6). Given that coal size is important and these two samples are of different coal type sieving was carried out and showed that the dull coal broke down to a smaller size. However, the difference in size distribution was not considered great enough to produce such marked leaching differences. To investigate the difference in water-soluble Cl with coal type, the associated cations were studied. This is shown in Table 2. Sample 6 has the highest Na, and sample 21 the lowest for the Yard-Ragman coals (Figure 4). Saunders[16] showed that Cl leachability is related to the water-soluble Na content. Similar patterns are seen in the Shallow Seam (Figure 7). The lowest Na is in a bright coal in the Deep Seam

(Figure 6). The Eight Feet and Park (Figures 10 and 11) show Na to be high but not highest in the dull coals, and in the Yard (Figure 8) there is very little difference except in the unmined roof. Only in the Lea Hall Shallow Seam (Figure 9) is there an exception where the only dull coal also have the lowest Na. The different size fractions (Table 2) shows Na extraction increasing with decreasing size for the Yard-Ragman bright coal sample (21) but reaching a peak in the 150-106μm and thereafter declining in the dull (6) coal sample. This, together with the association of Na with dull coal suggests a difference in pore size distribution between the coal types.

Using the standard error of the means for water-soluble Cl from the Yard-Ragman Seam it is seen that the bright coal has a significantly lower percentage than the dull banded or bright banded coals. The bright banded coal has a probably significant lower percentage of its Cl water-soluble than the dull banded coals and the dull coals have the highest water-soluble Cl (50%) but this is based on only two samples (Figure 5). Similar trends are to be seen in the 30-72 mesh B.S.S. Eight Feet Seam and to some extent in the <72 mesh B.S.S. Littleton Shallow profile and Lea Hall Deep Seam.

It can be seen from Figure 3 that the leaching characteristics of the coal changes with differing grain size. Caswell[25] has shown that in the hand specimen the most rapid leaching takes place in dull coal on account of its larger pores. In the 30-72 mesh B.S.S. mesh coals of the Eight Feet Seam, Cl leaching is marginally more rapid than from the bright coals. This relationship is obscured in the 150-200 mesh B.S.S. size range. The tema profile bears little resemblance tothe coarse fraction but between samples 8S1 and 8S8 corresponds very closely to the total Cl curve. There is a trend of dull coal leaching the most

Cl to the bright coal leaching the macimum. This provides further evidence of difference in pore size distribution in different coal types, which is supported by Harris and Yust[26,27]. Thomas and Damberger[28] show vitrinite, and hence bright coal, to have the greatest porosity of the maceral groups, but of sizes much smaller than dull coal. Bright coal is the major host of Cl (Saunders[16]; Caswell, Holmes and Spears[2]). Progressively finer grinding is therefore opening up smaller pores. Incomplete extraction with tema grinding suggests either that the smallest pores holding Cl are not being opened or that some proportion of the Cl is in a different form.

Form of Chlorine

Indirect evidence for the form of Cl can be deduced from a study of the associated water-soluble ions, namely Na, K, Ca, Mg, HCO_3, SO_4 and pH. As related in the Introduction two schools of thought on the form of Cl exist, either as chloride balanced by Na or K or in organic combination. The present work shows that between one-third and a half of the water-soluble Cl (tema ground) can be satisfied by the available Na. The K concentration is negligible. This corresponds with the findings of Edgcombe[10], Daybell and Pringle[11], and Gluskoter and Ruch[1], and suggests that the majority of Cl is in another form.

A study of the tema seam profiles (Figures 8-11) identify certain trends. The pH is low for the coals as would be expected from organic rich material. Values range from 2.80-6.95 ($\bar{x}$ = 4.49, S.C. = 1.1). The mudrock values are more neutral but vary with organic matter content. Closely corresponding with pH is Ca (r = +0.93), Mg(+0.50) and HCO_3(+0.83), all significant at the 99.9% significance level. There is no correlation between Ca and SO_4 nor XRD evidence of gypsum being prsent. The K values are low in the coals and roughly compare with ash content (+0.34, 95% significant). When the mudrocks are introduced the correlation coefficient is increased to +0.59 (99.9% significance). This suggests a correlation with the illite and degraded illite fraction of the ash. However, within the coal ash, the clay proportions are low and very variable, hence its reduced correlation coefficient. A small proportion, insignificant in terms of water-soluble Cl, could be contributed by groundwaters (Table 3). As much of the water-soluble Cl is thought to be associated with Na a close correlation is to be expected. Although variations in the coal Na profiles exist, they are not so marked as those exhibited by Ca, Mg, HCO_3 and pH. The Eight Feet Seam (Figure 10) shows comparable Na values between the seam and associated mudrocks. The Shallow Seam (Figure 9) has Na values approximately twice that of the mudrocks. There is a closer correlation between water-soluble Na and Cl in the <72 mesh B.S.S. profiles than in those that were tema ground seam profiles. The great majority of Na is easily water-soluble even from relatively coarse fractions. Similar leaching patterns are found by Neavel et al[29] and Saunders[16]. Cl leaching however, increases with smaller grain size.

The damp mudrock Y dbl was centrifuged and the solution analysed (Table 3). The Cl in the moisture originating from groundwaters, accounts for the total Cl of the sample (Caswell, Holmes and Spears[2]). Na balances 96% of the Cl. It is concluded that the readily water-soluble Cl in the coals, which can be predicted from the Na content,(Saunders[16]) is also groundwater held in the coal pores. Table 3 also shows the composition of moisture centrifuged from run-of-mine Shallow Seam coal. However, as the volume of water removed from the coal, compared to the mudrocks, was small in comparison to the moisture contents (9.98% compared to 5.80%) it suggests that the pores are far less accessible and perhaps far smaller, than in the mudrocks. Element ratios in the coal water are similar to that of the mudrock Ydbl but concentrations are lower by a factor of 10. As it is thought that the Na Cl is held in the moisture, and the centrifuged water is reduced in concentration, that a concentration gradient exists within the pores. Ca is slightly increased in the coal water, but Na is equivalent to 87% of the Cl. This is closely comparable to the groundwater figures associated with the Lea Hall Shallow Seam (Table 3).

It is notable that although the total dissolved solids weight changes, the ratio of major cations and Na (Cl equivalent) Cl ratio is remarkably similar within the Lea Hall groundwaters (Table 3). That there is a relationship between water-soluble Cl and water-soluble Na can be seen in the constant ratios in the <72 B.S.S. leachates (Table 4) from the three different collieries. As the ratio is reduced from that of the groundwaters (0.61 compared to 0.85 for the Lea Hall Deep Seam) it suggests that more than a NaCl brine is being released. An explanation of this phenomena is covered when considering the tema ground profiles.

It has been shown that total Cl is related to coal type, being highest in the bright and lowest in the dull coals, as a function of their internal surface area (Caswell, Holmes and Spears[2]). This relationship was based on coals from the Cannock Coalfield. However, the Yard-Ragman Seam from the North Staffordshire Coalfield shows a complete reversal of his trend. The water-soluble Cl, as already explained, is highest in the dull coals and lowest in the bright. If the total Cl has its water-soluble Cl contribution subtracted, then the distribution seen in the Cannock Coalfield also holds here. This suggests two distinct modes of occurrence of the Cl. It is believed therefore, that the readily water-soluble Cl is groundwater trapped in or in transit through the larger pores and consequently higher in the dull coal. This is Na associated and may be calculated from its water-soluble Na content. The remaining Cl is either held in less accessible pores, or in a different form, and the distribution of this Cl is controlled by rank imposed during the Hercynian Orogeny (Skipsey[30]) via its control on porosity. With grinding the water-soluble Na to water-soluble Cl ratio is seen to change from that of the groundwaters because of the dissolution of minerals in the coal.

Exchangeable Cations from the Associated Mudrocks

Evidence of Na-rich groundwater associated with the coals can be found from the relative abundances of exchangeable cations in the mudrock samples. Exchangeable cations are those which may be removed by ion exchange with a relatively concentrated ionic solution. They are associated predominantly with the clay minerals and reflect the type of clay minerals and the composition of the ground waters which have been in contact with them. $BaNO_3$ was chosen as an exchange medium because of its reduced dissolution of carbonates when compared to ammonium acetate. However, carbonates were negligible in all but 8R2 and 8R1 where siderite can be seen to vastly increase the exchangeable Ca and Mg values. The results are given in Figure 5. Results from the Yard-Ragman Seam were compared with non-marine mudstones of Spears[21]. This shows an increase in exchangeable Na at the expense of Ca in the Hem Heath samples. As the clay fraction varied between samples, notably those which are organic rich, the results were re-expressed as a percentage of the total C.E.C. (calculated in milliequivalents per 100 g). All samples except the siderite band 8R2 show Ca depletion. At Hem Heath there is a considerable gain in Na. This is especially notable in the intraseam dirt band, suggesting excessive channelling of Na rich groundwaters, even compared to the roof or floor measures. As the Na:Cl ratio has been shown to be high in the groundwaters, the exchangeable data indicates high Cl levels as shown in Table 3. Values from the Yard, Shallow, Eight Feet and Park seams show similar trends. Ca is reduced and in all but the Eight Feet Seam, at least some of the samples are enriched in Na. K values are also high. Na values are not as high as at Hem Heath and it is therefore concluded that the groundwaters are not so concentrated in the Cannock Coalfield. This is supported by groundwater analysis as indicated in Table 3. It is suggested that the very high salinities encountered at Hem Heath have allowed the 'normal' coal Cl relationship to be over-ridden by post rank groundwater additions even allowing for the low moisture contents. Lower salinities encountered in the Cannock Coalfield have enabled the original relationship to hold true. Ydb1 does show Na enrichment but as predicted, the lower salinities have expressed themselves in a relatively lower exchangeable Na percentage. It is interesting that only Ydb1 and the underlying dirty coal (Y1) exhibit notable Na concentrations. Perhaps the growth of epigenetic (secondary) minerals and other diagenetic processes have greatly reduced the throughflow of waters in all but the very fine grained intraseam dirt bands. Further evidence for Na enrichment from contemporary groundwaters is to be found in the non-mined Yard 'roof' section. Evaporation of these samples has led to abnormally high Cl values. The majority of this Cl may be balanced by Na, which is some two and a half times as high as that found in the freshly exposed seam samples, despite moisture contents being little higher than in the fresh seam.

Tema Ground Coal

The leaching characteristics of tema milled coal are somewhat different to that of the coarser fractions as seen from the Eight Feet

Seam (Figure 3). A comparison of the water-soluble ions associated with the Cl also show distinct differences (Figures 8-11). The proportion of Cl leached is increased but in none of the coal samples is 100% extraction achieved and totals are variable. This is seen clearly in the Park Seam (Figure 11). The water-soluble chlorine curve still follows that of the Na but there are notable exceptions. The Park Seam (Figure 11)is a good example, but similarities are to be found in the other three seams. High water-soluble chlorine peaks are found to correlate with high Ca (+0.75,=99.9%), HCO_3 (+0.57, =99.9%) and pH (+0.69, = 99.9%). There is a correlation with Mg (+0.27, = 90%) but this is not found in the Shallow Seam thus reducing the correlation coefficient. There is a stronger correlation between water-soluble Ca and Cl (+0.75) than with Na (+0.67, 99.9%). Where water-soluble Ca is low, so too is the pH, HCO_3 and water-soluble Cl, and vice versa. Ca and Mg are seen to have an irregular distribution through the seam profiles and this corresponds to the presence of calcite and ferroan-dolomite in the cleat. These minerals were identified by X.R.D. (X-ray diffraction) analysis of the coal ash. Dissolution of the carbonate will give rise to high concentrations of Ca, and to a lesser extent Mg, HCO_3 and consequently raise the pH. There is no evidence to believe that Cl is associated with the cleat carbonates and therefore the relationship with Cl must be indirect. A mass balance of the ions (excluding SO_4, which is unreliable) shows a close correlation. Na,Ca,Mg and pH is usually in excess of Cl and the difference is balanced by HCO_3. As the relationship between Cl and Ca is indirect, this suggests that ion exchange may be playing a role in releasing Cl over and above that balancedby Na,the relationship found in the coarser fractions and expected from the groundwaters. Similar leaching characteristics were found by Edgcombe[10],and Daybell and Pringle[11]. Daybell and Pringle[11] noted that 100% Cl leaching could not be attained, even under reflux, if the carbonate content was low. However, if sufficiently high, 100% extraction could be achieved. By adding carbonate, the coal with low concentrations could increase their Cl yield. This they attributed to ion-exchange between OH^- from water dissociation with Cl held in exchange sites on the organic matter. The pH would fall and exchange would stop when an appreciably acid concentration developed. Carbonates, however, if present would come into solution, the H^+ ions would combine with the $CO_3^=$ as HCO_3^-, thus the ion balance would be maintained. Tema grinding the coal would increase the surface area and allow surface reactions with organic matter to be at a maximum. This suggests that the Cl not balanced by Na is in combination with the organic matter. However, as the total chlorine has been shown to be related to moisture content and hence porosity (Caswell, Holmes and Spears[2]) it is thought that this Cl is attached to the internal surfaces of the coal micropores.

The Relationship of Water-Soluble Cations between Coal Seams

As expected, the total dissolved solids extracted from the seams increases with depth. This can be correlated to an increase in total dissolved solids in the groundwaters with depth, notable Na and Cl (Gluskoter[31], Downing and Howitt[32]). The Littleton Shallow Seam is an exception. Both water-soluble ions and the total Cl is considerably lower than the two seams studied higher in the geological succession from Littleton Colliery (0.39% total Cl compared to 0.82% in the Park Seam). However, if a ratio of water-soluble Na to total Cl is taken for all the Littleton seams a very constant ratio emerges (Table 6). This suggests that the lower water-soluble ions and total Cl content is controlled by the internal surface area of the coal which is reduced in the deeper

Shallow Seam. The water-soluble Na:total Cl ratios are remarkably constant for a given colliery (Table 6) but differ between Lea Hall and Littleton. The ratios for Littleton and Hem Heath are very similar. If the groundwaters of the North Staffordshire and Cannock Coalfields are similar in composition, similar Na:Cl ratios would occur if depth of burial, rank and hence internal surface area are similar. However, Hem Heath coals have groundwaters far more concentrated in Cl (Table 3). As the total Cl values are roughly comparable between the coalfields, the higher water-soluble Na and hence water-soluble Cl at Lea Hall suggests a fundamental difference in internal surface area between Lea Hall and Hem Heath. This is confirmed by a comparison of moisture contents (4-10% for the Lea Hall Shallow Seam and 2-3% at Hem Heath Yard-Ragman Seam). As water-soluble Na can be used to predict Cl leachability for <72 mesh B.S.S. coal (Saunders[16]) it is expected that the Lea Hall Cl leachability will be almost twice that of Littleton and Hem Heath.

Conclusions

1. The leachability of Cl depends upon the host rock. In the mudrocks with low organic matter content, all the chlorine is water-soluble.

2. In the coals, Cl leachability is a function of the ground size. However, this function may vary between samples, even from the same seam and certainly between collieries. Even with tema milling, 100% chlorine extraction cannot be achieved. Between the size fraction 150-200 mesh B.S.S. and tema milling there is a fundamental size distribution beyond which chlorine extraction is dramatically increased.

3. Groundwater analyses correspond closely to that of moisture centrifuged from an intraseam dirt band (Ydbl) and this accounts for its total

chlorine content. Moisture centrifuged from coal (Shallow Seam, Lea Hall) shows a similar ratio of ions, but levels are lower by a factor of ten. It is suggested that a concentration gradient exists in the coal pores and the moisture that can be centrifuged is only a part of the coal moisture. Further evidence of Na, and hence chlorine, rich groundwaters passing through coal seams is to be found from the exchangeable cations associated with the mudrocks. Na is considerably enriched at Hem Heath and this is backed up by National Coal Board groundwater analyses. Groundwaters in the Cannock Coalfield are not so concentrated but there is evidence that intraseam dirts channel recent brines through coal seams.

4. Water-soluble Na:total Cl ratios are remarkably similar between seams of a colliery. There is little difference between Littleton and Hem Heath collieries in different coalfields. Na contents are both low. Lea Hall shows a much higher Na content but all three collieries have similar total chlorine values. As readily water-soluble chlorine is higher at Lea Hall, it is thought that the relative proportion of readily accessible pores is greater at Lea Hall than Littleton or Hem Heath.

5. Chlorine appears to be in two forms:

i. A predominantly Na, Cl solution which are groundwaters temporarily trapped or 'in transit' through the larger pores and fissures in coal and making up the total Cl content of low organic matter mudrocks. This chlorine is readily water-soluble and the leachability of 72 mesh B.S.S. coal can therefore be predicted from the Na content of the vitrinite, being the predominant coal maceral group. After leaching, little or no Na remains. This water-soluble Cl is found to be highest in the dull coals, intermediate in the banded and lowest in the bright coals suggesting a fissure and macropore distribution which follows this trend. Water-soluble chlorine contents may be twice as high in the coals as in the surrounding mudrocks.

ii. Non-readily water-soluble Cl is thought to be held in the smaller pores. This Cl is fixed until finely ground, tema milling being essential to extract a significant proportion. It may represent ground waters held by the coal when rank, and hence pore distribution, was imposed during the Hercynian Orogeny. This Cl is no longer associated with Na. It is held predominantly in bright coal, followed by bright banded, dull banded and lowest in dull coal. The pore size range of vitrinite is smaller than that to be found in exinite and inertinite, however, the internal void space of vitrinite is greater. Tema ground leachates exhibit a correlation of high water-soluble Cl with high pH, high Ca, Mg and bicarbonate. Once the smaller 'fixed' Cl holding pores are opened, it is possible that an exchange process of Cl^- for OH^- takes place. The dissociated H^+ combines with carbonate dissolved by the low pH to form HCO_3^- and hence the Cl^- released can be correlated with the Ca and Mg of the carbonates. If insufficient carbonate is present exchange will be inhibited. Fine grinding is essential in opening up these sites and creating a maximum surface for reaction to take place.

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TABLE 1: Moisture Contents (% Weight)

Yard Seam		Shallow Seam		Eight Feet Seam		Park Seam		Yard-Ragman Seam	
YR3	1.78	SSR1	2.01	8R1	1.30	2R1	1.76	Roof	1.40
YR2	5.51	SSR2	1.67	8R2	1.90	2.1	6.37	1	2.40
YR1	4.75	SSR3	1.60	8S1	6.50	2.2	4.66	2	2.60
Y9	4.89	SS1	6.40	8S2	6.90	2.3	4.87	3	2.60
Y8	8.31	SS2	7.90	8S3	6.20	2.4	6.18	4	2.80
Y7	6.35	SS3	4.37	8S4	7.00	2.5	6.34	5	2.80
Y6	7.16	SS4	5.84	8S5	6.30	2.6	4.99	6	3.20
Y5	7.87	SS5	7.77	8S6	5.60	2.7	5.97	7	3.10
Y4	7.30	SS6	9.08	8S7	7.00	2.8	6.51	8	2.70
Y3	7.66	SS7	10.10	8S8	7.80	2.9	4.30	9	2.80
Ydb2	2.19	SS8	8.68	8S9	6.90	2.10	4.70	10	2.90
Y2	4.07	SS9	10.02	8S10	6.50	I.D.2.11	2.51	11	2.90
Ydb1	5.80	SS10	9.80	ID10	2.10	2.12	5.03	12	3.00
Y1	4.21	SS11	8.82	8S11	6.60	2F1	2.24	13	2.60
YF2	1.74	SSF1	1.32	8S12	5.90			14	2.70
YF1	1.49			8S13	6.80			Middle Dirt	2.30
				8F1	1.90			16	2.50
								17	2.80
								18	2.80
								19	3.00
								20	1.00
								21	2.50
								22	2.40
								23	2.40
								24	3.00
								25	3.00
								26	2.70
								27	2.50
								28	2.50
								Floor	1.70

TABLE 2: Total Cl and Water-Soluble Cl, Na, K, Ca and Mg Values (%) for Size Fractions of Two Samples from the Yard-Ragman Seam

Size Fraction µm	Total Cl	Water - Soluble				
		Cl	Na	K	Ca	Mg
Sample 6 - Dull Coal						
212-150 µm	1.30	0.93	0.431	0.002	0.069	0.022
150-106 µm	1.36	1.05	0.578	0.002	0.079	0.024
106- 76 µm	1.31	1.05	0.524	0.002	0.092	0.027
Less than 75 µm	1.27	1.03	0.481	0.002	0.108	0.031
Sample 21 - Bright Coal						
212-150 µm	0.62	0.04	0.015	0.001	0.009	0.002
150-106 µm	0.62	0.05	0.019	0.000	0.011	0.002
106- 75 µm	0.63	0.06	0.021	0.001	0.011	0.002
Less than 75 µm	0.70	0.13	0.059	0.001	0.014	0.003

TABLE 3: N.C.B. Ground Water Compositions and Water Centrifuged from Coal and Mudrock

µg/ml	Yard-Ragman^{+}	1131's Deep^{+}	1103's Deep^{+}	1014's Shallow^{+}	Shallow (coal)^{o}	Ydb1^{o}
Cl	138100	17570	24850	15370	2300	23000
Ca		1210	1410	905	330	1610
Mg		333	410	275	50	330
Na		9737	13760	8480	1305	14375
K		123	-	-	20	340
Relative % of Cations						
Ca		10.6	9.1	9.4	19.4	9.7
Mg		2.9	2.6	2.8	3.0	2.0
Na		85.4	88.3	87.8	76.4	83.3
K		1.1	-	-	1.2	2.0
Na(Cl eq.)		15017	21220	13078	2010	22170
Na(Cl eq.)/Cl		0.85	0.85	0.85	0.87	0.96

+ Ground Water
o Centrifuged Water

TABLE 4: <u>Less than 72 B.S.S. Mesh Leachates</u>

	Deep (Lea Hall)	Shallow (Lea Hall)	Yard-Ragman (Hem Heath)
$Na(Cl\ eq)/Cl^-$	0.61	0.61	0.63
Major Cations Relative %			
Ca	26.0	31.6	21.6
Mg	6.0	1.3	5.4
Na	66.8	65.8	72.3
K	0.7	1.3	0.7

TABLE 5: Exchangeable Cations

	Na	K	Ca	Mg	Total
Hem Heath Mudrocks (meq/100g)					
Roof	2.74	0.66	1.70	0.90	6.00
Intraseam Dirt (15)	8.22	1.13	1.45	1.07	11.87
Floor	4.48	1.07	2.89	1.48	9.92
Spears (1973) average	1.61	1.05	4.36	1.54	8.56
% of Total Exchangeable Cations Content (as equivalents)					
Hem Heath - Yard Ragman					
Roof	46	11	28	15	
Intraseam Dirt (15)	69	10	12	9	
Floor	45	11	29	15	
Littleton - Eight Feet					
8R1	11.5	45.6	15.8	26.1	
8R2	1.1	15.6	51.1	32.1	
I.D.10	15.1	49.8	13.6	21.4	
8F1	11.2	45.6	10.8	32.4	
Park					
2R1	28.0	23.0	26.9	22.1	
2.11	32.1	30.0	19.5	18.3	
2F1	42.1	21.7	19.9	16.4	
Lea Hall - Yard					
YR3	12.5	32.8	28.7	26.0	
YR2	15.1	73.4	4.3	7.2	
YR1	5.9	23.2	25.6	48.4	
Ydb2	0	35.0	36.9	28.1	
Y2	0	31.9	39.7	28.4	
Ydb1	44.7	16.7	23.1	15.5	
Y1	32.0	35.0	25.3	17.3	
YF2	5.5	42.1	24.4	28.0	
YF1	9.0	40.0	24.7	26.3	
Shallow					
SSR1	24.3	49.4	18.9	9.4	
SSR2	31.4	39.4	19.7	9.5	
SSR3	34.3	38.2	18.7	8.8	
SSF1	1.0	60.6	25.3	13.1	
Spears (1973)					
Non-marine Coal Measures Samples	19%	12%	51%	18%	

TABLE 6: Water-Soluble Na/Total Cl Ratios

(based on average values from coal leachates)

Hem Heath		Littleton		Lea Hall	
Yard-Ragman	0.13*	Eight Feet	0.14	Yard	0.24
		Park	0.15	Shallow	0.25
		Shallow	0.15*	Deep	0.20*

* <72 mesh - remainder are tema milled

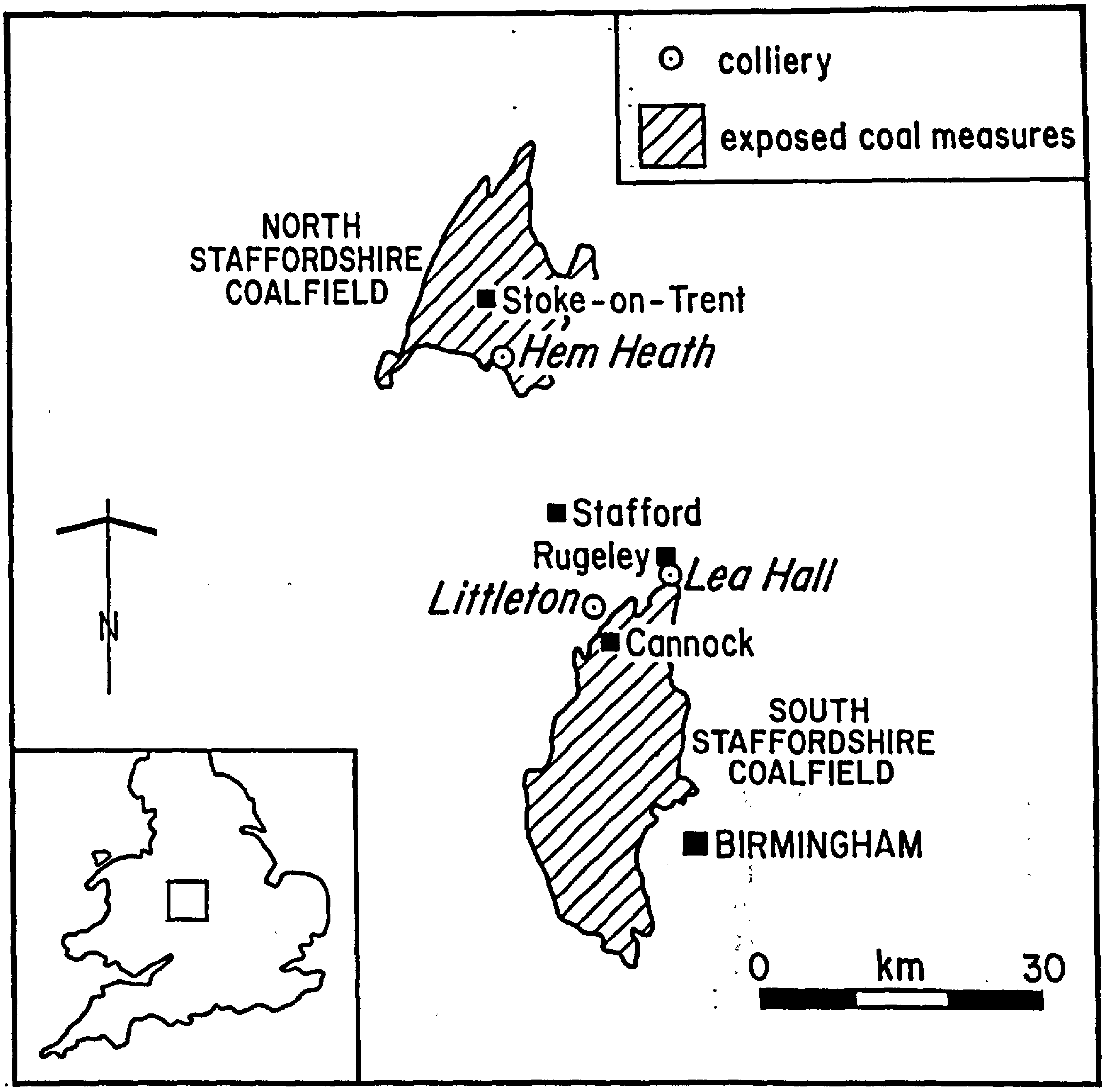

Figure 1: The location of Lea Hall, Littleton and Hem Heath Collieries.

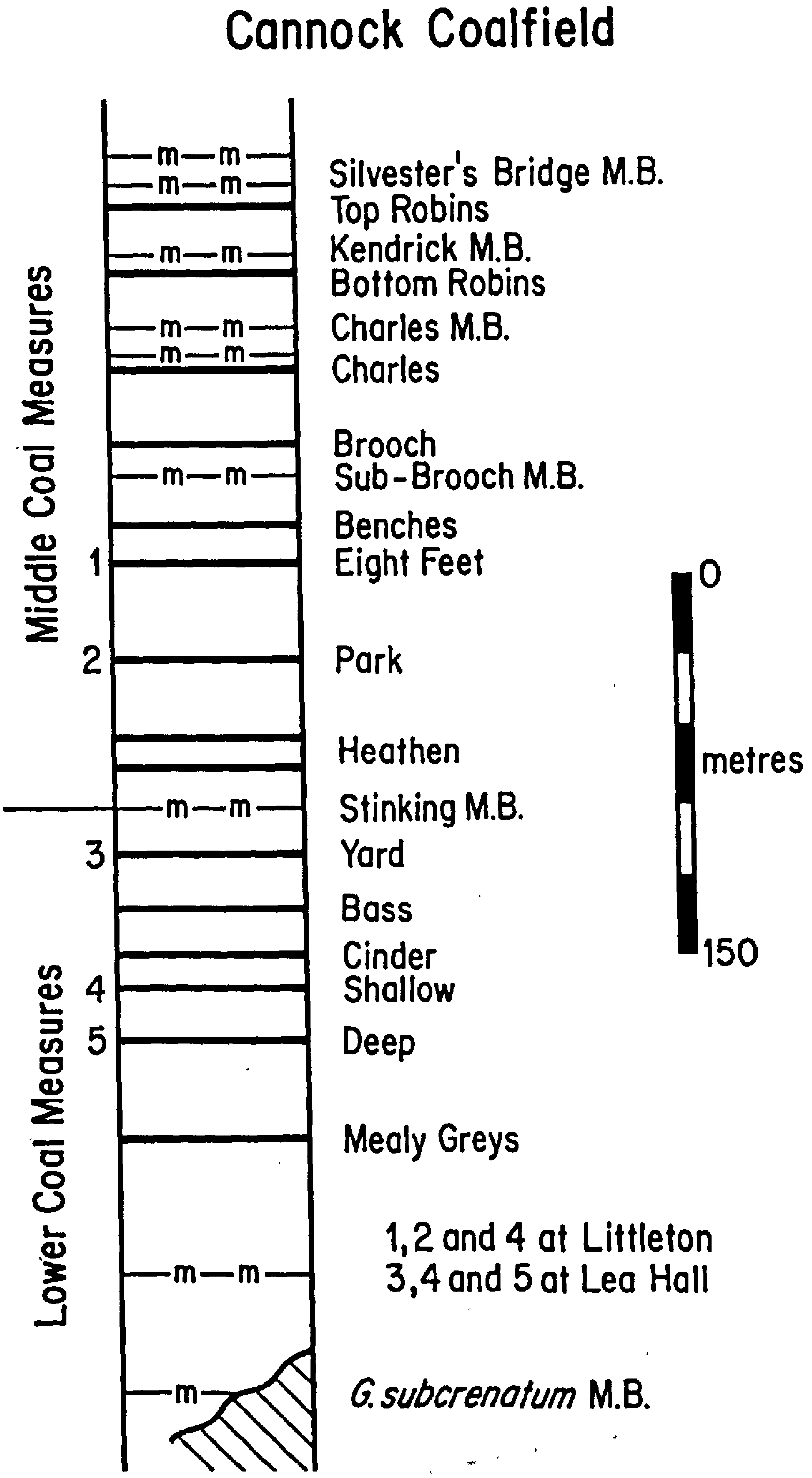

Figure 2: The general stratigraphic sequence in the Cannock (South Staffordshire) Coalfield and the seams sampled.

(Note: The Hem Heath, Yard-Ragman Seam (North Staffordshire Coalfield) correlates with the Benches Seam

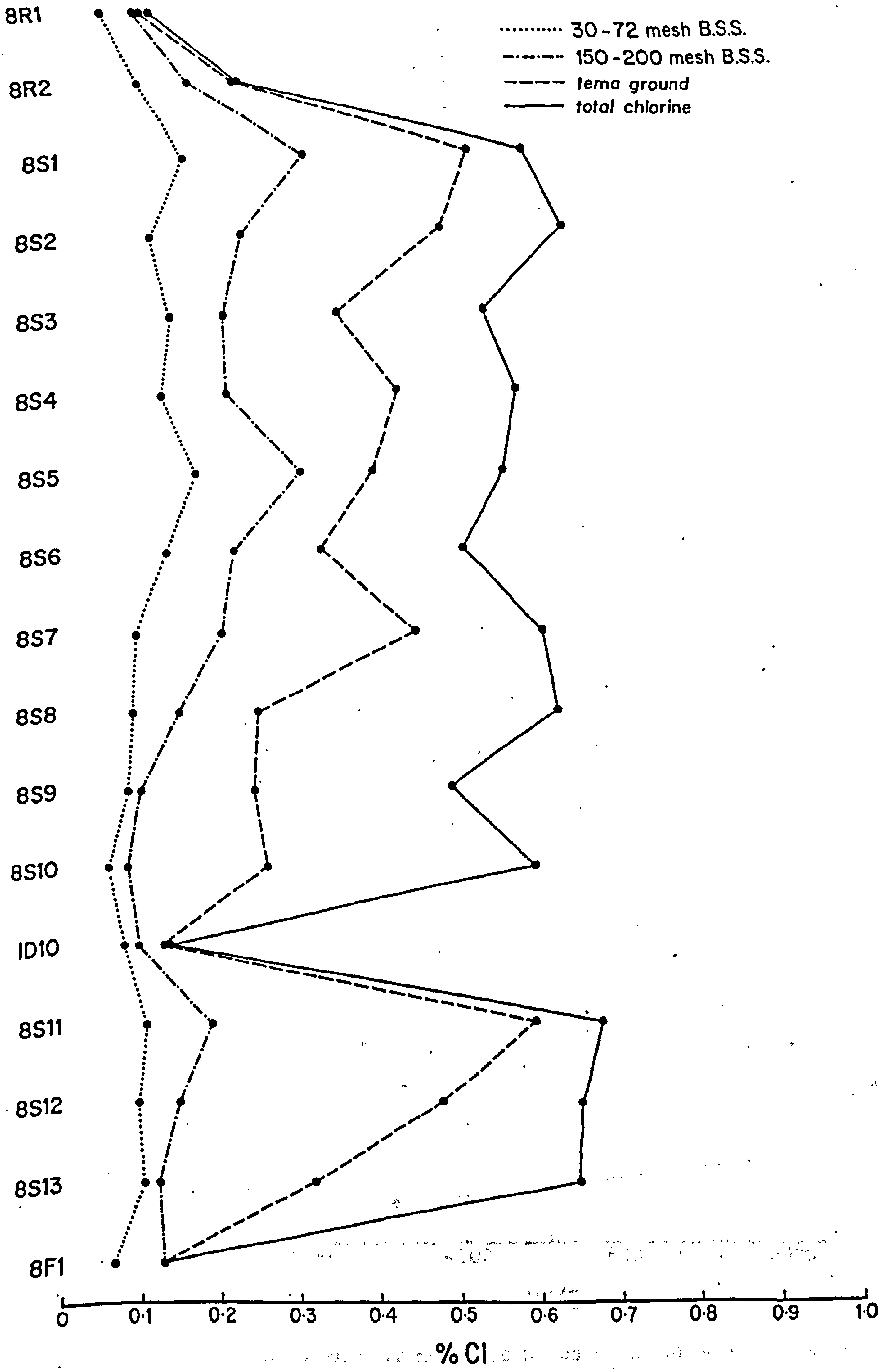

Figure 3: Water-soluble chlorine distribution from different size fractions from the Littleton Eight Feet Seam. Whole rock, as received.

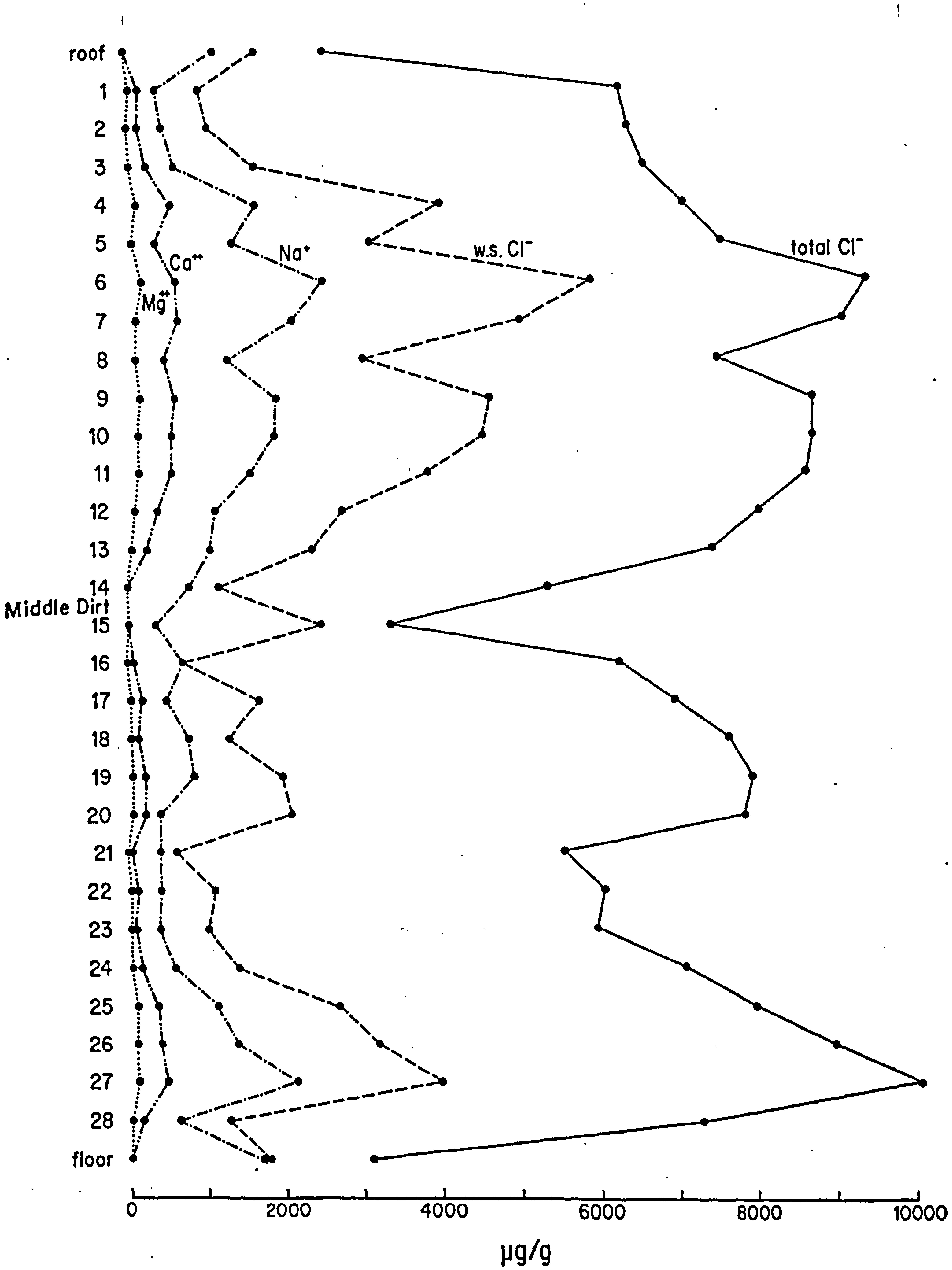

Figure 4: Less than 72 mesh B.S.S. water-soluble major cations, Cl and total Cl from the Yard-Ragman Seam. Whole rock as received.

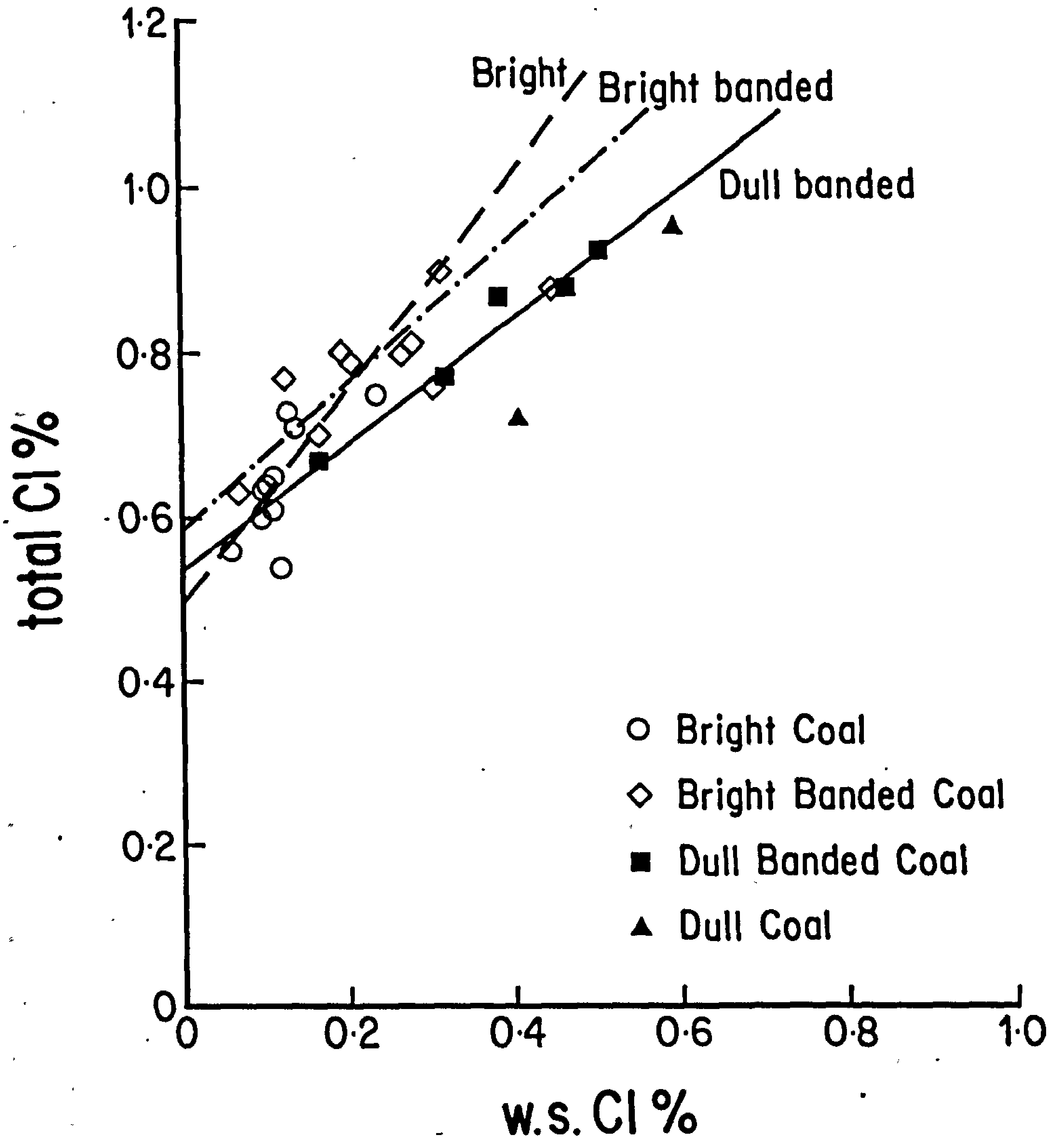

Figure 5: Regression equations for water-soluble vs. total Cl for different coal types from the Yard-Ragman Seam.

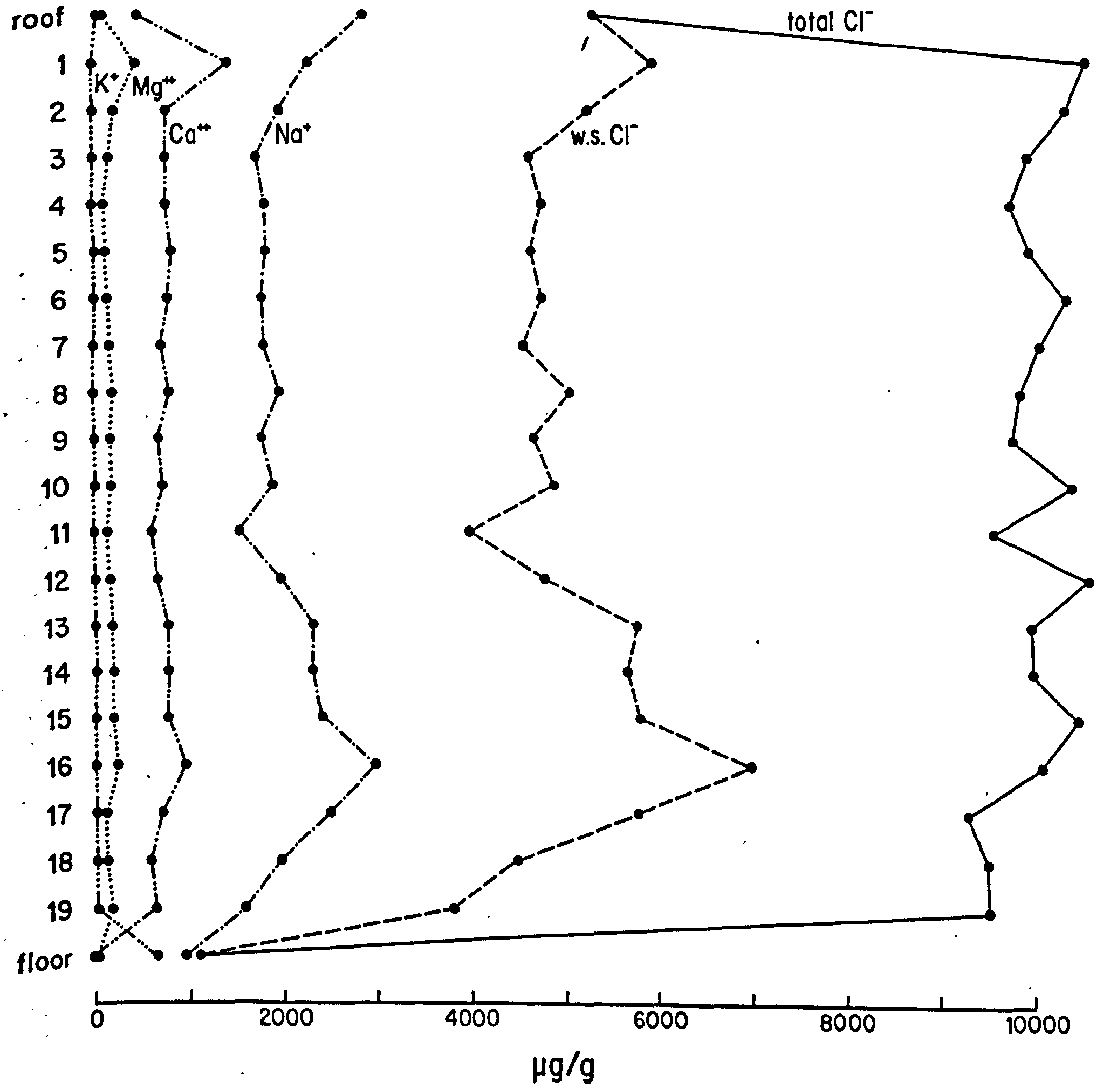

Figure 6: Less than 72 mesh B.S.S. water-soluble major cations, Cl and total Cl from the Lea Hall Deep Seam. Whole rock, as received.

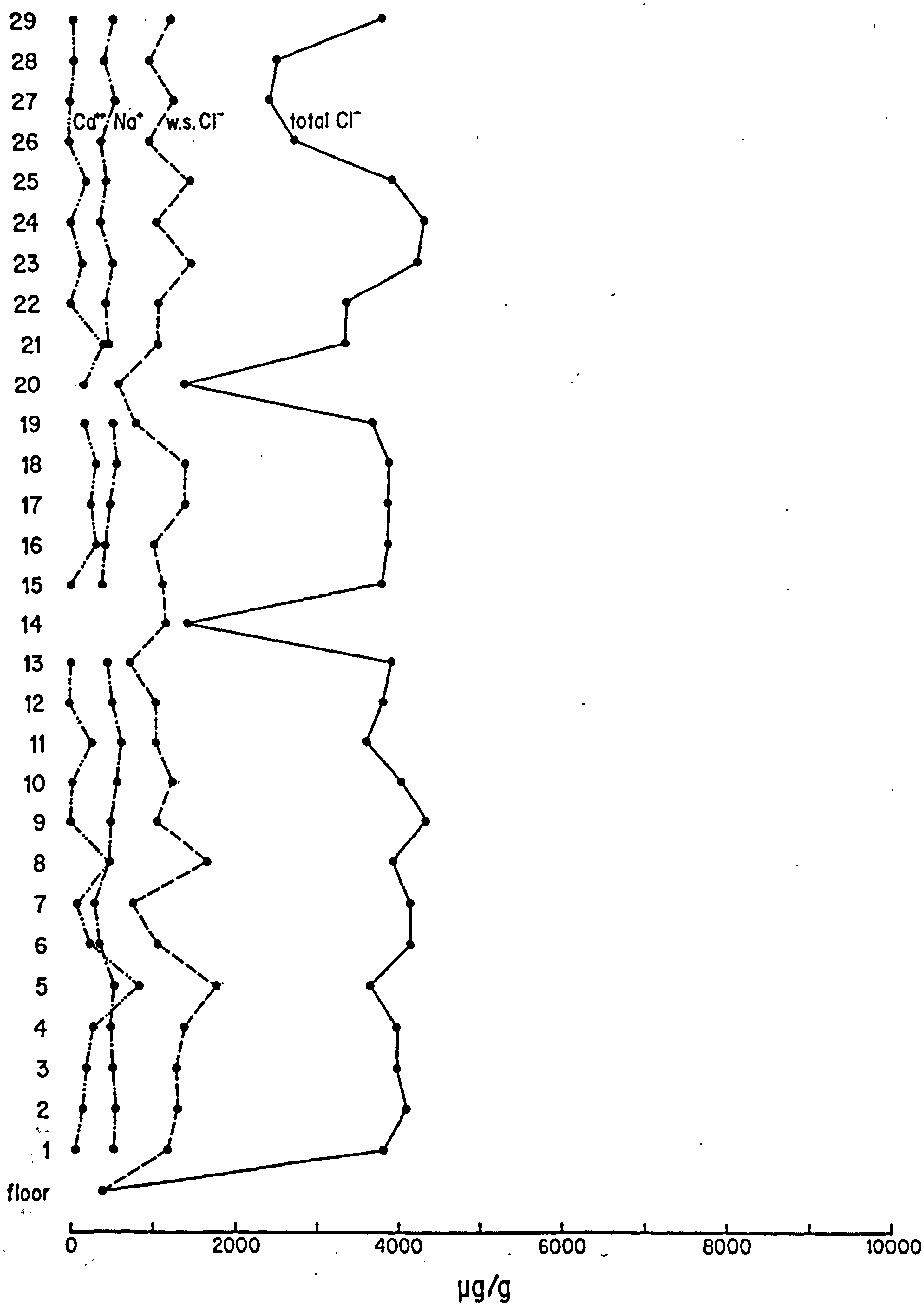

Figure 7: Less than 72 mesh B.S.S. water-soluble major cations, Cl and total Cl from the Littleton Shallow Seam. Whole rock, as received.

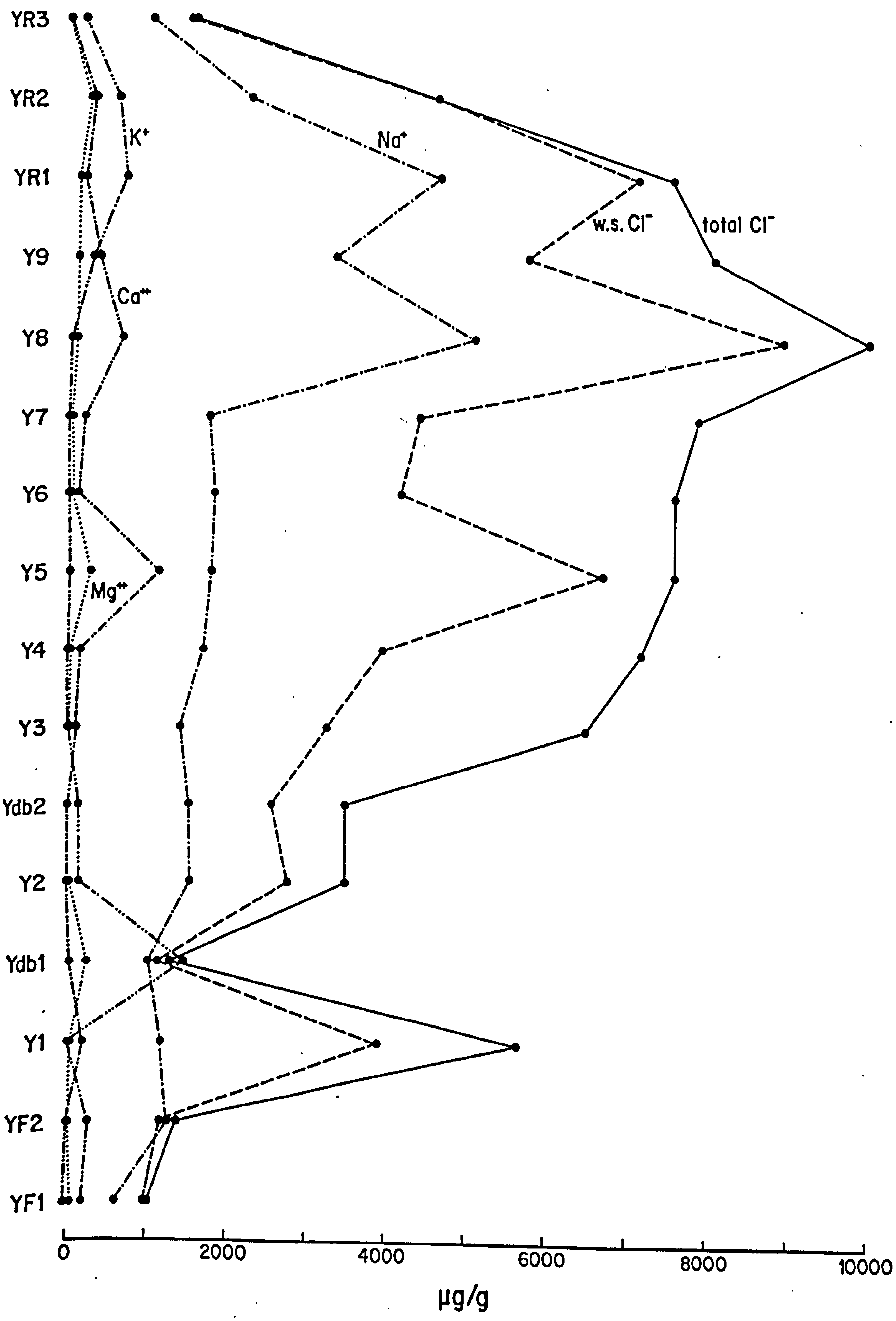

Figure 8: Water-soluble major cations, Cl and total Cl from the Lea Hall Yard Seam. Tema ground. Whole rock, as received.

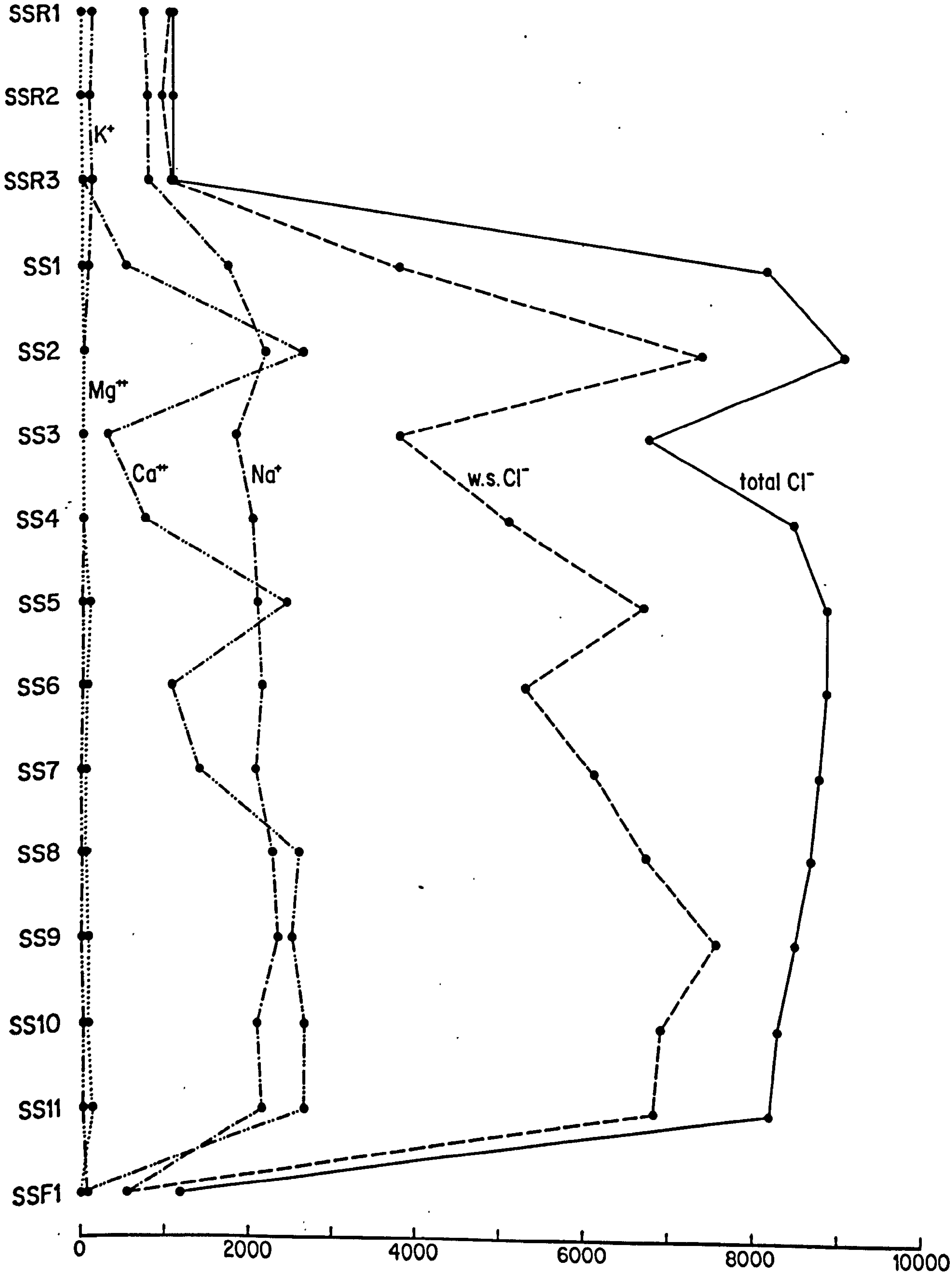

Figure 9: Water soluble major cations, Cl and total Cl from the Lea Hall Shallow Seam. Tema ground. Whole rock, as received.

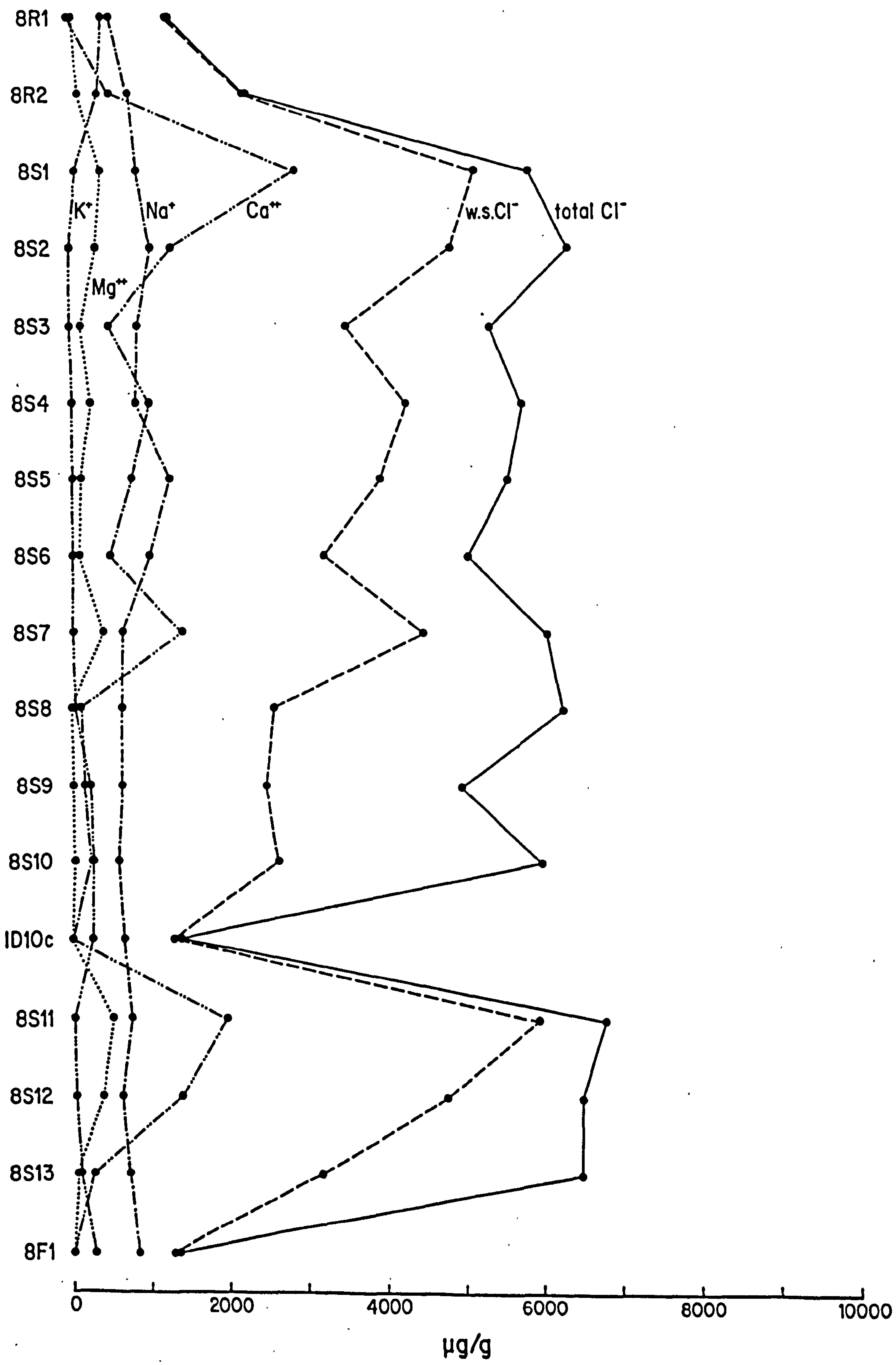

Figure 10: Water-soluble major cations, Cl and total Cl from the Littleton Eight Feet Seam. Tema ground. Whole rock, as received.

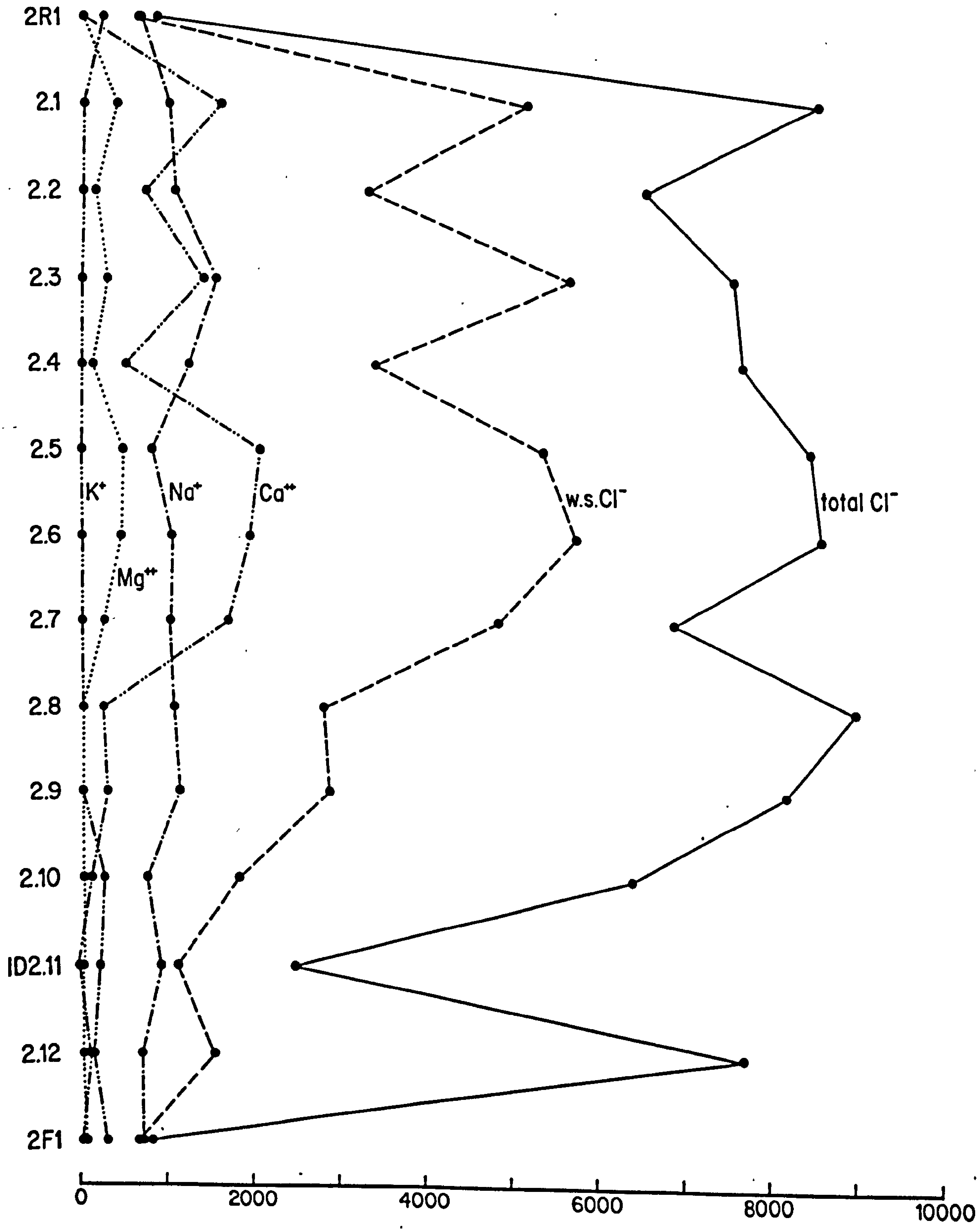

Figure 11: Water-soluble major cations, Cl and total Cl from the Littleton Park Seam. Tema ground. Whole rock, as received.

APPENDIX 3

THE DISTRIBUTION OF WATER-SOLUBLE CHLORINE IN COALS USING STAINS AND ACETATE PEELS

(Fuel, 1981)

A technique has been developed to show the distribution of readily leachable chlorine in high chlorine coals using silver nitrate as a stain. Acetate peels may be taken of the precipitated silver chloride for closer investigation of the relationships between the water-soluble chlorine and the coal lithotypes. High chlorine coals from Yorkshire Main Colliery (Barnsley Seam) and Thoresby Colliery (Top Hard Seam), Yorkshire and Nottingham respectively, showed that the durain fraction of coal will rapidly yield at least some of its water-soluble chlorine. However, vitrinite is the major host of water-soluble chlorine and the predominant component of bright coal. Bright coal shows no water-soluble chlorine component. This apparent discrepancy is explained by the size and distribution of pores and the permeability of different coal macerals. The water-soluble chlorine component is believed to be a NaCl solution held within coal pores. Pores found within the dull coal are much larger than those found in bright coal especially where the former has a high detrital mineral matter component. Bedding planes within durain bands which are coated by fossil remains or thin fusain layers are seen to be the major contributory fractions of the dull coal.

Introduction

The chlorine level found in coals varies dramatically from country to country, between coalfields, and even within one colliery, from a negligible level to 1.0% or more. Within England, high chlorine coals are found and present values vary between 0.1 and 1.0% (Ode[1]). High chlorine values are associated with high volatile bituminous coals and these coals are used extensively by the C.E.G.B. The chlorine liberated during combustion is a major cause of fireside corrosion to furnace walls and superheater tubes. Consequently the distribution of chlorine and its state of combination is an economic interest. Varying proportions of the chlorine is water-soluble and some of this may be removed in washeries prior to power station consumption. However, the distribution of water-soluble and organically bound chlorine is unclear, as are its origins (Edgcombe[2]; Daybell and Pringle[3]; Daybell and Gillham[4]; Gluskoter and Rees[5]). In this paper, a method is presented to distinguish the distribution of easily leached water-soluble chlorine at a macro-scale.

The distribution of high chlorine coals (greater than 0.4% by weight) in the U.K., has been documented by Skipsey[6,7] and shown to be associated with high volatile bituminous rank coals. Skipsey[6] showed that a positive relationship existed between total chlorine and increasing rank until a threshold value of 84% carbon (d.m.m.f.) is attained. At higher rank, the chlorine value is seen to fall dramatically. This he explained by the results of work done by Bond and Hirsch and summarised in van Krevelen[8]. Bond postulated that the coal pore structure changes in response to increasing rank. Using X-ray diffraction, Hirsch developed a model in which he distinguished three types of coal structures characterised by differing carbon contents. At about 85% carbon, coal passes from a highly porous structure to one in which pores are practically absent. Hence the chlorine holding capacity would be drastically reduced at this rank. Skipsey argued that the increasing chlorine values with depth is related to increasing chlorine concentration in deep ground waters. High chlorine coals in the U.K. are restricted to the coalfields of Lancashire, Staffordshire, Nottinghamshire, Yorkshire and East

Durham. With a trend towards deeper mining it is reasonable to suppose that chlorine will provide problems in the future if untreated.

Staining and Acetate Peels - A Background

The use of stains has long been a standard geological technique to distinguish otherwise optically similar minerals. A stain specific to a mineral of a certain chemical composition will colour that mineral and leave any other minerals unaffected. Some minerals show tonal variations in response to differing crystal orientation so that crystal faces may be identified. The technique is commonly used in carbonate mineral study but its uses extends far beyond the field of carbonate petrology. If the mineral under study is etched by acid to produce a surface relief, an acetate peel of the resulting impression can be taken and used for microscopic investigation. This is made possible by wetting the rock surface with acetone which allows an imprint to be made on acetate sheet. A similar technique is presented using silver nitrate as stain, which when combined with chlorine leaves the white precipitate of silver chloride.

Method

1) a) Select a smooth surface, for example a cleat fracture with the mineralisation removed - or -

   b) (i) Carefully saw a section normal to the bedding, then smooth the surface by file and finally by emery paper.

      (ii) Remove dust which will clog pores by high frequency vibration in a ultrasonic bath.

      (iii) Dry the coal in an oven or in air.

2) Apply a concentrated silver nitrate solution by an aerosol spray onto the smooth surface.

3) Dry the sample rapidly.

4) Carefully wet the coal surface with acetone.

5) Place acetate sheet on wetted coal surface and remove bubbles with careful pressure.

6) Leave to dry (c. 60 seconds).

7) Remove acetate peel.

8) Place in photographic developing solution then wash in water.

9) Place in photographic 'fixer' and wash in water for about 20 minutes.

10) Mount between glass slides.

Variations on this method are possible and stages may be omitted depending upon the purpose of the study.

Note: It is recommended to use the technique soon after mining ensuring that the coal moisture is at a maximum.

Discussion of the Method

Any smooth surface normal to the bedding is suitable to study lithotype variations and water-soluble chlorine relationships. If a detailed peel showing surface ornamentation is to be used, a cleaned natural surface is recommended. Peels are taken more easily but surface detail is reduced if a surface is cut and smoothed. Natural fractures such as cleat surfaces are frequent in bright coal because of its brittle nature but are relatively infrequent in the dull fraction and tend to be more uneven. This limits the convenience of this approach. Sawn sections must then be used. The samples must be carefully packed or encased in resin to prevent fracturing. A sawn surface must then be smoothed using a file and finally by emery paper. This leads to the clogging of the surface pores with fine dust. This must be removed before silver nitrate is applied. The sample should be placed cut side down in an ultrasonic bath and vibrated for 15 to 30 seconds. As it is the distribution, and not the amount of chlorine present, that is of interest, the chlorine lost into the bath is of no consequence. Drying may be carried out by simply leaving the moisture to evaporate or by heating the specimen for a few minutes. However, it should be noted that prolonged oven drying will eventually remove all the coal moisture and render the method unusable for reasons to be given. The experiment may be repeated several times with gradually failing results as the chloride rich pore waters are exhausted from the surface of the coal. Further oven drying or standing unused for several hours allows the moisture to be drawn back to the surface and the experiment to be continued. If required, a small amount of surface relief may be introduced to the coal at this stage by low temperature 'plasma ashing' of the sample.

The use of an aerosol spray to apply the silver nitrate solution to the coal surface reduces any 'preferred orientation' effect introduced by other application methods such as 'painting'. The silver nitrate combines with the water-soluble chlorine and forms a white precipitate, silver chloride. Care should be taken not to use too much solution for danger of dispersing the precipitate from its source. Rapid drying helps to prevent this. This will provide a more rapid, simple technique to show the relationship of coal lithotypes and water-soluble chlorine if a peel is not taken.

If an acetate peel is to be taken, the coal surface is carefully flooded with acetone and acetate sheet carefully spread onto the surface and bubbles removed. Too much pressure will melt the acetate sheet. Once dry, the peel may be removed taken with it the silver chloride and some pattern, usually slight, of the coal structures. The white precipitate is seen more easily if developed in photographic developer and hence turned black. However, problems may now arise in distinguishing the stain from coally material adhering to the peel. It is essential, therefore, in the initial preparation to clean away any loose coally material. This is a major reason in preferring surfaces smoothed flat at the expense of surface relief and structural detail. The resulting peel may then be mounted between glass slides for observation.

Discussion of Observations

Two high chlorine coals from the Eastern Pennines Coalfield were investigated. These were samples taken from the Barnsley Seam (Yorkshire Main Colliery) and the Top Hard (Thoresby Colliery). The following observations were made at the lithotype (hand specimen) scale. 'Bright coal', composed essentially of the lithotypes vitrain and clarain showed no silver chloride precipitation, nor did the thick fusain bands in the 'dull coal'. Of the durain fraction, however, some portions exhibited a marked precipitation. The amount varied between samples from small white silver chloride stains to whole dull coal bands. In the latter case this was seen to be evenly distributed through the dull coal although a possible explanation of this could be dispersion of the silver chloride before drying. On close inspection the major silver chloride precipitation was seen to correspond to horizons of cannel coal. Within this type of coal, areas of non-organic matter, apparently fossil residue, and thin fusain films both in the cannel and true durains often showed a higher concentration of precipitation than the background.

Saunders[9], using S.E.M. fitted with E.D.A.X. showed that the water-soluble chlorine extracted from 72 B.S.S. coal in 24 hours is related to the sodium content of the vitrinite. For coals of this size, the leachate is essentially a NaCl solution. It is believed, therefore, that the water-soluble chlorine component of 72 B.S.S. coal is in fact a NaCl solution held within the coal pores. It is interesting, therefore, to note the apparent discrepancy between the E.D.A.X. microanalysis with that of the hend specimen observations. An explanation is offered by the nature and distribution of the coal porosity.

Vitrinite is the dominant maceral group in the majority of bituminous coals. Its pores lie in the meso- and micropore range measuring 2 to 20nm in diameter and Harris and Yust[11] consider them to be interconnected and thus permeable. Exinite is found in banded coal and inertinite is the dominant maceral group of dull coal. Harris and Yust[10] described exinite to be least porous but relatively large pores are found extending from the interface between inertinite into the spore exines. These pores fall into the meso- and macropore range measuring 20 to 100nm in diameter. Inertinites are most porous but the pore size falls predominantly into the mesopore range and varies between 2 and 50nm and apparently have a high permeability[10]. The different size fraction and leaching time between the work of Saunders[9] and the present method would therefore indicate a difference in the accessability of different maceral groups resulting from their differing porosities and permeabilities. During the short time interval taken for the acetate peel method, only the largest pores and fractures, such as cleat, would yield sufficient quantity of precipitate to be visible to the naked eye. This would explain the apparent concentration of water-soluble chlorine within certain horizons in durain and notably cannel coal. Major fusain bands with their high permeability would be expected to give a high chlorine yield but it is though that this would rapidly dry out or percolate into the surrounding coal. However within durain bands, areas of marked precipitation correlate with thin fusain films or lenses and with bedding planes covered by fossil debris. It is proposed that the higher permeability of these horizons leads to the relatively rapid loss of chloride bearing moisture. Vitrinite would have a slow leaching rate on account of its small pore size especially where concentrated into vitrain or clarain portions of 'bright coal', even though it may be the host of the majority of water-soluble chlorine.

The 'macroporosity' distribution was determined using a variation of the silver nitrate peel technique. A potassium solution was adsorbed into the coal and the surface then dried. Sodium cobaltinitrate, a potassium stain, was then sprayed onto the coal surface precipitating a yellow stain. The distribution was comparable with that of the silver chloride and thus attributable to the 'macropore' (used as a general term) and fissure distribution in the coal.

The use of silver nitrate as a stain therefore demonstrates the distribution of rapidly leachable water-soluble chlorine at the macro-scale. It demonstrates the 'macropore' distribution, which is dominated by the inertinite fraction of the durain, fossil horizons along certain bedding planes and cannel coal. Acetate peels facilitate microscopic studies of the relationship between rapidly water-soluble chlorine and the coal lithotypes.

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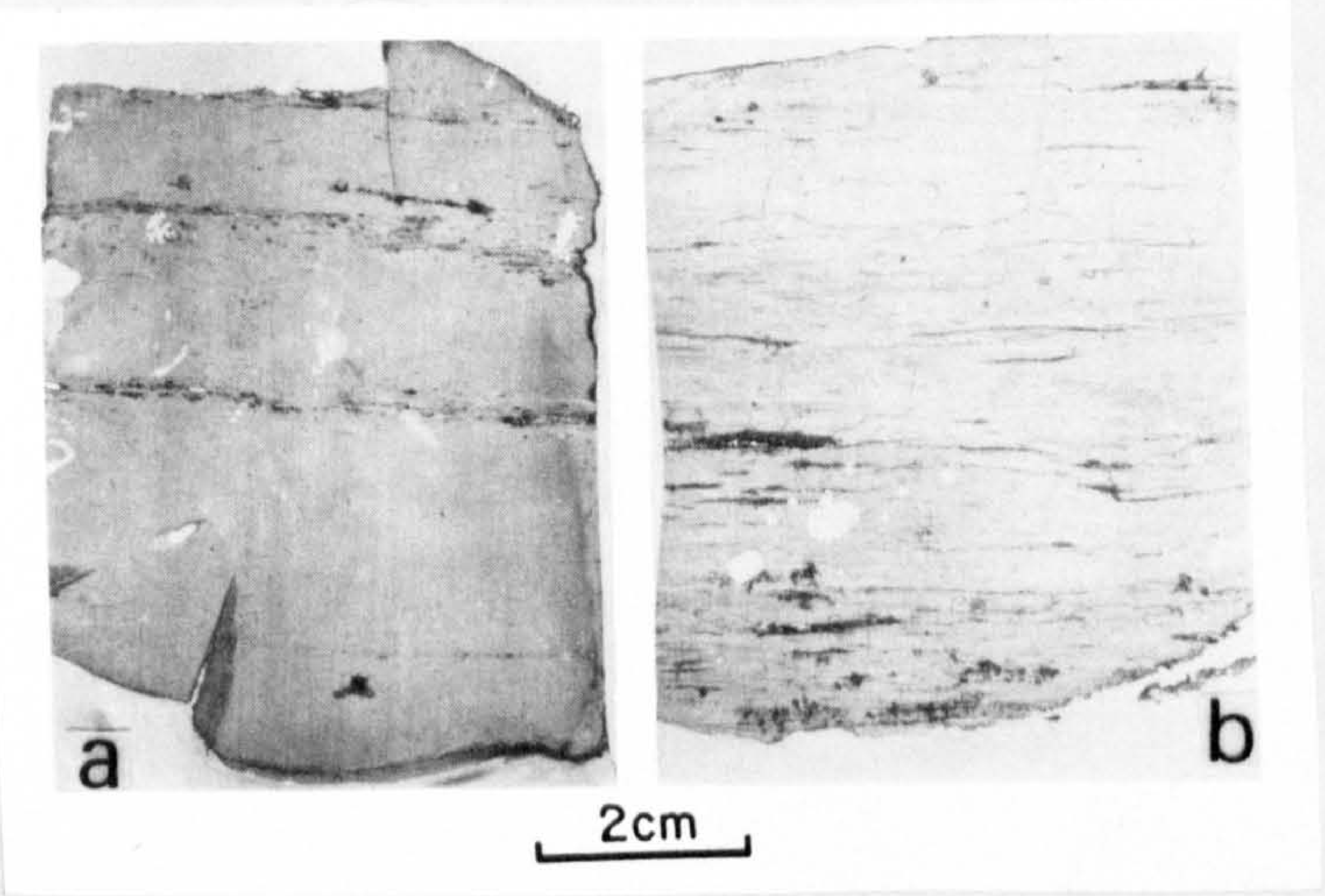

Chlorine distribution in Thoresby Colliery coal

A. Dull coal showing readily leached chlorine along bedding planes rich in mineral matter.

B. Bright banded coal with lenses of chlorine corresponding to fusainous partings.

The vertical cracks in both A and B are cleat fractures.