Copy #3

DEPARTMENT OF
NATIONAL RESOURCES

BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

RECORD 1975/127

009700

FACTORS IN THE DEPOSITION AND MINERALIZATION OF A BLACK SHALE WEST OF MARY KATHLEEN, QUEENSLAND

by

B.A. Duff

RECORD 1975/127

FACTORS IN THE DEPOSITION AND MINERALIZATION OF A BLACK SHALE WEST OF MARY KATHLEEN, QUEENSLAND

by

B.A. Duff

CONTENTS

FIGURES

TABLES

F. D. Atkinson, Commonwealth Government Printer

4. R-mode statistics
5. R-mode eigenvalues
6. Interfactor correlations (R-mode)
7. Element associations
8. Factor-element associations
9. Comparison of black shale with other metal-rich shales
10. Comparison of black shale with shales from established environments
11. Analytical data comparison of black shale with shale of other studies

SUMMARY

This study presents the results of a geochemical study on a black shale from the eastern succession of the Mount Isa geosyncline. According to the criteria of Vine & Tourtelot, the shale is enriched in Zn, Co, Cu, Ni, and V relative to common black shales, but is low in Pb.

The black shale constitutes the upper unit of the Corella Formation, and is considered to have been deposited in a local - probably euxinic - trough within a broad shelf on which mainly carbonates were deposited. This view, supported by factor analysis of the chemically determined elements, is taken to indicate a slow rate of deposition in a stable trough, with little carbonate precipitation.

From an interpretation of the factor analysis,it is suggested that the main geological factors controlling the element variance were rate of deposition, opportunity for absorption and complexing processes, post-depositional enrichment of metal sulphides, and proximity to shoreline. These controls are related to proportions of heavy metal/hydrolysate, chalcophile, and evaporitic-type elements.

A syngenetic origin for the sulphides in the shale is considered unlikely,and a process including migration of sulphide and metal ions, and subsequent localization in discrete concordant layers, is suggested. Such a process may account for many of the cross-cutting veinlets of sulphide and carbonate.

The composition of the shale - in which a high level of Zn does not correlate with high values of Ag and Pb, and there is no correlation of C with S, or hydrolysate with chalcophile elements - differs from that of the black shales in the Mount Isa and McArthur River deposits.

INTRODUCTION

This Record presents geochemical results from a systematic and detailed investigation of a sulphide-bearing shale in the eastern succession of the Mount Isa Geosyncline (Carter, Brooks, & Walker, 1961). Seventy samples from a black shale in the upper section of the Corella Formation about 12 km west northwest of Mary Kathleen (Fig. 1) were analysed, most for a total of 24 major and minor elements; major oxide determinations were made on 10 of the samples. All samples were taken from a diamond drill-core 42 m long recovered by a BMR rig in 1971 from BMR Cloncurry No. 5 (Fig. 2). A detailed description of the core is presented in Hill & Duff (1975).

Primary objectives of the project were:

a) to evaluate the metal enrichment of the shale

b) to establish or confirm the palaeo-environment of deposition and provenance using minor element indicators and associations

c) to elucidate the geological factors controlling the variable chemistry of the sediment and their relation to processes of element dispersion using multivariate data analysis.

d) to determine whether particular element associations are syngenetic, diagenetic, metamorphic, or other post-depositional features.

e) to provide a basis for comparison with recent detailed geochemical studies in other regions of the Precambrian in northwest Queensland (Smith & Walker, 1972; G.M. Derrick, pers. comm).

Geological setting

The sampled shale represents sedimentation in a local depression within a carbonate shelf (Derrick et al., 1974; fig. 3), and is from the westernmost of a series of shale lenses within the Corella Formation. About 4.5 km west of the drill site, quartzite underlying the Corella Formation unconformably overlies the Kalkadoon-Leichhardt metamorphic basement.

Only 300-500 m of the black shale is preserved at the top of the Corella Formation,and it is overlain with angular unconformity by the Deighton Quartzite. The shale forms an elongate north-trending discontinuous outcrop 18 km long and 1 to 2 km wide containing abundant pyrrhotite and numerous gossanous zones. It overlies a sequence of carbonates and pelitic sediments which locally contain scapolite and cordierite (Fig. 3).

Correlation of the shale with the graphitic metal-rich Dugald River sequence has been proposed (G.M. Derrick, pers. comm.); in both areas shale overlain by quartzite represents the uppermost part of the Corella Formation.

DESCRIPTION OF THE SHALE

Both sulphides and evaporites are distributed inhomogeneously throughout the black carbonaceous shale, generally as discrete layers up to 8 cm thick (stratiform) or finely disseminated within the shale, but also as cross-cutting veinlets and joint and fracture fillings.

Some textural features may indicate mobilization of stratiform sulphides and evaporites after deposition, probably during consolidation; they include intricate near-vertical contortion of veinlets (Fig. 4a, b) and the breaching or warping of laminations by small 'diapir'-like domes rising from concordant sulphide layers (Fig. 5a, b). Some veinlets are terminated by bedding, failing to breach the layering, and others are contorted only at particular places along their length. An origin that includes differential compaction, upward injection of sulphide and water, and subsequent contortion of veins by the weight of overburden is suggested (see, for example, Conybeare & Crook, 1968, p. 188). If redistribution occurred during compaction, re-mobilization of elements during metamorphism may be of relatively little significance.

Metamorphism to the middle grade of the greenschist facies has affected the shale, as indicated by the presence of much pyrrhotite relative to pyrite (Lambert, 1973).

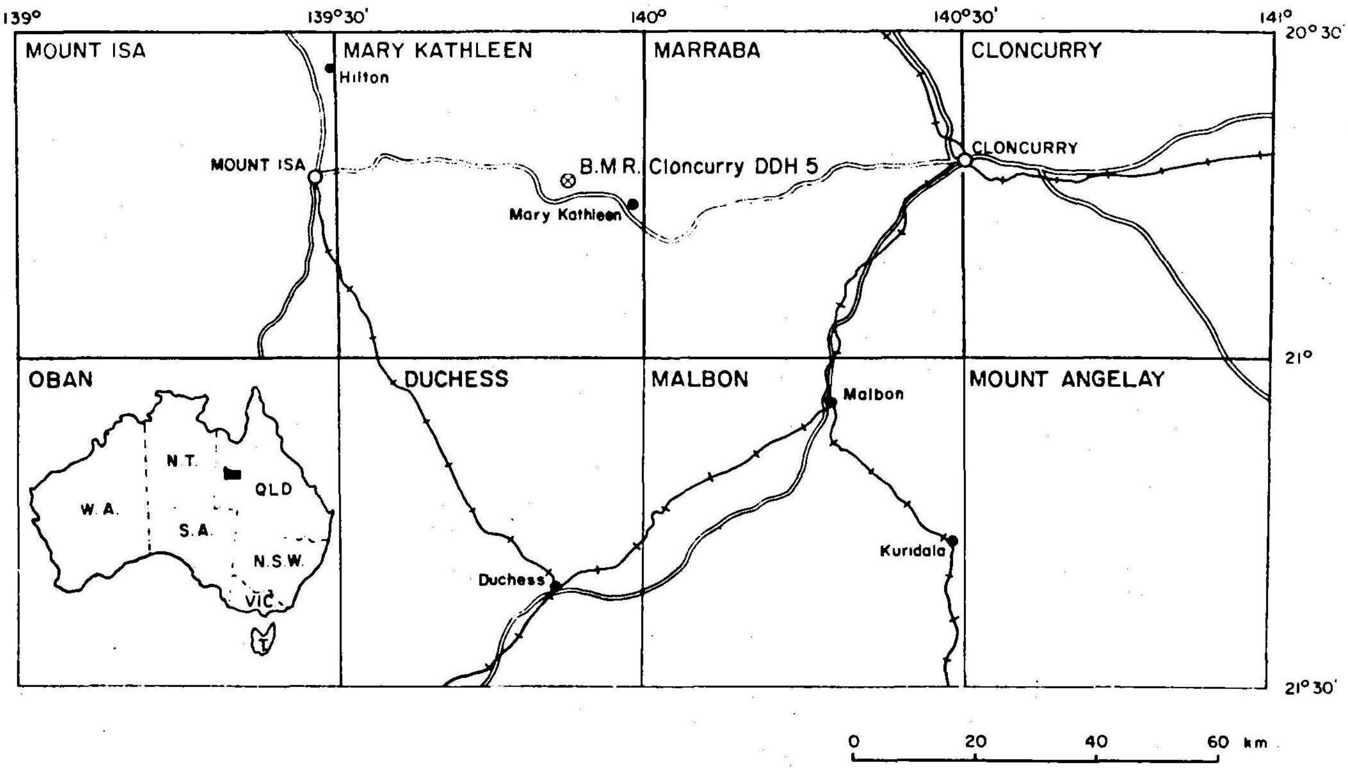


Fig. I Location map showing 1:100 000 Sheet areas

Record 1975/127 KJ F 54/A2/136

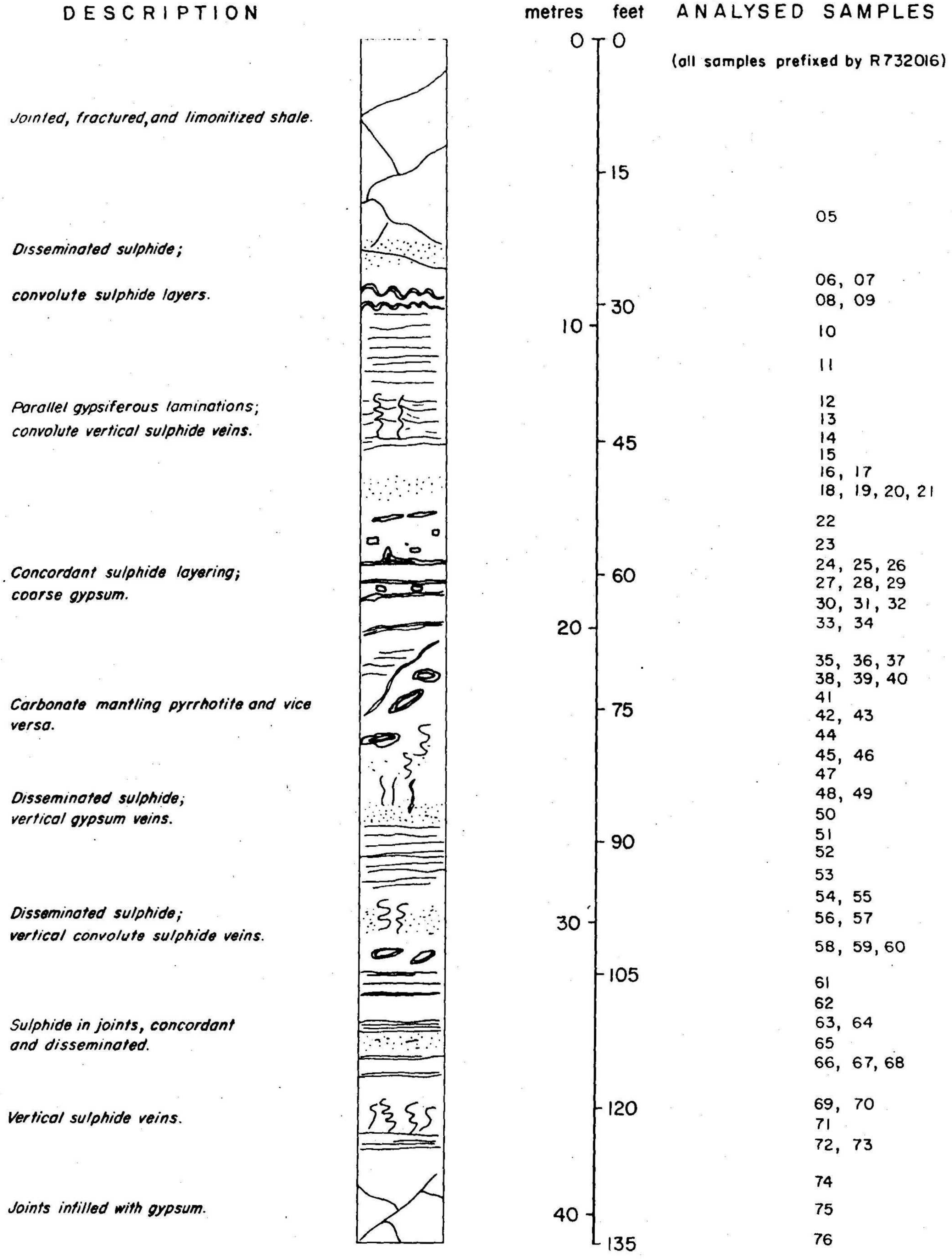


Fig. 2 Generalized log of the black shale.
Analysed samples and corresponding depths are shown.
(B M R -Cloncurry DDH 5)

Record 1975/127

KJ F54/A2/137

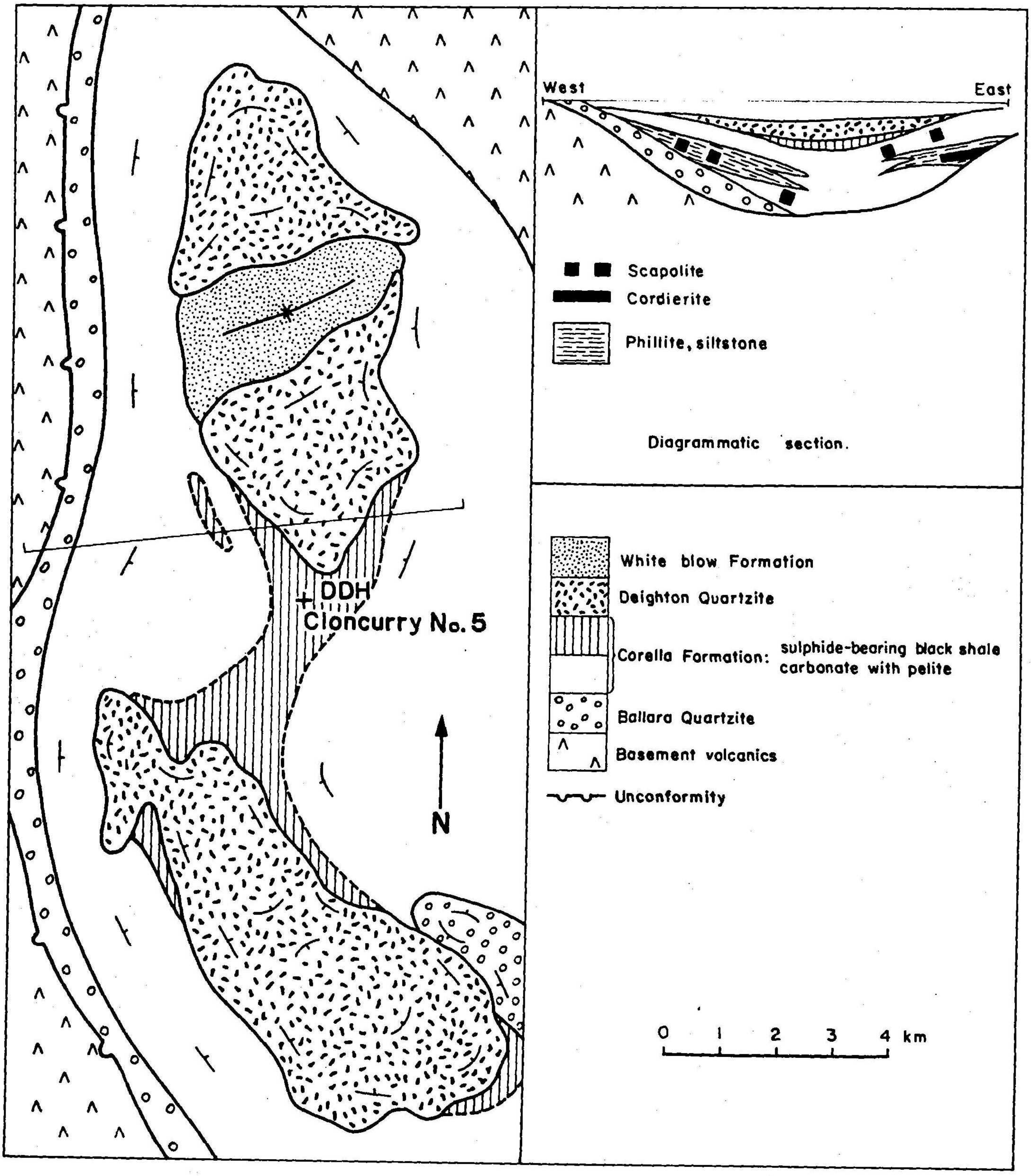
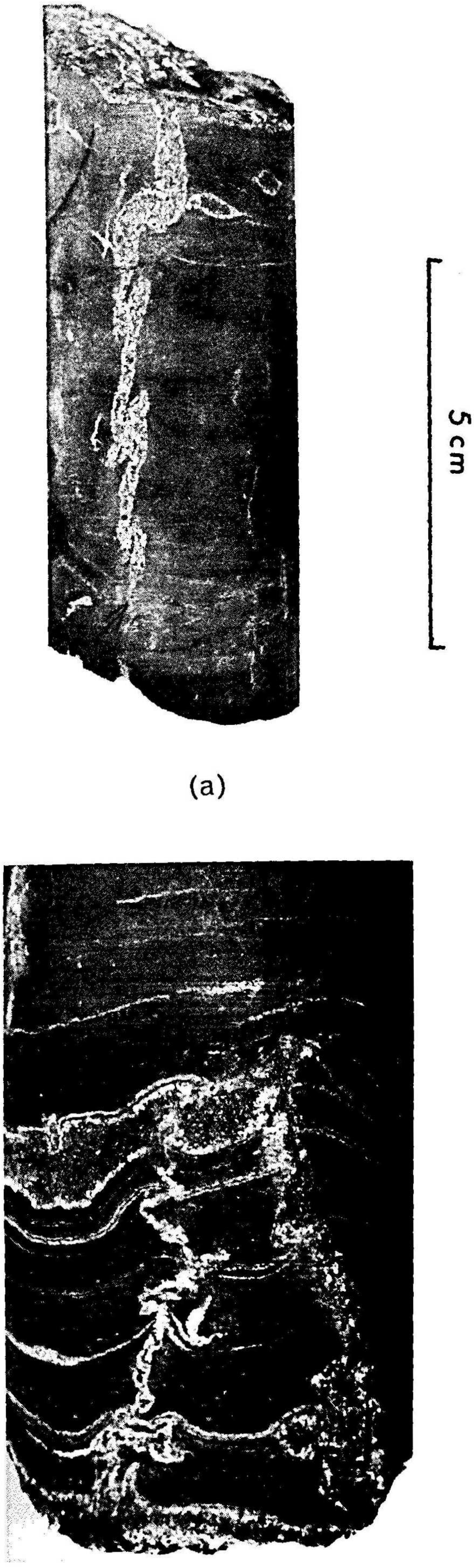


Fig. 3 Geology in vicinity of DDH Cloncurry No. 5

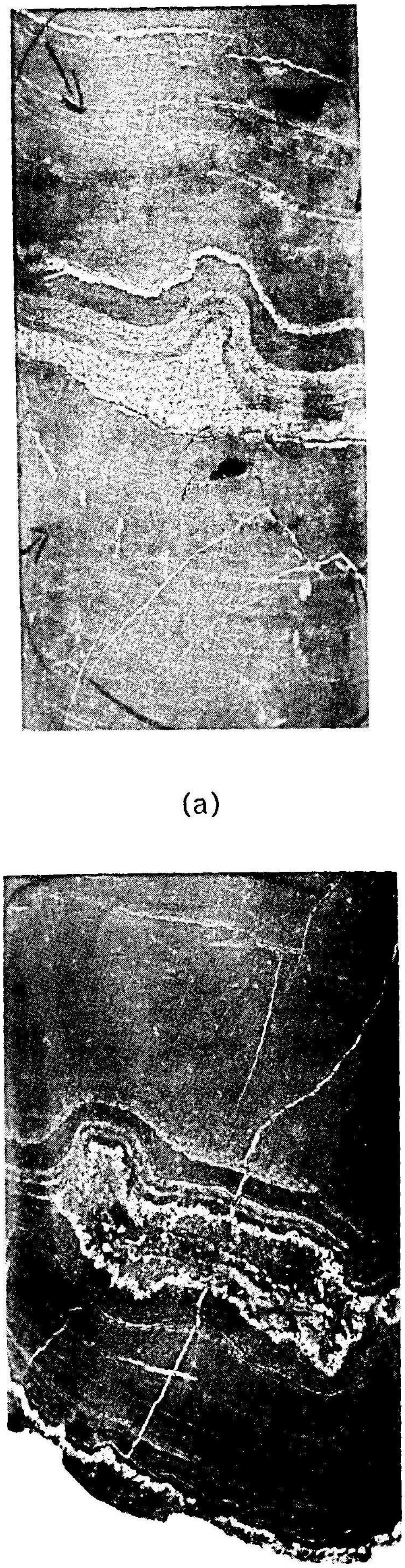
Record 1975/127

F54/A2/146



(b)

Fig. 4. Contortion of vertical sulphide and carbonate veinlets in shale. Carbonate (white) mantles pyrrhotite in both veins and concordant lenses.



(a)

(b)

Fig. 5. Deformed concordant sulphide and carbonate layering in shale.

Mineralogy

Thin section and XRD study reveal a quartz-muscovite/clay-plagioclase (andesine or bytownite)-biotite-chlorite-scapolite assemblage for the detrital component of the shale, associated with much carbonaceous material (1-5 percent). Evaporites in the shale are represented by calcite-gypsum-anhydrite assemblages. The principal metal sulphide phase is pyrrhotite, which is accompanied by lesser pyrite, and minor chalcopyrite, sphalerite, and galena forming blebs in pyrrhotite.

ANALYTICAL TECHNIQUE

Seventy samples were taken at roughly 0.6 m intervals down the full length of the black shale core (Fig. 2), and all variations within the black shale were represented.

Atomic absorption spectroscopy (AAS) and direct-reading optical spectroscopy (DROS) were undertaken at BMR for Ag, Bi, Cd, Co, Cu, Ni, Pb, Zn, and Zr (AAS), and for Ca, Fe, Mg, Mn, Ti, Ba, Sc, V, Y, and Zr (DROS); accuracies are generally ± 10 percent for AAS, and ± 20 percent for DROS. In addition, ten major oxide analyses were carried out using X-ray fluorescence (XRF) with accuracy ± 3 percent. AMDEL determined Se and As using XRF (± 3 percent), and CO_2 and B using gravimetric and spectrophotometric methods (± 10 percent); S was determined volumetrically (± 10 percent). Organic carbon was determined in CSIRO Division of Applied Organic Chemistry (Australian Microanalytical Service).

The minor element analyses for the black shale are shown in Appendix I, and the ten major element analyses in Table 1.

STATISTICAL ANALYSIS

1. Multivariate data

In order to extract the maximum information from a correlation array, and to account for the 'control' of groups of variables, various methods of

TABLE 1. Major element analyses (wt. percent) for ten black shale samples

SAMPLE NO.	1616	1619	1621	1633	1639	1646	1657	1665	1666	1675
SiO_2	64.86	51.57	67.36	47.72	59.99	67.20	70.08	69.04	60.31	67.98
TiO_2	0.69	0.53	0.74	0.37	0.39	0.53	0.49	0.55	0.55	0.68
Al_2O_3	18.30	14.38	17.83	9.78	13.77	17.20	13.26	15.66	13.32	15.18
Total iron as Fe_2O_3	3.40	23.84	3.93	33.04	12.20	2.92	7.39	3.08	4.74	6.19
MnO	0.04	0.06	0.03	0.08	0.06	0.04	0.06	0.04	0.19	0.08
MgO	3.10	3.22	2.89	2.76	1.04	2.25	3.28	2.50	0.76	4.63
CaO	2.95	1.14	0.99	3.25	8.52	2.85	2.68	4.73	19.64	2.70
Na_2O	0.88	0.29	0.58	0.48	1.06	1.03	0.95	2.58	0.53	1.75
K_2O	4.87	4.57	5.25	2.11	1.56	4.34	3.30	1.84	0.59	2.95
P_2O_5	0.23	0.19	0.23	0.10	0.11	0.17	0.16	0.12	0.16	0.13
Loss on ignition	7.31	12.51	7.60	9.43	8.30	5.56	4.02	5.00	10.58	2.80

Analysed in B.M.R. Laboratory by XRF.

multivariate analysis can be used which consider the multiple variables in combinations. These include factor analysis (one population), and discriminant analysis (two or more populations). As computer programs are widely available for both these techniques, it is possible to interpret the results obtained in the same time or less that it takes to analyse the data array by 'hand'.

For a comprehensive account of multivariate analysis see Cooley & Lohnes (1971). Krumbein & Graybill (1965) give several examples of the geological application of the various methods. Imbrie (1963) and Hirst & Kaye (1971) have applied factor analysis to geological problems.

2. Factor analysis

The theory of factor analysis is fully outlined in Harman (1960), and has been used in this study to establish geochemical associations that might reflect real processes contributing to element variance in the sedimentary environment.

Factor analysis represents the variance[*] of a variable, Zj, in terms of several underlying factors F_1, F_2, Fn (where n is the number of variables) which account successively for the variance according to the model:

$$Zj = Aj\ F + Aj_2\ F_2 + \ldots\ldots + Ajn\ Fn + E \quad (j = 1,2,\ldots\ldots n) \quad \ldots\ldots(1),$$

where the Aj coefficients are the factor-loading for variable j, and E represents variance unaccounted for by the factors owing to error.

The factors are found by obtaining the eigenvectors and eigenvalues of the correlation matrix (principal components solution); each variable can then be written as a linear combination of the factors (eigenvectors) as in (1). Because of experimental error, very small factors from the principal components solution are taken to be zero.

Final interpretation of the factors is aided by rotation of the principal component matrix to produce an orthogonal varimax solution in which

---

[*] Variance is a measure of the 'spread' of a distribution.

each factor represents an independent dimension of the data. In contrast, subsequent oblique promax rotation allows a solution in which factors may be correlated.

Factor analysis can be applied to examine relations among individuals or samples (Q-mode) or to establish relations between variables measured in each sample(R-mode). Mathematically, the two processes are identical for the varimax solution, and the only difference is in the initial matrix, which is a similarity matrix for the Q-mode and a matrix of correlation coefficients for the R-mode.

Details of the factor analysis used here are given by Mayo & Long (in prep.). This incorporates, with additional options, the Q-mode technique of Klovan & Imbrie (1971), and the R-mode technique of Dixon (1971).

RESULTS

Q-mode analysis

The samples fell into three groups: a barren shale group, a sulphide group, and an evaporite group, and Q-mode factor analysis was carried out on the twenty-four elements measured in each sample

in order to:

(1) determine the degree of mixing between the groups;

(2) separate samples into distinct groups for R-mode analysis so that possible within-group associations would not be diluted and disguised;

(3) identify any other groups not obvious in the core; and

(4) determine, if possible, the partitioning of elements in the groups.

The general statistics for each element in the seventy are presented in Table 2, and eigenvalues with the associated cumulative amount of variance are shown in Table 3. Three Q-mode factors, shown in Figure 6, were taken as significant in explaining 88 percent of the variance. The normalized(transformed so that the loadings for each variable sum to 1) varimax factor

TABLE 2. General Statistics for Untransformed Data (Q-mode)

	Average	Standard Deviation	Minimum Value	Maximum Value
Ca	2.00	1.48	1.00	8.00
Fe	5.32	2.85	1.50	10.00
Mg	1.78	.68	.30	3.80
Mn	.04	.01	.02	.12
Ti	.30	.09	.10	.52
Ag	1.88	.80	1.00	4.00
Ba	246.28	99.47	100.00	610.00
Bi	8.48	5.87	6.00	44.00
Cd	3.37	4.85	1.00	27.00
Co	60.77	72.81	6.00	393.00
Cu	358.70	441.44	9.00	2310.00
Ni	67.44	80.10	3.00	426.00
Pb	10.02	4.71	3.00	36.00
Sc	15.60	2.54	10.00	23.00
V	169.25	67.98	17.00	300.00
Y	33.48	9.11	18.00	68.00
Zn	1211.44	2015.84	15.00	10800.00
Zr	130.64	43.88	100.00	370.00
Se	3.22	2.95	2.00	18.00
As	313.40	1088.99	2.00	6300.00
B	175.28	76.92	20.00	320.00
CO_2	1.04	1.94	.05	11.20
C	2.46	1.26	.30	5.44
S	4.23	5.93	.12	33.50

No. of samples = 70

Ca to Ti and CO_2 to S in percent; Ag to As in p.p.m.

TABLE 3. Eigenvalues (Q-mode analysis)

Factor	Eigenvalue	Cumulative variance %
1	51.42	73.46
2	7.37	83.99
3	2.76	87.94

loadings for each sample are given in Appendix II. These have been used in a ternary plot of the three factors (Fig. 6). The geochemical significance of the factors can be determined either by inspecting the main component in particular samples identified with each of the factors, or by inspection of the scaled varimax factor scores (Appendix IIB). These indicate that V, B, Ti, Sc, C, Ba, and Mg are most strongly associated with Q-mode factor 1 (Group I); Fe, Ag, Ni, S, Co, Cu, and Se with Q-mode factor 2 (Group II); and Ca, Mn, and CO_2 with Q-mode factor 3 (Group V). The groupings of elements with each Q-mode factor are regarded as indicating their geochemical association with the organo-detrital, sulphide, and evaporitic processes in the sedimentary environment. Given this assumption, the ratio of respective eigenvalues gives the relative contribution of each component to the total composition of the shale. As well as groups I, II, and V, a group of organo-detrital/sulphide samples (Group III), and a group of mixtures of all three components (Group IV) can be recognized (Fig. 6), reflecting the fine-scale mixing of the components.

The last step in the Q-mode process computes an oblique-rotated factor matrix in which single samples most representative of a particular Q-mode factor have the value 1.0 for that factor, and zero for others. These 'reference' samples represent the most divergent compositions, and all other samples can be thought of as mixtures of the three reference samples (numbers 7, 14, and 61, Appendix IIc). On the basis of the oblique rotation, down-hole levels for each factor are logged separately in Figure 7. The top 17 m of the core are relatively low in sulphides and evaporites, and high in the organo-detrital portion. The alternating sulphide-rich and organo-detrital section of the core is represented in the interval 17 m to 32 m. Below this all parts are intermixed in roughly equal amounts. At the level of 32 m evaporites are enriched relative to the other components.

TABLE 4. Statistics for the four Q-mode shale groups

	Group I		Group II		Group III		Group IV	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Ca	1.46	0.40	2.12	1.39	1.32	0.50	3.90	1.01
Fe	3.42	1.10	*	*	7.16	2.26	5.57	2.26
Mg	2.02	0.55	1.22	0.54	1.92	0.54	1.59	0.77
Mn	0.03	0.01	0.04	0.01	0.04	0.01	0.06	0.02
Ti	0.36	0.07	0.16	0.04	0.29	0.05	0.25	0.04
Ag	1.37	0.49	3.27	0.47	2.08	0.29	2.00	0.53
Ba	303.51	84.43	157.27	50.02	246.67	70.62	140.00	26.18
Bi	6.81	1.60	16.91	10.97	6.67	1.30	7.50	4.24
Cd	2.49	2.10	5.63	8.15	6.25	7.21	*	*
Co	19.76	11.77	189.73	99.40	70.67	25.27	65.12	31.66
Cu	109.19	94.02	865.64	671.66	608.67	462.71	439.37	214.65
Ni	19.73	11.91	210.64	102.90	86.83	32.48	68.37	25.67
Pb	10.65	2.95	9.82	9.13	9.58	5.10	8.87	2.64
Sc	16.57	2.24	13.64	2.16	16.17	1.70	14.00	2.61
V	212.57	44.18	100.54	49.40	175.00	33.64	86.87	19.69
Y	31.05	7.84	36.91	9.61	31.50	6.17	40.00	12.60
Zn	879.40	944.60	1950.36	3325.06	2477.42	2956.20	111.37	101.47
Zr	136.08	53.88	124.09	28.00	122.50	20.50	128.75	43.57
Se	*	*	8.27	4.86	2.92	1.31	2.75	0.89
As	73.46	208.27	1179.91	2460.11	227.42	425.92	426.50	1002.12
B	217.30	64.49	121.82	57.59	155.83	69.73	92.50	40.62
CO_2	0.24	0.16	1.59	1.92	0.48	0.30	2.65	1.10
C	2.84	1.33	1.58	0.64	2.54	1.15	1.53	0.62
S	1.12	0.78	14.73	8.32	5.49	2.87	2.84	1.28

Ca to Ti and CO_2 to S in percent; Ag to B in p.p.m.

* Elements omitted from the R-mode analysis

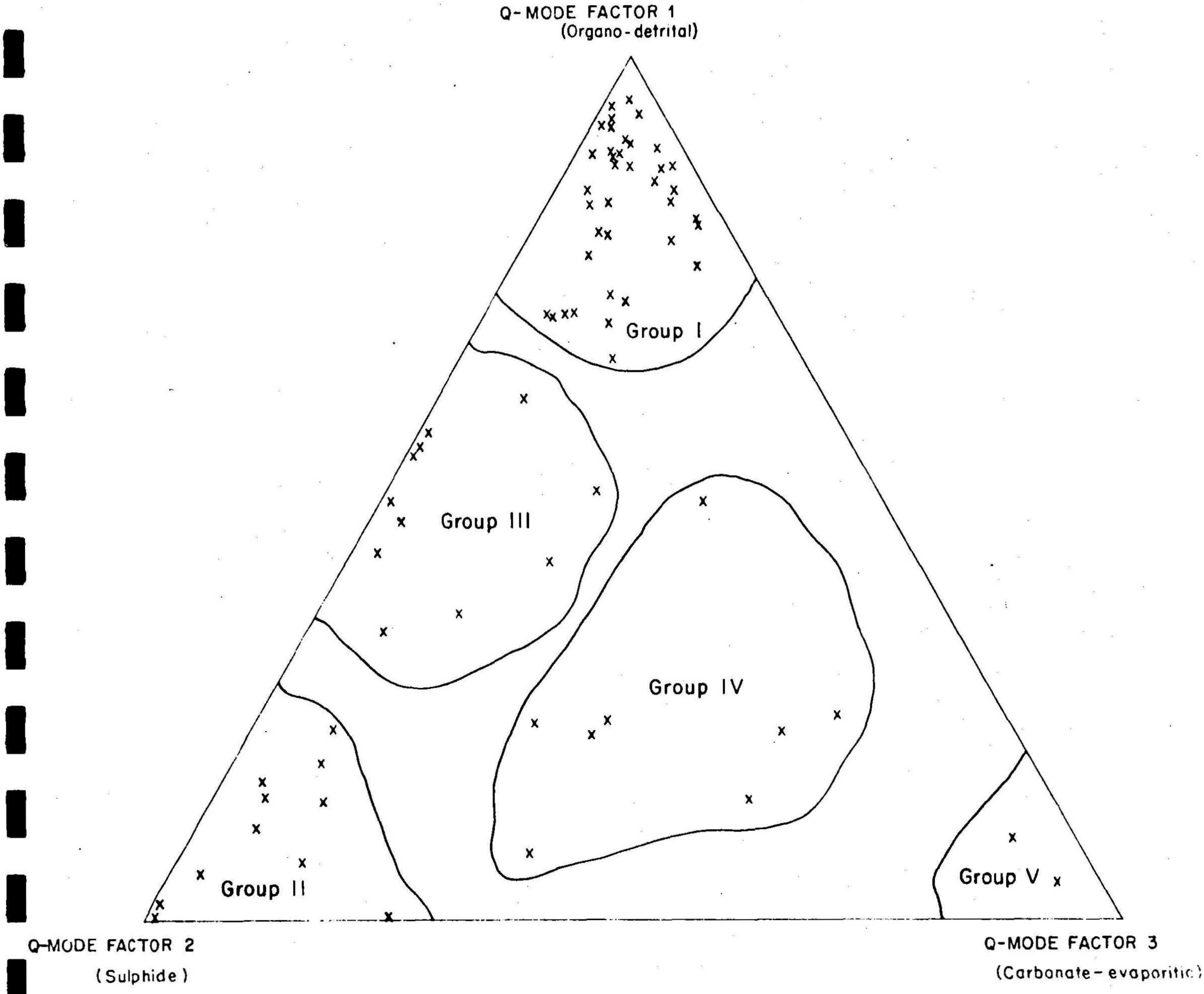


Fig.6 Ternary projection of the sample groupings with the Q-mode factors (B M R - Cloncurry DDH 5).

Record 1975/127

KJ F 54/A2/139

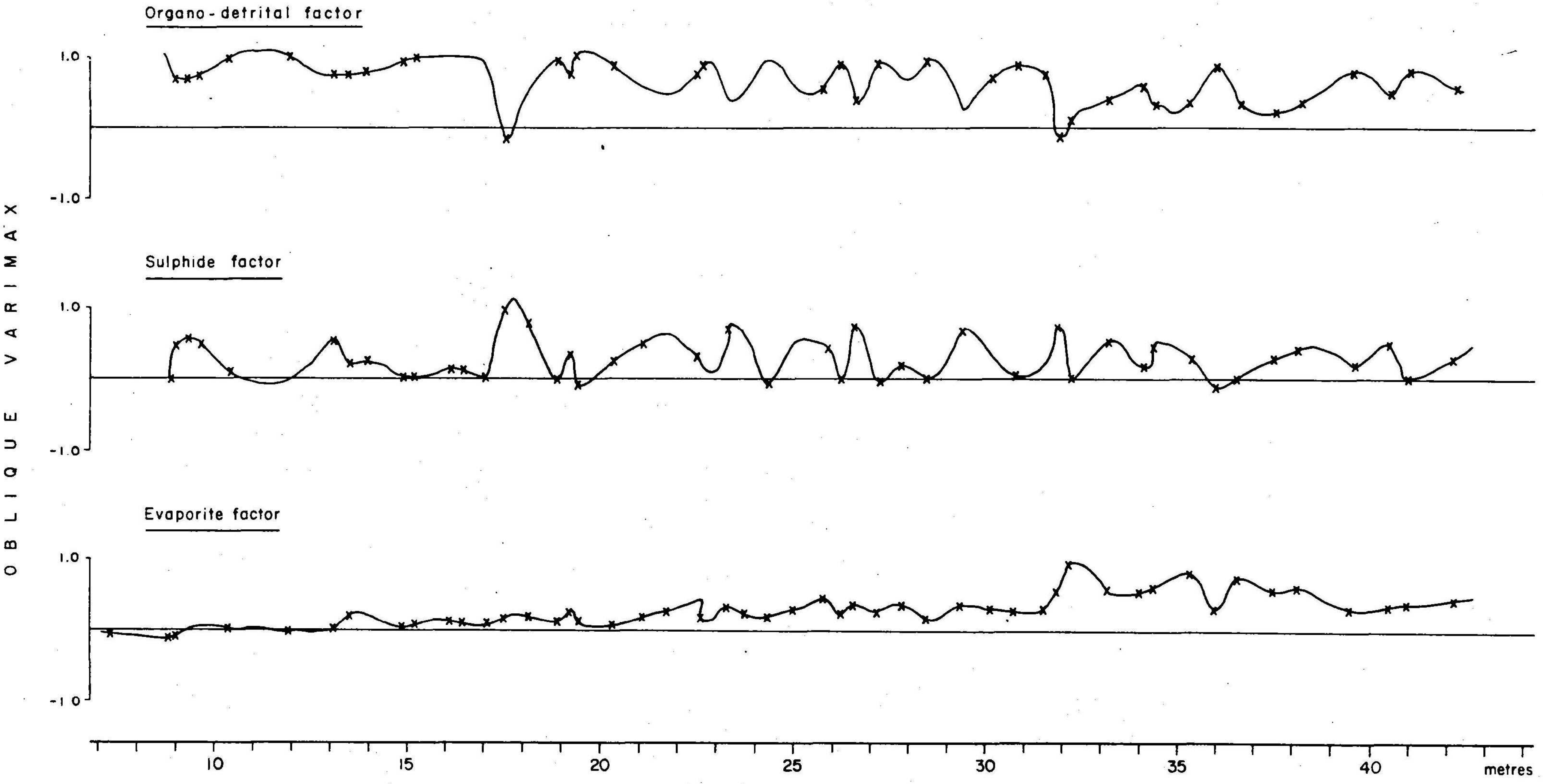


Fig. 7 Major components as fractions of reference samples, plotted against drill-hole depth. (B.M.R. - Cloncurry DDH 5).

Record 1975/127

KJ F 54/A2/138

R-mode analysis

Groups I and II were treated separately by R-mode analysis in order to detect within-group element relations; there were insufficient samples for analysis of the carbonate-evaporite group. In addition, the two mixed groups, III and IV, were analysed separately. Se in Group I, Fe in Group III, and Cd in Group IV were omitted from the analysis, these elements having values at the upper or lower limits of detection.

Means and standard deviations for the elements in Groups I - IV are presented in Table 4. The number of significant R-mode factors was determined by checking the amount of variance accounted for by successive factors, and by determining the consistency of factor loadings for different numbers of factors. The significant factors for each group with the cumulative variance accounted for is shown in Table 5, and the correlations between the R-mode promax factors in each group are presented in Table 6. The interpreted element associations for each group (see Table 7) have been given with their respective R-mode factors in Table 8. The correlation and factor matrices from which these associations were determined are presented in Appendix III, and a factor loading diagram (Fig. 8) shows the relative control of each R-mode factor on particular elements for each of the four Q-mode groups.

GEOCHEMICAL ASSOCIATIONS

Organo-detrital group (I)

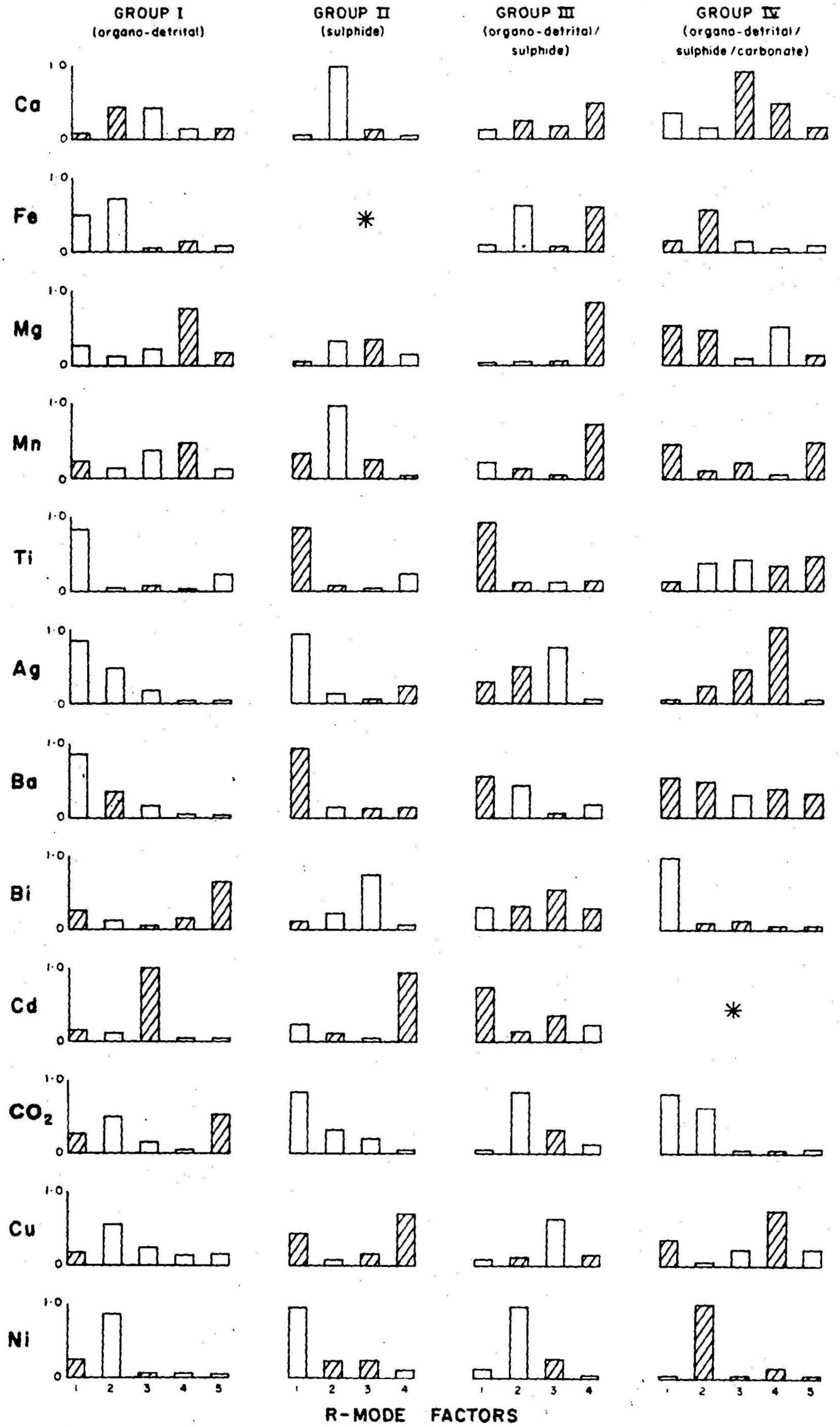
Five R-mode factors account for 68.96 percent of the total variance (Table 5).

Factor 1 'controls' Sc, Ba, Ti, Ag, C, and V, and is considered to reflect organic adsorption or complexing processes. The high correlation between these two groups may be expected where elements are either adsorbed on clays (probably illite from the high values of K_2O, Table 1), or fixed by organic material. This factor, then, reflects a syngenetic process - the rate of deposition.

TABLE 5. R-mode eigenvalues for the four Q-mode groups

Group	R-mode factor	Eigenvalue*	Cumulative percentage variance
I	1	6.014	26.147
	2	3.447	41.136
	3	2.922	53.839
	4	1.972	62.412
	5	1.506	68.960
II	1	10.305	44.802
	2	4.950	66.322
	3	3.117	79.873
	4	1.789	87.649
III	1	7.657	31.904
	2	4.404	50.253
	3	3.487	64.783
	4	3.037	77.438
IV	1	8.392	36.490
	2	5.513	60.461
	3	3.179	74.285
	4	2.414	84.782
	5	1.997	93.463

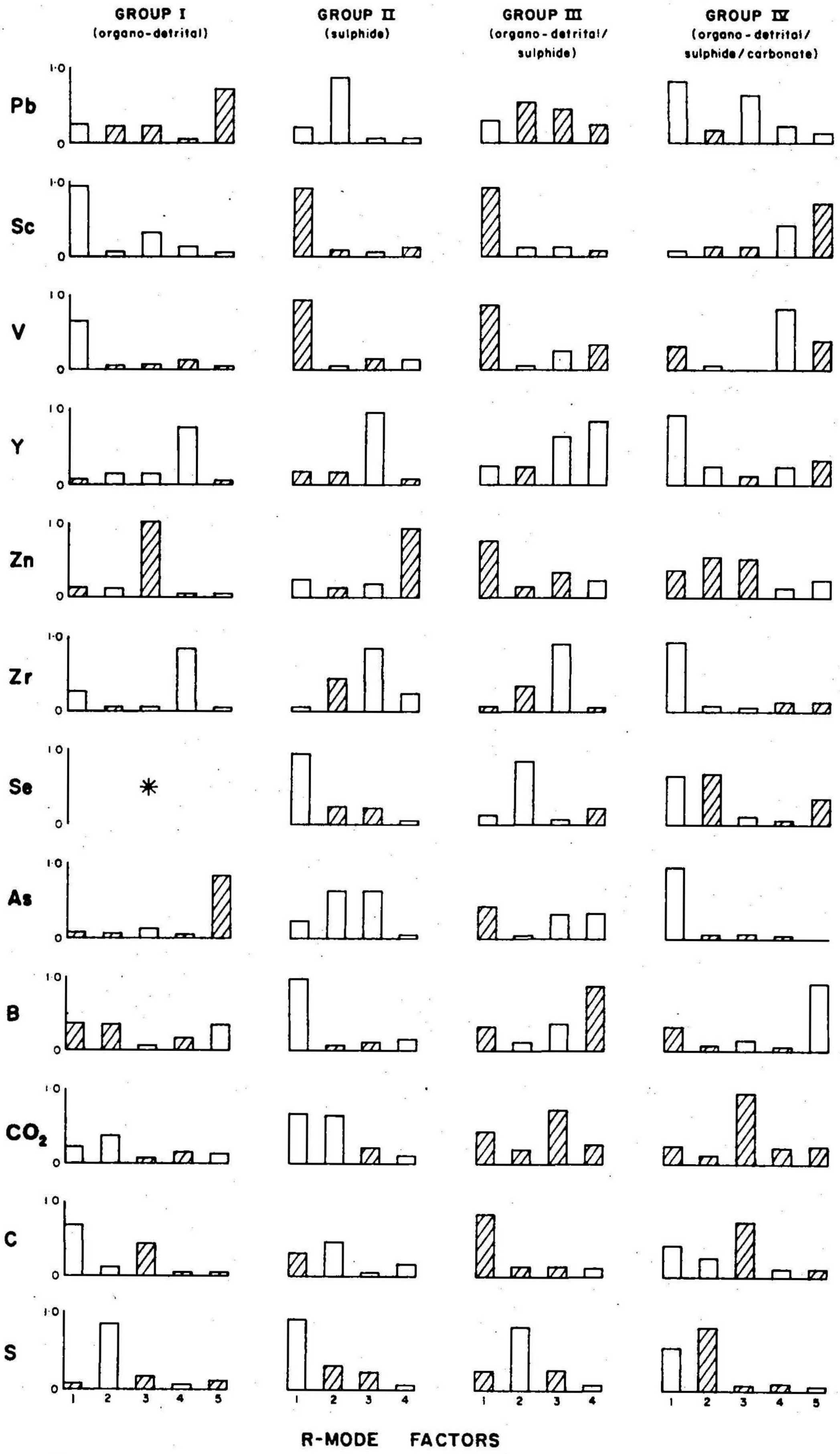
* Only those factors deemed to be significant are tabulated.



* Omitted from R-mode analysis.

Fig. 8a The loadings of elements and CO_2 with the R-mode factors in each group. Negative and positive factor loadings are denoted by filled and empty columns respectively.

F54/A2/147a



* Omitted from R-mode analysis.

Fig. 8 b

TABLE 6. Correlation between R-mode factors for the Q-mode groups.

Group I (organo-detrital)

R-mode Factor	1	2	3	4	5
1	1.00	-0.18	-0.36	-0.03	0.16
2		1.00	0.26	-0.01	-0.25
3			1.00	-0.12	0.07
4				1.00	-0.14
5					1.00

Group II (sulphide)

R-mode Factor	1	2	3	4
1	1.00	0.12	-0.08	-0.06
2		1.00	0.14	0.23
3			1.00	0.27
4				1.00

Group III (organo-detrital/sulphide mixed)

R-mode Factor	1	2	3	4
1	1.00	-0.24	0.03	-0.33
2		1.00	0.00	0.17
3			1.00	-0.10
4				1.00

Group III (organo-detrital/sulphide/carbonate mixed)

R-mode Factor	1	2	3	4	5
1	1.00	0.05	-0.19	0.03	0.10
2		1.00	0.14	-0.32	0.18
3			1.00	-0.37	0.03
4				1.00	-0.12
5					1.00

The negative correlation* of S, identified with R-mode factor 2, with C (Appendix III), and the separate grouping of the chalcophile elements (Ni, Fe, Cu, Co) of r-mode factor 1, may reflect secondary remobilization into the barren shale of sulphides. As suggested already, some mobility may have been associated with compaction and diagenesis. R-mode factor 2, therefore, is considered to reflect sulphide redistribution and concentration. It is associated with the pyrrhotite, pyrite, and chalcopyrite in the core.

R-mode factor 3 controls Zn and Cd, and is not correlated with any of the other factors. Each element shows a weak correlation with C, but not with S (Appendix III), which is a surprising result in view of the presence of sphalerite in minor amounts. No explanation is offered for the independent behaviour of Cd and Zn.

The Zr, Y association of R-mode factor 4 probably reflects the resistate mineral zircon. This factor is therefore probably a detrital factor. As, Pb, Bi, and Co are associated with R-mode factor 5, and may be an insignificant association. On the other hand they are all chalcophile elements, and some sulphide depletion process may be indicated.

Sulphide group (II)

Four R-mode factors account for 87.65 percent of the total variance (Table 5). V, B, Sc, Ti, and Ba of the factor 1 (Table 8) have negative loadings, and Fe, Se, Ag, Ni, S, and Co have positive loadings. The process associated with factor 1 is considered to involve enrichment of the chalcophile elements relative to the hydrolysate elements; the opposed loadings (presence of both negative and positive loadings)may be due to the metal sulphide deposition in the shale being a diagenetic or metamorphic process rather than a syngenetic process as in R-mode factor 1 of the organo-detrital group. If this is correct, the stratiform sulphides as well as the remobilized sulphides in the shale are probably not syngenetic; instead it is suggested that they originated in post-depositional processes involving

---

* Correlation was taken to be significant at the level $|r| = 0.5$.

TABLE 7. Element correlation in the four components of the black shale. Elements are listed in order of decreasing positive or negative correlation (1 r 1 0.5)

	Organo-detrital group		Sulphide group		Organo-detrital/sulphide mixed group		Organo-detrital/sulphide/carbonate mixed group	
	+ correlation	- correlation	+ correlation	- correlation	+ correlation	- correlation	+ correlation	- correlation
Ca	-	-	Pb, Mn, Co_2	-	Bi, Mn,	-	C, Co_2, Bi, Y, Ag	-
Fe	S, Ni, Co	-	*	*	S, Ni, Se,	Y	S, Se, Co, Ni,	Cu, Ti
Mg	-	-	B, T, V, Ba, Sc	S, Se, Ni, Ag, Co	Mn, B	Y	V, Zn, Ni, Sc	Zr
Mn	-	C	Ca, Pb, C	-	Mg, Ca,	Ba, C,	Ba, Sc,	-
Ti	Sc, C, Ba, Ag	Co	B, V, Mg, Ba, Sc	Ag, Se, S, Ni, Co	Sc, Zn, Cd, C	-	Cu	Fe, S
Ag	Sc, Ti, C	-	Se, Ni, S, Co,	B, Sc, Ti,	Zr, Y	Ni, Co,	Ca, Cu	V
Ba	Sc, Ti, C, V	Co	Sc, V, Ti, Mg	Se, Ni, Co, Ag, S	S, Se, Ni, C	Mn, Pb,	Mn	Y, As, Zr
Bi	-	-	As, Y,	-	Pb, Ca,	Sc, Ti	As, Co, Y, Fe, Pb, S, C,	Ba, Mg
Cd	Zn,	-	Zn,	-	Zn, As, C, Ti, Sc,	-	*	*
Co	As, Ni, S, Fe, Cu	Ti, Ba	Co_2, Ag, Se, Ni,	Sc, V, B, Ba, Ti, Mg	Ni, S, Se, As,	-	Se, Fe, S, Bi, As, Y, Pb	-
Cu	Ni, Co,	-	Ba	-	-	-	Ti, Ag,	C, V, Sc, Zn
Ni	S, Fe, Co, Cu	-	S, Se, Ag, Co, Co_2	Sc, Ti, V,	Co, S, Se,	Ag	S, Se, Fe, Mg, Zn, Co	-
Pb	-	-	Ca, Co_2, As, Mn, Co	-	Bi	Ba, V, Sc	As, Bi, Co, Y	Co_2
Sc	Ti, Ba, C, V	-	V, B, Ba, Ti,	Ag, Co, Se, S	Ti, C, Ba, V,	Bi, Pb	V, Co_2, Mg, Mn	B, Cu
V	C, Ti, Ba, Sc	-	B, Ti, Sc, Ba,	Se, Co, Ni, S	Sc, Ti, C,	Pb,	Mg, Sc,	Ag, Cu
Y	Zr,	-	Zr, Bi	-	Ag, Zr,	Mg, Fe	As, Bi, Zr, C	Ba, Cu, B
Zn	Cd, C	-	Cd,	-	Cd, As, C, Sc	-	Mg, Co_2, Ni	Pb
Zr	Y	-	Y	-	Ag, Y	-	Bi, As, Y	Mg

	Organo-detrital group		Sulphide group		Organo-detrital/sulphide mixed group		Organo-detrital/sulphide/carbonate mixed group	
	+ correlation	- correlation	+ correlation	- correlation	+ correlation	- correlation	+ correlation	- correlation
Se	*	*	Ni, S, Ag, Co	V, B, Ti, Ba, Mg	Co, Ni, S, Fe	-	S, Fe, Co, Ni,	B
As	Co	-	Pb, Bi, Ca, Co,	-	Cd, Zn, C, Co,	-	Bi, Zr, Y, Co	Ba, Mg
B	-	-	V, Ti, Mg, Ba,	Ag, Se, Co, S, Ni, Co_2	Mg	-	-	Sc, V, Se
Co_2	-	-	Co, Pb, Ca, Ag,	Sc, Ti, B,	Zn, Cd,	Zr	Ca, C, Zn, V	Pb
org. C	Ti, V, Ba, Zn	Mn,	-	-	Sc, Zn, Cd, Ba, Ti	Mn	Ca, Y, Bi, As, Co_2	Ba, Cu
S	Ni, Fe, Co,	-	Ni, Se, Ag, Co,	V, B, Ti, Sc, Ba	Ni, Co, Fe, Se	-	Fe, Co, Se, Ni,	-

* Elements omitted from the R-mode analysis

migration of sulphur and chalcophile metals.

Ca, Pb, and CO_2 associated with R-mode factor 2 are opposed by Zr (Table 8). This may indicate that some depletion of detrital material relative to carbonate enrichment has occurred, possibly due to proximity to a shoreline.

R-mode factors 3 and 4 are similar to those of the organo-detrital group.

Organo-detrital/sulphide mixed group III

77.44 percent of the total variance is accounted for by four R-mode factors. Factor 1 again controls Ti, Sc, V, Zn, Cd, and C, and is regarded as reflecting the rate of deposition associated with an adsorption process. The positive correlation of C with these elements (Appendix III) supports this contention;

R-mode factor 2 represents sulphide enrichment (Ni, Se, Co, S, Fe), and is negatively correlated with factor 1 (Table 6). The strong S-Fe correlation ($r=0.70$) reflects the presence of disseminated pyrrhotite in the shale.

No interpretation of R-mode factors 3 and 4 is given; it is possible that they represent statically insignificant associations.

Organo-detrital/sulphide/evaporite mixed group (IV)

Five R-mode factors account for 93.46 percent of the total variance. Factor 1 comprises As, Bi, Zr, Y, Co and Pb, and may reflect syngenetic complexing and adsorption processes. Factor 2 is a sulphide-depletion factor with negatively loaded elements Ni, S, Se, Co, and Fe, and is probably bipolar with respect to factor 1 in the sulphide group. Factor 3 is associated with a carbonate-depletion process; CO_2 and Ca have negative loadings. Factors 4 and 5 are left uninterpreted.

TABLE 8. Elements loaded in association with each R-mode factor for four Q-mode groups.

Group	R-mode factor	Element association
Organo-detrital	1	Sc, Ba, Ti, Ag, C, V, Fe
	2	S, Ni, Fe, Cu, Co
	3	- Cd, Zn
	4	Zr, -Mg, Y
	5	-As, -Pb, -Bi, -Co
Sulphide	1	-V, -B, Fe, Se, Ag, Ni, -Sc, S, -Ti, -Ba, Co
	2	Mn, Ca, Pb, CO_2, -Zr
	3	Zr, Y, Bi, As
	4	Cd, Zn
Organo-detrital/sulphide mixed	1	-Ti, -Sc, -V, -C, -Zn, -Cd
	2	Ni, Se, Co, S, Fe
	3	Zr, Ag, -CO_2, Cu, Y
	4	-B, -Mg, Y, -Mn, -Fe
Organo-detrital/sulphide/evaporite mixed	1	As, Bi, Zr, Y, Co, Pb
	2	-Ni, -S, -Se, -Co, Y, -Fe
	3	-CO_2, -Ca, -C, Pb
	4	-Ag, V, -Cu, Mg
	5	B, -Sc

ELEMENT DISTRIBUTION AND PARTITIONING

The geochemical associations related to the three Q-mode factors, taken from the scaled Q-mode factor scores (Appendix IIB), give the overall partitioning of elements into each component of the black shale:

1) V, B, Ti, Sc, C, Ba, and Mg with the organo-detrital fraction.
2) Fe, Ag, Ni, S, Co, Se, and Cu with the sulphide fraction.
3) Ca, Mn, Y, and CO_2 with the carbonate or evaporite fraction.

Information about the possible processes giving rise to sulphide and evaporite segregation or deposition is provided by examining each of these fractions separately using the R-mode approach. This analysis indicates that a possible process for the formation of the concordant metal sulphide layers, as well as the clearly remobilized sulphide in cross-cutting structures, is post-depositional migration of sulphur and chalcophile metals to sites where other elements are either depleted or replaced. Such a process may have operated during compaction and diagenesis, and may have been associated with the veining and contortion attributed to differential compaction. It seems that metamorphism played only a minor role in element redistribution: the original syngenetic/diagenetic element distributions appear to be little disturbed.

Models for the post-depositional origin of sulphide layers have previously been proposed by Lambert & Bubela (1970) and Lambert (1973). They involve diffusion of metals into unconsolidated sediments or release of metals from fixed sites in clay or organic matter, or both, during diagenesis or metamorphism. In the presence of free sulphide ions, these can form discrete metal sulphide bands.

The elements Sc, Ba, Ti, Ag, V, Ni, Co, Zn, Cd may have been fixed during deposition by adsorption and complexing processes in clays and with organic material.

Mobility of the carbonate fraction (Q-mode factor 3) - elements Ca, Mn, Y, and CO_2 is evident in the mixed groups. The positive carbonate association in the sulphide group may reflect direct precipitation of evaporites following the suggested marine transgression. That this process accompanied the sulphide enrichment process (R-mode factor 1) may have important implications for the palaeo-environment of sulphide mineralization in that the deeper and quieter water suggested by the transgression (R-mode factor 2) may have favoured metal sulphide concentration.

Most of the variance in the element populations can thus be accounted for by a model that includes:

1) syngenetic segregation of elements into clay and organic matter group by adsorption and complexing, respectively, and into carbonate by direct precipitation
2) post-depositional - possibly prediagenetic - localization of mobile sulphide and metal ions in concordant sulphide layers accompanied by possible minor remobilization of evaporites
3) remobilization of sulphides producing cross-cutting relations.

METAL ENRICHMENT

Vine & Tourtelot (1970) have devised a scheme for deciding whether a black shale is metal-enriched. They computed the 90th percentile for minor element distributions in a set of samples, and defined a shale as metal-rich if any element occurred in excess of this class interval. The minor-element enrichment index allows comparison of black shales with different element enrichments. It is determined by summing the percentage of samples that are metal-rich with respect to a given number of minor elements.

In Table 9 the index of Vine & Tourtelot (1970) has been adjusted to apply to 14 of the minor elements determined in this study. The resulting enrichment index for these elements in Cloncurry No. 5 black shale is 263. The shale is enriched in B, Co, Cu, Ni, and Zn, and is almost as enriched as

TABLE 9. A comparison of minor-element enrichment indices (percent of samples that are enriched in minor elements); modified after Vine & Tourtelot (1970)

Element	Percent of samples enriched in each set														
	Set numbers														
	1	3	4	5	6	8	9	10	13	14	16	17	18	19	This study
Ti											10				
Mn	15						28	10		5	100				
Ag		11		5	74					37	15				
B			12			16	30					7	7	11	43
Ba			59						9		10	14	5	7	
Co								82	6						56
Cu		22	9		14			71				5			53
Ni		57			23			69		5					72
Pb				13			7	10			60				
Sc							40								
V		73	17		30					37					
Y			5		77			25		11	25				
Zn		32			56			22							32
Zr			7		5			16	12						7
Totals (enrichment index)	15	195	109	18	279	16	105	305	27	97	220	21	17	18	263

the second most enriched shale (Houy Formation) examined by Vine & Tourtelot, and on their criteria is classed as enriched relative to average black shales.

PALAEO-ENVIRONMENT OF DEPOSITION

Consideration of the processes controlling the element variance in the sulphide group has led to the suggestion that some deepening of the black shale basin may have occurred. The main geological factor controlling the variance in both organo-detrital and sulphide groups is related to adsorption and complexing processes, and it is suggested that the shale was deposited slowly in a quiet environment - probably a local embayment - in which the detrital contribution was of relatively minor significance. It is suggested that this environment of slow deposition in a stable local embayment has been the main control on element distribution, and that this can be distinguished from one of rapid detrital deposition in unstable near-shore conditions or in a rapidly subsiding basin. The distinction can be made because the high loadings of the hydrolysate or resistate (detrital) elements are in the primary factor that accounts for the bulk of the element variance. The loading of C and elements complexed or adsorbed by organic matter with factor 1 and the hydrolysate group further attest to slow quiet deposition.

The general lack of correlation between C and S (Appendix III) does not preclude the possibility of a syngenetic association of organic and chalcophile element groups, because subsequent redistribution of the chalcophile elements may have masked any association. Therefore a restricted euxinic environment might be invoked to provide an initial source of sulphides. In this connection, Lambert (1973) has shown that the conversion of pyrite to pyrrhotite with attendant loss of sulphur proceeds more rapidly in the presence of carbonaceous material.

Deposition of evaporites was a less significant process than organo-detrital and sulphite deposition, accounting for only 3.95 percent of the total variance in the Q-mode analysis. This suggests that concentrations in

TABLE 10. Comparison of the black shale with two shales with different palaeoenvironments

	Houy Formation	Belden Shale	This study
Ag ppm	1.20	-	1.88
Co "	140	11	60.77
Cu "	210	40	358.70
Ni "	490	39	67.44
Pb "	52	26	10.03
V "	210	110	169.26
Zn "	920	-	1211.44
C %	5.1	1.3	2.47

the restricted trough occasionally reached the level for direct precipitation. The presence of scapolite (Hill, 1968; Ramsay & Davidson, 1970), and the very high level of B in the shale (Degens, Williams, & Keith, 1957) support the interpretation of high salinity.

Therefore, minor element distributions support the view that the black shale was deposited under quiet restricted marine conditions - probably in a local embayment on a shallow epicontinental shelf. Deposition took place at a slow rate, probably in a euxinic basin, which provided a sink for metal enrichment and sulphide deposition.

In Table 10 the black shale is compared with partial analyses (Ag, Co, Cu, Ni, Pb, V, Zn, C) presented for black shales representing two different trough environments (Vine & Tourtelot 1970); the Houy Formation was deposited in a local basin on a shallow epicontinental marine shelf, whereas the Belden Shale represents rapid dumping and burial in a subsiding trough. The former reflects a stable tectonic environment; the latter, tectonic instability. The Houy Formation, which is close in total enrichment to the Cloncurry No. 5 black shale, is enriched in the listed elements relative to the Belden Shale. These elements appear to indicate palaeotectonic stability, supporting the palaeo-environmental interpretation given above for the Cloncurry No. 5 black shale.

Because of the diversity of possible element dispersion and concentration processes in the sedimentary environment, it is generally impossible to gain any idea of provenance from minor elements in sediments, and a more fruitful approach is to examine the constituent minerals. For Cloncurry No. 5 shale, marked enrichment in the base metals (Co, Cu, Ni, Zn) may be related to the proximity of basic rocks contributing detritus.

COMPARISON WITH OTHER BLACK SHALE STUDIES

The average black shale composition for the 70 samples is used as a basis for comparison with black shale compositions from other sources

TABLE 11. Analytical data: comparison of black shale with shale of other studies

	Average shale a	Average black shale b	Average for this study	Average for the Urquhart Shale c	Average for black shales from the Cloncurry region d
Ca	2.21	1.50	2.01	8.80	*
Fe	4.72	2.00	5.33	4.30	*
Mg	1.50	0.70	1.78	4.30	*
Mn	0.08	0.02	0.04	0.26	*
Ti	0.46	0.02	0.30	0.15	*
Ag	0.07	1.00	1.88	44.00	*
Ba	580.00	300.00	246.28	381.00	800.00
Bi	*	*	8.48	*	*
Cd	0.30	*	3.37	67.00	*
Co	19.00	10.00	60.77	32.00	61.00
Cu	45.00	70.00	358.70	254.00	97.00
Ni	68.00	50.00	67.44	22.00	17.00
Pb	20.00	20.00	10.03	2607.00	9.00
Sc	13.00	10.00	15.60	14.00	*
V	130.00	150.00	169.25	33.00	132.00
Y	26.00	30.00	33.48	32.00	41.00
Zn	95.00	300.00	1211.44	3963.00	7.00
Zr	160.00	70.00	130.64	188.00	180.00
Se	0.60	*	3.23	*	15.00
As	13.00	*	313.40	*	*
B	100.00	50.00	175.29	*	21.00
Co_2	*	*	1.05	*	4.10
C org	*	3.20	2.47	*	4.10
S	0.24	*	4.23	*	0.18

a. Turekian & Wedepohl (1961)
b. Vine & Tourtelot (1970)
c. Smith & Walker (1972)
d. G. Derrick, unpublished data

Ca to Ti in percent; Ag to B in p.p.m;
Co_2 to S in percent.

* not included in analysis

(Table 11). The Cloncurry No. 5 shale is markedly enriched in most of the base metals (Co, Cu, Ni, V, Zn) compared with the average shales determined by Turekian & Wedepohl (1961; column a in Table 11) and Vine & Tourtelot (1970; column b in Table 11). Pb, however, is lower in the shale studied than in either of the average shale compositions (a and b), but is similar to the mean value of 34 samples of black shale from the Corella Formation and Marino Slate in the Cloncurry region (G.M. Derrick, unpublished results; column d in Table 11). In this study, the black shale is enriched in B relative to the average shales (a and b) and to the black shales farther east (d). The Co value is identical with that in d and is about twice that in the Urquhart Shale (Smith & Walker, 1972). Zn, Ni, Cu, and V are all enriched,in the shale studied. Relative to d, the shale studied is enriched in Zn, Ni, Cu, and V - Zn by about two orders of magnitude. The Urquhart Shale is higher in Ag and Pb (by three orders of magnitude), but lower in Cu, Ni, Co, and V.

The linear relation that Smith & Walker (1972) found in the Mount Isa sequence between Cd and Zn is evident also in the Cloncurry No. 5 shale (Appendix III; Table 7); in general Zn and Cd are highly correlated, and group under the same factor.

Within and surrounding the silica-dolomite body of the Urquhart Shale, Co was found to be a good indicator of Cu, which Smith & Walker (1972) considered had been derived from basement basic volcanics. No such correlation was found in this study, and it is likely that here a different process localized copper mineralization.

For shales in the McArthur River region, Lambert & Scott (1973) found a good correlation between C and S, and argued that this supported a syngenetic origin for the sulphides. This correlation is not apparent in the results from Cloncurry No. 5, although, as already noted, an initial syngenetic C-S association may have been disguised by subsequent remobilization. A major difference between the two regions is in grade of metamorphism; at McArthur River there has been essentially no metamorphism, in contrast to the middle greenschist metamorphic grade of the Corella Formation, which may have contributed to redistribution of the chalcophile elements.

Base-metal enrichment has taken place in graphitic shale of the Dugald River sequence, northwest of Cloncurry, and geochemical similarities between this sequence and the Cloncurry No. 5 shale are expected from geological considerations: both sequences represent the upper part of the Corella Formation.

CONCLUSIONS

It is considered that the Cloncurry No. 5 black shale was deposited slowly in a local - probably euxinic - embayment surrounded by a broad marine shelf; the basin was an effective base metal 'sink',and the shale is enriched in Zn, Co, Cu, Ni, and V, although it is surprisingly low in Pb - a feature it shares with black shales farther east in the Corella Formation and the Marino Slate.

The lack of correlation of high Zn levels with Ag and Pb, and the absence of any C-S correlation or correlation between hydrolysate and chalcophile group elements, further distinguish the mineralization from the Mount Isa-McArthur River type. This distinction may result from :

1) distinct environments of syngenetic mineralization. Various workers (e.g., Smith, 1969; Lambert & Scott, 1973) have emphasized the possible genetic significance of major penecontemporaneous faults and volcanism for the Mount Isa-McArthur River type
2) different grades of metamorphism which may have contributed to remobilization
3) different processes of post-depositional element redistribution.

Besides being used to elucidate depositional environment, element associations from factor analysis suggest that chalcophile elements may have been concentrated in discrete layers during a post-depositional process; hence the concordant sulphide layers may not be syngenetic in origin, although the base metals,may have been involved in syngenetic complexing and adsorption processes before redistribution.

REFERENCES

Carter, E.K., Brooks, J.H., & Walker, K.R., 1961 - The Precambrian mineral belt of northwestern Queensland. *Bur. Miner. Resour. Aust. Bull*. 51.

Conybeare, C.E.B. & Crook, K.A.W., 1968 - Manual of sedimentary structures. *Bur. Miner. Resour. Aust. Bull*. 102.

Cooley, W.W., & Lohnes, P.R., 1971 - MULTIVARIATE DATA ANALYSIS. Sydney, Wiley & Sons.

Degens, E.T., Williams, E.G., and Keith, M.L., 1958 - Environmental studies of Carboniferous sediments. Part II: Application of geochemical criteria. *Bull. Amer. Ass. Petrol. Geol*., 42, 981-97.

Derrick, G.M., Wilson, I.H., Hill, R.M., Glikson, A.Y., & Mitchell, J.E., 1974 - Geology of the Mary Kathleen 1:100 000 Sheet area, Queensland. *Bur. Miner. Resour. Aust. Rec*. 1974/90 (unpubl.).

Dixon, W.J., 1971 - BIOMEDICAL COMPUTER PROGRAMS. *Univ. Calif. Publications*.

Harman, H.H., 1960 - MODERN FACTOR ANALYSIS. Chicago, Univ. Chicago Press.

Hill, R.M., 1968 - Geology of Sunset area, Mary Kathleen, Queensland. *Univ. Qld B. Sc. Hons. Thesis* (unpubl.).

Hill, R.M., & Duff, B.A., 1975 - Metalliferous diamond drilling, Mount Isa area, 1971. *Bur. Miner. Resour. Aust. Rec*. 1975/84 (unpubl.).

Hirst, D.M., & Kaye, M.J., 1971 - Factors controlling the mineralogy and chemistry of an Upper Visean sedimentary sequence from Rook Hope, County Durham. *Chem. Geol*., 8, 37-59.

Imbrie, J., 1963 - Factor and vector analysis programs for analysing geologic data. *Office Naval Res., Geography Branch, Tech. Rep*. 6.

Klovan, J.E., & Imbrie, J., 1971 - An algorithm and FORTRAN IV program for large-scale Q-mode factor analysis and calculation of factor scores. *Math. Geol*., 3, 61-79.

Krumbein, W.C., & Graybill, F.A., 1965 - AN INTRODUCTION TO STATISTICAL MODELS IN GEOLOGY. New York, McGraw-Hill.

Lambert, I.B., 1973 - Post-depositional availability of sulphur and metals and formation of secondary textures and structures in stratiform sedimentary sulphide deposits. J. geol. Soc. Aust., 20, 205-15.

Lambert, I.B., & Bubela, B., 1970 - Banded sulphide ores: the experimental production of monomineralic sulphide bands in sediments. Mineral Deposita, 5, 97-102.

Lambert, I.B., and Scott, K.M., 1973 - Implications of geochemical investigations of sedimentary rocks within and around the McArthur Zinc-Lead-Silver deposit, Northern Territory. J. Geochem. Expl., 2., 307-30.

Mayo, W., & Long, K.A., in prep. - Documentation of Geological Branch computer programs. Bur. Miner. Resour. Aust. Rec. (unpubl.).

Ramsay, C.R., & Davidson, L.R., 1970 - The origin of scapolite in the regionally metamorphosed rocks of Mary Kathleen, Queensland. Contr. Mineral. Petrol., 25, 41-51.

Smith, S.E., & Walker, K.R., 1972 - Primary element dispersions associated with mineralization at Mount Isa, Queensland. Bur. Miner. Resour. Aust. Bull. 131.

Smith, W.D., 1969 - Penecontemporaneous faulting and its likely significance in relation to Mount Isa ore deposition. Geol. Soc. Aust. spec. publ. 2, 225-36.

Turekian, K.K., & Wedepohl, K.H., 1961 - Distribution of the elements in some major units of the earth's crust. Bull. Geol. Soc. Amer., 72, 175-92.

Vine, J.D., & Tourtelot, E.B., 1970 - Geochemistry of black shale deposits - a summary report. Econ. Geol., 65, 253-72.

APPENDIX 1. Analyses of the black shale (Cloncurry No. 5)

Sample	Ca%	Fe%	Mg%	Na%	Ti%	S%	C%	CO_2%	LOSS ON IGNITION	Ag ppm	Ba ppm	Bi ppm	Cd ppm	Co ppm	Cu ppm	Ni ppm	Pb ppm	Sc ppm	V ppm	Y ppm	Zn ppm	Zr ppm	Se ppm	As ppm	B ppm
1605	ND	2.5	1.5	ND	0.52	0.30	5.44	0.25	9.94	2	440	ND	1	6	75	9	11	22	250	20	369	160	-2	65	70
1606	ND	2.0	1.7	0.02	0.38	0.86	4.86	0.05	8.33	1	330	ND	6	8	24	10	10	16	210	25	2,380	130	-2	5	90
1607	ND	6.6	1.9	0.04	0.36	7.3	3.96	0.9	12.12	2	290	6	26	98	350	98	8	18	210	28	10,300	ND	3	1,350	100
1608	ND	6.3	1.1	ND	0.28	7.7	3.78	0.1	12.21	2	250	ND	6	100	513	104	6	17	180	35	2,100	120	3	850	90
1609	ND	5.6	1.3	0.03	0.33	6.95	3.43	1.05	11.25	2	350	6	12	70	425	94	11	17	150	35	5,130	ND	2	220	90
1610	ND	4.0	1.6	0.03	0.38	2.40	3.82	0.1	8.63	1	310	ND	5	26	64	38	8	17	220	28	1,630	100	-2	12	190
1611	ND	2.9	1.4	0.03	0.37	0.65	3.83	0.55	7.15	1	310	ND	5	18	59	30	13	16	210	21	2,650	110	-2	-2	230
1612	ND	9.8	1.9	0.03	0.33	5.6	3.76	0.45	10.15	2	290	6	10	53	498	75	7	18	210	27	4,250	120	2	90	180
1613	ND	6.0	3.8	0.07	0.40	1.9	3.75	0.75	9.25	2	240	ND	3	21	125	23	7	17	220	26	810	100	-2	2	90
1614	1.4	5.6	2. 4	0.03	0.43	2.55	3.18	0.7	7.61	2	250	ND	2	29	198	38	11	18	185	35	725	120	-2	28	100
1615	2.0	2.9	2.7	0.03	0.46	0.5	5.11	0.25	5.77	2	610	6	1	10	23	10	17	23	270	18	413	ND	-2	4	210
1616	1.7	2.5	2.3	0.03	0.44	0.44	4.27	0.3	6.87	2	350	ND	4	9	189	7	12	18	245	25	1,330	120	-2	2	210
1617	1.4	4.3	2.2	0.03	0.48	1.90	3.84	0.25	7.04	2	310	ND	4	21	144	25	9	18	240	34	1,580	140	-2	8	240
1618	ND	+10.0	0.5	ND	ND	23.5	0.76	1.35	12.64	4	ND	10	27	244	1,640	321	3	12	36	33	10,800	ND	15	100	40
1619	ND	+10.0	2.4	0.04	0.33	10.2	2.33	0.3	9.76	2	320	ND	4	99	293	135	8	18	180	32	1,530	120	5	18	180
1620	ND	4.6	2.3	0.04	0.43	1.37	4.37	0.15	7.51	2	390	ND	2	19	130	21	7	18	250	28	1,510	120	-2	8	240
1621	ND	3.1	2.3	0.03	0.47	0.35	4.29	0.15	7.36	2	380	ND	1	6	10	3	11	19	260	36	475	140	-2	-2	210
1622	ND	2.2	2.1	0.03	0.40	0.17	3.83	0.05	6.54	2	320	ND	1	7	9	3	10	17	260	30	578	130	-2	2	290
1623	ND	+10.0	0.3	ND	ND	33.5	0.76	3.45	16.69	4	ND	10	3	296	258	426	3	10	17	30	900	140	18	10	30
1624	2.2	+10.0	1.0	0.05	0.14	12.4	2.68	1.55	8.25	3	220	6	13	122	1,000	155	8	17	125	40	4,960	130	4	22	140
1625	1.7	3.6	1.8	0.04	0.38	1.42	3.50	0.25	6.64	1	300	10	6	19	24	21	15	17	240	30	2,280	120	-2	40	230
1626	1.6	3.9	1.9	0.04	0.44	2.60	3.48	0.20	6.42	2	270	10	4	24	38	26	13	16	215	34	1,960	120	-2	100	230
1627	1.9	2.8	1.8	0.03	0.37	0.62	3.82	0.15	5.85	1	280	ND	3	13	173	10	13	15	230	30	1,100	120	-2	110	210
1628	1.9	2.1	2.2	0.04	0.45	0.32	3.34	0.25	5.45	1	320	ND	6	8	24	5	11	16	255	23	2,860	140	-2	2	290
1629	2.5	8.0	2.0	0.05	0.33	4.25	3.05	0.7	5.73	2	250	8	2	50	175	67	9	17	215	23	845	130	3	-2	230
1630	2.0	+10.0	0.7	0.03	ND	-	-	-	8.17	4	125	14	7	243	1,130	333	6	10	50	28	2,670	ND	-	-	-
1631	1.1	1.5	1.7	0.02	0.37	0.28	3.61	0.25	5.85	1	320	ND	7	7	19	3	13	15	215	33	2,530	200	-2	28	280
1632	ND	+10.0	2.1	0.03	0.26	7.0	2.21	0.3	7.03	2	280	8	6	78	400	104	8	15	150	30	2,630	120	2	2	200
1633	2.1	+10.0	2.0	0.04	0.20	13.6	1.85	0.85	8.37	3	180	13	8	140	1,510	194	9	14	125	32	3,100	100	7	- 2	180
1634	1.2	2.5	1.3	0.03	0.36	0.69	3.86	0.25	6.24	1	300	ND	7	20	59	10	11	17	250	50	2,550	300	-2	240	210
1635	1.4	+10.0	1.0	0.03	0.16	11.0	2.32	0.6	8.04	3	140	13	2	123	585	158	10	14	110	47	688	160	7	5	130
1636	1.5	4.2	1.9	0.03	0.27	2.0	2.58	0.2	5.23	2	300	10	6	31	185	32	19	15	175	40	2,210	170	-2	220	180
1637	1.4	4.4	1.8	0.04	0.32	1.80	3.03	0.2	5.78	3	230	ND	5	28	1,290	27	8	17	215	43	2,180	180	-2	22	220
1638	1.7	4.4	1.0	0.03	0.45	1.90	3.02	0.3	5.86	2	390	ND	1	25	123	30	11	21	220	50	71	370	-2	2	130
1639	5.2	9.2	0.6	0.04	0.22	4.8	2.47	2.7	5.28	2	ND	18	1	130	203	72	13	15	70	68	67	230	4	2,900	60
1640	1.2	5.4	2.1	0.04	0.32	2.10	2.24	0.15	4.70	1	230	8	1	30	110	37	11	14	185	26	158	105	-2	10	240

APPENDIX 1. (contd.)

Sample	Ca%	Fe%	Mg%	Na%	Ti%	S%	C%	CO_2%	LOSS ON IGNITION	Ag ppm	Ba ppm	Bi ppm	Cd ppm	Co ppm	Cu ppm	Ni ppm	Pb ppm	Sc ppm	V ppm	Y ppm	Zn ppm	Zr ppm	Se ppm	As ppm	B ppm
1641	2.8	>10.0	1.8	0.04	0.21	9.15	1.58	0.5	6.30	3	190	8	ND	107	463	141	6	15	175	30	405	105	5	50	160
1642	1.3	>10.0	1.2	0.03	0.15	19.4	1.49	1.35	11.27	3	130	18	ND	227	393	267	9	14	110	31	60	110	10	60	140
1643	ND	4.5	3.0	0.05	2.37	1.22	2.57	0.35	5.43	2	370	ND	ND	23	108	25	13	16	300	25	132	ND	<2	60	270
1644	2.0	2.4	2.1	0.04	0.33	0.45	2.22	0.25	4.20	1	340	ND	1	10	42	11	15	15	250	27	95	120	<2	2	240
1645	2.1	>10.0	1.1	0.03	0.19	7.4	1.38	0.15	5.57	3	160	44	ND	253	463	120	12	14	100	60	63	180	4	6,300	130
1646	2.1	2.2	1.9	0.03	0.36	0.64	2.51	0.3	5.04	1	350	ND	1	19	59	10	10	16	220	44	66	170	<2	190	220
1647	2.1	5.4	2.2	0.05	0.20	2.65	2.13	0.7	6.61	2	130	10	ND	53	195	58	23	13	130	28	268	110	2	20	100
1648	1.8	3.4	3.0	0.05	0.36	1.07	2.08	0.1	3.97	1	280	10	1	19	81	18	8	18	230	30	105	130	<2	20	300
1649	1.5	>10.0	1.8	0.04	0.18	7.6	1.58	0.4	5.39	3	160	15	ND	91	610	133	5	15	130	42	268	140	5	80	180
1650	2.1	2.8	2.4	0.04	0.33	0.87	1.45	0.2	3.41	1	260	ND	1	16	98	16	9	15	130	21	104	105	<2	18	260
1651	1.2	4.3	2.5	0.05	0.22	1.63	1.47	0.25	5.14	1	160	10	1	70	150	28	13	14	160	31	123	105	<2	1,250	120
1652	1.1	3.5	2.1	0.04	0.31	1.12	1.67	0.1	3.56	1	330	10	1	20	164	19	9	15	240	30	288	110	<2	8	250
1653	2.3	>10.0	1.6	0.05	0.19	6.2	0.82	0.6	5.83	3	250	28	ND	91	2,310	103	7	15	140	30	66	100	4	350	170
1654	1.8	>10.0	2.0	0.05	0.24	8.35	1.48	0.55	8.11	2	250	6	ND	106	1,020	141	5	15	190	28	58	120	6	110	210
1655	2.4	3.7	2.0	0.06	0.31	1.23	1.89	0.2	5.30	1	280	ND	ND	19	175	25	8	16	230	29	173	100	<2	90	220
1656	1.5	2.4	1.7	0.04	0.33	0.55	1.85	0.1	3.86	1	220	ND	1	13	68	11	9	16	220	46	86	120	<2	2	230
1657	1.4	4.6	1.8	0.04	0.26	2.45	1.47	0.1	4.00	1	170	10	1	34	270	42	10	15	175	38	80	110	2	55	240
1658	1.7	4.2	1.5	0.03	0.21	2.25	2.19	0.15	3.91	1	160	8	ND	30	124	37	8	14	150	36	75	110	<2	105	200
1659	8.0	>10.0	1.1	0.07	ND	1.83	2.16	6.7	12.58	4	ND	21	ND	393	290	273	36	10	38	31	144	ND	12	5,000	40
1660	>8.0	3.2	0.3	0.12	0.30	2.15	4.20	11.2	9.62	2	ND	10	ND	28	305	48	8	13	50	50	174	115	<2	60	170
1661	2.8	6.0	1.8	0.04	0.23	3.45	0.66	0.85	2.92	2	150	6	ND	79	543	84	12	10	78	30	91	ND	3	170	150
1662	2.3	4.2	1.8	0.05	0.28	1.62	1.11	1.5	3.10	1	130	ND	ND	43	480	41	9	15	97	38	96	130	<2	90	110
1663	4.4	7.5	2.6	0.06	0.21	3.80	1.80	4.4	7.66	2	140	ND	ND	78	383	101	5	16	100	31	356	ND	3	2	100
1664	3.8	4.9	1.6	0.09	0.21	2.50	1.76	3.5	5.10	2	150	ND	ND	44	290	68	9	14	90	35	89	ND	2	10	120
1665	2.0	2.1	1.2	0.03	0.30	0.40	0.30	0.45	1.23	1	290	ND	ND	19	118	13	11	12	85	25	535	140	<2	4	140
1666	>8.0	2.3	0.3	0.12	0.31	1.80	3.02	8.8	7.52	2	ND	ND	ND	39	423	45	6	10	32	41	15	130	<2	40	110
1667	1.7	2.7	1.9	0.05	0.39	0.12	0.91	0.35	2.52	1	400	ND	ND	11	18	8	5	19	160	30	125	140	<2	2	320
1668	5.0	2.8	1.3	0.05	0.25	1.15	2.18	2.85	4.96	2	110	ND	ND	36	363	31	7	13	100	46	65	110	2	190	70
1669	4.2	3.0	0.5	0.05	0.31	1.77	1.09	2.5	3.24	3	160	ND	ND	40	903	52	7	11	50	31	29	140	2	140	110
1670	1.3	2.7	1.8	0.06	0.27	0.38	0.68	0.25	2.45	4	230	ND	ND	16	98	12	8	14	160	25	136	ND	<2	4	270
1671	3.5	7.0	2.5	0.08	0.28	3.65	1.21	2.9	4.40	2	180	ND	ND	71	350	98	9	18	110	41	38	120	4	10	20
1672	2.7	4.7	0.7	ND	0.23	-	-	-	2.60	2	100	ND	ND	69	333	100	9	14	76	32	405	ND	-	-	-
1673	1.4	4.2	1.4	0.05	0.27	1.45	1.03	0.22	3.72	2	250	ND	ND	36	518	40	6	17	190	32	110	120	<2	8	280
1674	1.3	4.8	1.3	0.04	0.26	2.60	0.74	0.15	3.28	2	210	ND	ND	61	495	74	6	14	130	42	278	130	3	35	30
1675	1.4	3.9	2.6	0.06	0.38	0.38	0.71	0.1	2.59	1	210	ND	ND	13	144	16	9	16	160	38	136	140	<2	8	310
1676	1.8	5.0	3.1	0.06	0.28	1.47	0.63	0.35	5.80	2	110	ND	1	52	1,650	65	16	15	140	27	160	120	<2	10	240

APPENDIX IIA.

NORMALIZED VARIMAX FACTOR COMPONENTS

Index No.	Sample Number	Communality		Q-mode Factors	
			1	2	3
1	73201605	.7876	.9236	.0740	.0024
2	73201606	.8583	.9478	.0519	.0003
3	73201607	.7367	.5393	.4589	-.0017
4	73201608	.9162	.4864	.5097	.0038
5	73201609	.8621	.5679	.4279	.0042
6	73201610	.9645	.8889	.0994	.0117
7	73201611	.9452	.9308	.0587	.0104
8	73201612	.9402	.5488	.4468	.0045
9	73201613	.8240	.7058	.2094	.0849
10	73201614	.9110	.7054	.2378	.0568
11	73201615	.8834	.9210	.0634	.0156
12	73201616	.9514	.8922	.0775	.0303
13	73201617	.9779	.8315	.1301	.0384
14	73201618	.8006	-.0004	.9928	-.0068
15	73201619	.9506	.4645	.5077	.0278
16	73201620	.9685	.8483	.1235	.0281
17	73201621	.9560	.8878	.0784	.0338
18	73201622	.9562	.9083	.0555	.0362
19	73201623	.7897	-.0204	.9758	.0038
20	73201624	.9110	.1578	.8028	.0393
21	73201625	.9688	.8807	.0799	.0393
22	73201626	.9645	.7988	.1364	.0647
23	73201627	.9628	.9020	.0526	.0455
24	73201628	.9628	.9358	.0274	.0368
25	73201629	.9463	.6052	.3115	.0833
26	73201631	.9178	.9529	.0294	.0178
27	73201632	.9329	.4278	.5523	.0198
28	73201633	.9445	.1421	.8086	.0493
29	73201634	.8059	.8905	.0722	.0373
30	73201635	.9360	.1073	.8352	.0576
31	73201636	.9108	.7010	.2381	.0609
32	73201637	.8689	.6048	.3104	.0848
33	73201638	.7071	.7719	.1609	.0672
34	73201639	.7254	.0764	.5712	.3524
35	73201640	.9304	.7962	.1311	.0726
36	73201641	.9336	.2203	.6989	.0808
37	73201642	.8954	.0513	.9186	.0301
38	73201643	.9379	.8339	.1090	.0571
39	73201644	.9591	.8974	.0288	.0738
40	73201645	.6399	.0654	.8107	.1239
41	73201646	.9445	.8721	.0381	.0897
42	73201647	.8080	.4142	.3799	.2058
43	73201648	.9453	.8575	.0513	.0912
44	73201649	.9288	.1833	.7278	.0889
45	73201650	.9007	.8475	.0349	.1177
46	73201651	.8258	.6484	.1989	.1527
47	73201652	.9406	.8753	.0672	.0575
48	73201653	.7714	.1385	.7500	.1114
49	73201654	.8932	.3345	.5914	.0741
50	73201655	.9509	.7908	.0687	.1405
51	73201656	.9272	.8370	.0432	.1198
52	73201657	.9025	.7170	.1529	.1301
53	73201658	.9013	.7269	.1625	.1107
54	73201659	.7247	-.0014	.7546	.2440
55	73201660	.7941	.0934	.0718	.8348
56	73201661	.8648	.2275	.4878	.2847

APPENDIX IIA.

2.

		COMM.	1	2	3
57	73201662	.8998	.4864	.1892	.3244
58	73201663	.8774	.4320	.6208	.5527
59	73201664	.9362	.4485	.4804	.7101
60	73201665	.8016	.8077	.1549	.3539
61	73201666	.8077	.1841	.2056	.8553
62	73201667	.8713	.8735	.1449	.2957
63	73201668	.8574	.4514	.3915	.7073
64	73201669	.7342	.3186	.4816	.6330
65	73201670	.8646	.8360	.1671	.3712
66	73201671	.8388	.4418	.5890	.5447
67	73201673	.8744	.7789	.3978	.3309
68	73201674	.8160	.5393	.6407	.3386
69	73201675	.8777	.8154	.2236	.4034
70	73201676	.7323	.6034	.4626	.3928

APPENDIX IIB

SCALED VARIMAX FACTOR SCORES

	Q-mode Factors		
	1	2	3
Ca	-.429	-.101	2.644
Fe	-.148	3.078	.013
Mg	1.406	.376	.661
Mn	-.009	-.071	2.568
Ti	2.002	-.207	.697
Ag	-.411	2.076	.468
Ba	1.462	.058	-.612
Bi	-.179	.552	.111
Cd	.261	.716	-.963
Co	-.331	1.259	.076
Cu	-.220	1.036	.435
Ni	-.312	1.409	-.075
Pb	.550	.221	.570
Sc	1.556	.566	-.129
V	2.297	.336	-.322
Y	.252	.682	1.567
Zn	.345	.741	-.990
Zr	.315	.112	.179
Se	-.325	1.035	-.294
As	-.161	.350	.205
B	2.027	-.092	.848
CO_2	-.414	.070	1.681
C	1.548	.479	-.235
S	-.242	1.269	-.347

APPENDIX IIC

OBLIQUE PROJECTION PROGRAM

NAME	INDEX	7	14	61
73201605	1	.921	.040	-.052
73201606	2	.981	.000	-.096
73201607	3	.698	.487	-.080
73201608	4	.716	.570	.036
73201709	5	.751	.478	.025
73201610	6	.986	.083	.017
73201611	7	1.000	.000	.000
73201612	8	.770	.517	.031
73201613	9	.771	.208	.238
73201614	10	.822	.261	.194
73201615	11	.957	.007	.027
73201616	12	.966	.029	.089
73201617	13	.939	.123	.129
73201618	14	.000	1.000	.000
73201619	15	.688	.561	.159
73201620	16	.951	.116	.093
73201621	17	.963	.030	.101
73201622	18	.973	-.022	.103
73201623	19	-.149	.986	.167
73201624	20	.371	.804	.248
73201625	21	.962	.031	.120
73201626	22	.900	.124	.199
73201627	23	.968	-.033	.130
73201628	24	.991	-.102	.097
73201629	25	.761	.346	.270
73201631	26	.990	-.083	.028
73201632	27	.659	.601	.135
73201633	28	.351	.823	.283
73201634	29	.884	.014	.102
73201635	30	.293	.843	.311
73201636	31	.817	.260	.203
73201637	32	.728	.330	.262
73201638	33	.755	.138	.180
73201639	34	.140	.542	.622
73201640	35	.879	.111	.212
73201641	36	.432	.716	.333
73201642	37	.198	.908	.248
73201643	38	.911	.079	.172
73201644	39	.950	-.108	.192
73201645	40	.159	.681	.370
73201646	41	.922	-.083	.227
73201647	42	.537	.377	.448
73201648	43	.914	-.048	.234
73201649	44	.385	.739	.356
73201650	45	.877	-.095	.271
73201651	46	.716	.186	.349
73201652	47	.936	-.002	.164
73201653	48	.290	.692	.369
73201654	49	.538	.607	.291
73201655	50	.861	-.015	.327

APPENDIX IIC

2.

NAME	INDEX	7	14	61
73201656	51	.883	-.073	.281
73201657	52	.698	.133	.320
73201658	53	.810	.149	.289
73201659	54	-.132	.733	.571
73201660	55	.106	.023	.942
73201661	56	.369	.498	.581
73201662	57	.596	.173	.578
73201663	58	.343	.457	.646
73201664	59	.323	.266	.816
73201665	60	.798	-.109	.312
73201666	61	.000	.000	1.000
73201667	62	.884	-.124	.233
73201668	63	.327	.168	.804
73201669	64	.200	.316	.745
73201670	65	.825	-.106	.329
73201671	66	.355	.421	.632
73201673	67	.773	.171	.312
73201674	68	.510	.497	.380
73201675	69	.795	-.045	.376
73201676	70	.567	.273	.417

APPENDIX III

Correlation coefficients for group I (organo-detrital component), 37 samples

	Ca	Fe	Mg	Mn	Ti	Ag	Ba	Bi	Cd	Co	Cu	Ni	Pb	Sc	V	Y	Zn	Zr	As	B	Co_2	C	S
Ca	1.00																						
Fe	- 0.23	1.00																					
Mg	- 0.00	0.38	1.00																				
Mn	0.00	0.44	0.53	1.00																			
Ti	- 0.13	- 0.12	0.10	-0.31	1.00																		
Ag	- 0.28	0.36	0.25	-0.11	0.53	1.00																	
Ba	0.04	- 0.33	0.03	-0.38	0.67	0.41	1.00																
Bi	- 0.00	0.25	0.07	0.11	-0.38	-0.12	-0.32	1.00															
Cd	- 0.20	- 0.21	-0.20	-0.37	0.19	-0.08	0.03	0.06	1.00														
Co	- 0.00	0.07	0.03	0.28	-0.58	-0.05	-0.55	0.50	-0.18	1.00													
Cu	0.04	0.46	-0.07	0.26	-0.40	0.21	-0.38	0.11	-0.24	0.50	1.00												
Ni	- 0.14	0.79	-0.07	0.17	-0.41	0.07	-0.45	0.38	-0.11	0.72	0.88	1.00											
Pb	0.13	-0.14	-0.03	-0.46	0.08	0.15	0.28	0.26	0.34	0.01	-0.23	-0.09	1.00										
Sc	-0.08	0.07	0.11	-0.20	0.75	0.58	0.73	-0.22	-0.07	-0.32	-0.14	-0.19	0.01	1.00									
V	-0.22	-0.08	0.25	-0.15	0.58	0.39	0.55	-0.13	0.19	-0.38	-0.28	-0.27	0.22	0.53	1.00								
Y	0.02	0.12	-0.32	-0.09	-0.15	-0.01	-0.28	0.16	0.05	0.23	0.12	0.14	-0.05	-0.02	-0.05	1.00							
Zn	-0.22	-0.22	-0.28	-0.40	0.29	-0.00	0.12	0.04	0.98	-0.21	-0.29	-0.14	0.35	-0.03	0.23	-0.05	1.00						
Zr	0.01	-0.15	-0.46	-0.34	0.24	0.11	0.21	-0.13	0.24	-0.07	-0.11	-0.14	0.11	0.30	0.09	0.94	0.18	1.00					
As	-0.05	0.12	0.07	0.18	-0.38	-0.14	-0.31	0.40	-0.03	0.74	0.08	0.13	0.22	-0.23	-0.19	0.14	-0.07	0.00	1.00				
B	0.15	-0.22	0.08	0.30	-0.13	-0.28	-0.04	0.02	-0.08	-0.21	-0.02	-0.17	-0.19	-0.16	0.09	-0.00	-0.06	-0.18	-0.28	1.00			
Co_2	0.00	0.28	0.23	0.18	0.18	0.25	0.04	-0.25	0.07	0.08	0.05	0.11	0.05	0.09	-0.11	-0.15	0.08	0.23	-0.01	-0.39	1.00		
C	-0.32	-0.10	0.06	-0.56	0.71	0.48	0.56	-0.21	0.47	-0.40	-0.36	-0.26	0.32	0.59	0.88	-0.18	0.54	0.14	-0.15	-0.37	0.04	1.00	
S	-0.12	0.02	0.05	0.08	-0.21	0.21	-0.41	0.45	0.05	0.05	0.38	0.87	-0.01	+0.11	-0.16	0.24	0.01	-0.06	0.16	-0.30	0.11	-0.03	1.00

Primary Factor R-mode Pattern Matrix for Group I

Factors	1	2	3	4	5
Ca	-.886	-.408	.430	.131	-.142
Fe	.475	.003	-.620	-.134	.003
Mg	.294	.113	.223	-.776	-.100
Mn	-.254	.108	.300	-.403	.107
Ti	.821	.810	-.000	-.003	.220
Ag	.021	.474	.174	.000	.075
Ba	.838	-.332	.108	.029	-.040
Bi	-.246	.108	-.000	-.100	-.025
Cd	-.137	.118	-1.002	.048	.022
Co	-.279	.407	.156	.035	-.510
Cu	-.104	.505	.232	.140	.107

Primary Factor Pattern Matrix for Group I (Contd')

Factors	1	2	3	4	5
Ni	-.242	.848	-.068	.083	-.014
Pb	.262	-.247	-.224	-.030	-.704
Sc	.058	.075	.311	.157	.058
V	.671	-.051	-.093	-.154	-.041
Y	-.055	.158	.140	.750	-.023
Zn	-.124	.101	-1.015	-.010	.044
Zr	.262	-.020	.036	.832	.033
As	-.099	-.072	.166	-.033	-.835
B	-.363	-.355	.077	-.176	.306
Co_2	.210	.385	-.074	-.166	.103
C	.695	.110	-.460	-.042	-.058
S	-.083	.877	-.178	.062	-.114

Correlation coefficients for group II (Sulphide component), 11 samples

	Cu	Hg	Mn	Ti	Ag	Ba	Bi	Cd	Co	Cr	Ni	Pb	Sc	V		Zn	Zr	Se	As	B	CO_2	C	S
Cu	1.00																						
Hg	0.19	1.00																					
Mn	0.87	0.43	1.00																				
Ti	-0.14	0.04	0.07	1.00																			
Ag	0.25	-0.78	-0.87	-0.87	1.00																		
Ba	-0.08	0.01	0.35	0.71	-0.74	1.00																	
Bi	0.19	0.10	0.10	0.28	-0.18	0.11	1.00																
Cd	-0.27	-0.41	-0.38	-0.43	-0.39	-0.17	-0.40	1.00															
Co	0.47	-0.08	0.08	-0.72	0.78	-0.78	0.23	0.05	1.00														
Cr	-0.20	0.23	0.07	-0.28	-0.13	0.54	0.03	-0.45	-0.43	1.00													
Ni	-0.08	-0.71	-0.38	-0.81	0.82	-0.78	-0.34	0.29	0.70	-0.28	1.00												
Pb	0.03	0.03	0.74	-0.27	0.29	-0.27	0.29	-0.28	0.81	-0.31	0.04	1.00											
Sc	-0.29	0.56	0.10	0.88	-0.88	0.82	-0.03	-0.04	-0.85	0.31	-0.80	-0.41	1.00										
V	-0.11	0.82	0.21	0.98	-0.91	0.80	0.01	-0.34	-0.84	0.21	-0.84	-0.27	0.87	1.00									
Y	-0.15	-0.08	-0.20	0.26	-0.37	0.05	0.58	-0.13	-0.08	-0.25	-0.47	0.00	0.29	0.11	1.00								
Zn	-0.27	-0.39	-0.30	-0.42	-0.38	-0.17	-0.41	0.39	0.03	0.45	0.28	-0.30	-0.03	-0.33	-0.13	1.00							
Zr	-0.30	-0.28	-0.37	0.11	-0.25	-0.09	0.40	-0.29	-0.03	-0.46	-0.21	-0.14	0.12	-0.03	0.88	-0.29	1.00						
Se	-0.98	-0.72	-0.37	-0.83	-0.89	-0.82	-0.31	0.33	0.70	-0.21	0.98	0.05	-0.87	-0.88	-0.45	0.33	-0.21	1.00					
As	0.67	-0.10	0.38	-0.11	0.22	-0.24	0.73	0.27	0.65	-0.33	-0.07	0.75	-0.35	0.30	0.45	-0.28	0.29	0.05	1.00				
B	-0.29	0.85	0.18	0.91	-0.95	0.70	0.11	-0.36	-0.84	0.27	-0.82	-0.30	0.85	0.94	0.19	-0.35	0.04	-0.87	-0.30	1.00			
CO_2	0.72	-0.39	0.49	-0.72	0.75	-0.54	-0.10	-0.06	0.80	-0.34	0.60	0.76	-0.74	-0.68	-0.39	-0.07	-0.29	0.59	0.45	-0 .72	1.00		
C	0.42	0.23	0.52	0.08	-0.35	0.17	-0.23	-0.13	-0.14	-0.31	-0.38	0.44	0.37	0.30	0.26	-0.13	0.15	-0.43	0.12	0.26	0.14	1.00	
S	-0.14	-0.74	-0.40	-0.81	0.80	-0.72	-0.39	0.33	0.65	-0.25	0.99	-0.04	-0.75	-0.82	-0.45	0.32	-0.17	0.98	-0.13	-0.81	0.55	-0.35	1.00

Primary Factor Pattern Matrix for group II

Factors	1	2	3	4
Cu	.055	.908	-.106	.048
Hg	-.082	.328	-.385	.172
Mn	-.328	.970	-.283	-.028
Ti	-.878	-.071	.015	.237
Ag	.902	.128	-.086	-.202
Ba	-.903	.149	-.128	-.158
Bi	-.104	.204	.702	.044
Cd	.222	-.128	.031	-.909
Co	.883	.305	.204	.049
Cr	-.423	.081	-.185	-.898

Primary Factor Pattern Matrix for group II (Cont')

Factors	1	2	3	4
Ni	.931	- .245	- .255	.105
Pb	..217	.898	.069	.085
Sc	- .911	-..088	.036	- .165
V	- .962	.011	- .182	.164
Y	- .181	- .140	.967	- .087
Zn	.212	- .122	.019	- .903
Zr	.047	- .407	.838	.234
Se	.952	- .228	- .208	.031
As	.235	.604	.628	- .007
B	- .954	- . 054	- .108	.172
Ce$_2$	.672	.603	- .228	.111
C	- .327	.480	.033	.019
S	.911	- .302	- .241	.068

Correlation coefficients for group III (mixed), 12 samples

	Ca	Fe	Mg	Ti	Ag	Ba	Bi	Cd	Ce	Co	Ni	Pb	Sc	V	Y	Zn	Zr	Sn	As	B	Co_2		C	S
Ca	1.00																							
Fe	-0.06	1.00																						
Mg	0.07	0.19	1.00																					
Na	0.54	-0.16	0.73	1.00																				
Ti	-0.27	0.18	-0.04	-0.18	1.00																			
Ag	0.05	-0.36	-0.07	0.00	0.18	1.00																		
Ba	-0.35	0.58	-0.47	-0.05	0.02	-0.07	1.00																	
Bi	0.00	0.01	0.21	0.25	-0.51	-0.16	-0.33	1.00																
Cd	-0.43	0.00	-0.23	-0.38	0.03	-0.05	0.57	-0.20	1.00															
Ce	-0.35	0.43	-0.16	-0.28	-0.04	-0.53	0.43	-0.27	0.38	1.00														
Co	-0.24	-0.31	0.40	0.41	-0.08	0.48	-0.46	-0.44	-0.28	-0.27	1.00													
Ni	-0.31	0.06	-0.04	-0.21	-0.04	-0.58	0.51	-0.28	0.12	0.03	-0.28	1.00												
Pb	0.33	-0.41	0.48	0.49	-0.40	-0.10	-0.03	0.07	-0.21	-0.40	0.02	-0.42	1.00											
Sc	-0.34	0.22	-0.16	-0.43	0.38	0.15	0.71	-0.55	0.59	0.19	-0.14	0.17	-0.51	1.00										
V	0.11	0.37	-0.00	-0.13	0.04	0.37	0.43	-0.31	0.38	0.04	-0.07	-0.08	-0.52	0.78	1.00									
Y	-0.32	-0.51	-0.55	-0.33	-0.03	0.59	0.09	-0.38	-0.08	-0.18	0.20	-0.25	-0.29	-0.05	-0.17	1.00								
Zn	-0.43	0.01	-0.24	-0.40	0.06	-0.03	0.55	-0.28	0.99	0.25	-0.27	0.09	-0.21	0.80	0.31	-0.07	1.00							
Zr	0.19	-0.24	-0.22	0.06	0.05	0.02	-0.19	-0.14	-0.38	-0.58	0.46	-0.54	-0.23	-0.04	0.34	0.53	0.38	1.00						
Sn	0.00	0.52	0.04	0.18	-0.07	-0.22	0.24	-0.28	-0.17	0.69	-0.03	0.78	-0.44	0.09	0.27	-0.12	-0.21	-0.09	1.00					
As	-0.33	-0.13	-0.34	-0.35	0.31	-0.15	0.25	-0.28	0.80	0.53	-0.20	0.23	-0.73	0.42	0.31	-0.04	0.78	-0.38	0.04	1.00				
B	0.18	0.46	0.67	0.43	0.17	0.29	-0.11	0.01	-0.29	-0.23	0.48	-0.06	-0.02	0.17	0.42	-0.43	-0.28	0.40	0.11	0.43	1.00			
Co_2	0.24	-0.01	0.06	0.17	0.30	-0.29	0.27	0.22	0.51	0.07	-0.34	0.07	0.32	0.14	0.08	-0.48	0.52	-0.58	-0.07	0.25	-0.12	1.00		
C	-0.11	0.12	-0.46	-0.03	0.56	0.13	0.01	-0.08	0.68	0.11	-0.44	-0.02	-0.23	0.75	0.64	-0.08	0.70	-0.10	-0.21	0.57	-0.12	0.35	1.00	
S	-0.35	0.71	-0.20	-0.47	0.23	-0.40	0.76	-0.26	0.35	0.87	-0.43	0.90	-0.49	0.49	0.26	-0.19	0.34	-0.43	0.61	0.35	-0.07	0.15	0.38	1.00

Primary factor Pattern Matrix for group III

Factors	1	2	3	4
Ca	.118	-.251	-.172	-.409
Fe	.091	.586	-.041	-.571
Mg	.012	.032	-.051	-.631
Na	.293	-.148	-.040	-.718
Ti	-.844	-.106	.112	-.155
Ag	-.205	-.452	.758	.003
Ba	-.575	.417	-.056	.198
Bi	.288	-.318	-.517	-.228
Cd	-.784	-.130	-.362	.206

Primary Factor Pattern Matrix for group III (Cont'd)

Factors	1	2	3	4
Co	.072	.844	-.333	.163
Cu	.100	-.126	.632	-.176
Ni	.123	.972	-.280	-.007
Pb	.298	-.542	-.465	-.262
Sc	-.927	.126	.148	-.087
V	-.889	.054	.281	-.377
Y	.254	-.208	.622	.817
Zn	-.784	-.164	-.350	.204
Zr	-.072	-.314	.894	-.031
Se	.153	.863	.073	-.222
As	-.449	.006	-.834	.359
B	-.325	.119	.372	.882
Co_2	-.445	-.199	-.710	-.272
C	-.835	-.178	-.193	.132
S	-.229	.830	-.264	.042

Correlation coefficients for group IV (mixed), 8 Samples

	Ca	Fe	Mg	Mn	Ti	Ag	Ba	Bi	Co	Cu	Ni	Pb	Sc	V	Y	Zn	Zr	Se	As	B	Co_2	C	S
Ca	1.00																						
Fe	0.19	1.00																					
Mg	-0.43	0.25	1.00																				
Mn	-0.10	-0.02	0.46	1.00																			
Ti	-0.28	-0.54	-0.23	-0.11	1.00																		
Ag	0.50	-0.14	-0.45	0.00	0.21	1.00																	
Ba	-0.49	-0.11	0.44	0.57	0.39	0.31	1.00																
Bi	0.51	0.65	-0.51	-0.39	0.31	0.00	-0.62	1.00															
Co	0.32	0.93	-0.07	-0.33	-0.47	-0.02	-0.32	0.83	1.00														
Cu	-0.27	-0.58	-0.31	-0.29	0.70	0.53	0.42	-0.44	-0.47	1.00													
Ni	-0.06	0.76	0.59	0.30	-0.30	0.11	0.48	0.06	0.55	-0.25	1.00												
Pb	-0.15	0.45	-0.32	-0.30	-0.20	-0.20	-0.23	0.83	0.61	-0.30	0.08	1.00											
Sc	0.08	0.50	0.54	0.51	-0.09	-0.41	0.08	0.15	0.24	-0.81	0.39	-0.17	1.00										
V	-0.20	0.11	0.82	0.48	-0.23	-0.64	0.09	-0.35	-0.15	-0.60	0.21	-0.27	0.68	1.00									
Y	0.58	0.47	-0.45	-0.27	-0.20	-0.15	-0.68	0.90	0.63	-0.59	-0.15	0.53	0.32	-0.06	1.00								
Zn	0.06	0.41	0.88	0.14	-0.48	-0.18	0.04	-0.18	0.18	-0.24	0.58	-0.51	0.40	0.43	-0.29	1.00							
Zr	0.44	0.48	-0.63	-0.43	-0.02	0.06	-0.53	0.94	0.68	-0.21	-0.10	0.58	0.13	-0.46	0.86	-0.33	1.00						
Se	0.19	0.89	0.22	-0.04	-0.22	0.00	0.06	0.57	0.86	-0.45	0.72	0.47	0.49	0.14	0.50	0.17	0.47	1.00					
As	0.51	0.62	-0.53	-0.43	-0.31	-0.01	-0.65	0.99	0.82	-0.44	0.02	0.65	0.11	-0.35	0.90	-0.20	0.93	0.55	1.00				
B	-0.43	-0.32	-0.18	-0.24	-0.20	0.00	0.01	-0.32	-0.27	0.43	-0.14	0.23	-0.74	-0.40	-0.58	0.06	-0.38	-0.57	-0.30	1.00			
Co_2	0.01	0.23	0.24	0.54	-0.36	0.24	0.00	0.02	0.03	-0.35	0.32	-0.60	0.54	0.28	0.05	0.59	-0.80	0.08	-0.03	-0.36	1.00		
C	0.84	0.29	-0.28	0.02	-0.49	-0.01	-0.72	0.61	0.34	-0.65	-0.15	-0.03	0.35	0.11	0.73	0.12	0.48	0.16	0.61	-0.45	0.61	1.00	
S	0.20	0.88	0.19	-0.03	-0.51	0.03	-0.01	0.62	0.93	-0.47	0.81	-0.48	0.36	-0.02	0.40	0.35	0.45	0.90	0.59	-0.25	0.18	0.20	1.00

Primary Factor Pattern Matrix for group IV

Factor	1	2	3	4	5
Ca	.332	.115	-.890	-.451	-.112
Fe	-.124	-.537	.126	.013	.055
Mg	-.522	-.472	.096	.509	-.180
Mn	-.478	-.119	-.227	.088	-.491
Ti	-.134	.385	.435	-.331	-.481
Ag	-.058	-.232	-.463	-1.088	.022
Ba	-.535	-.492	.300	-.381	-.307
Bi	.969	-.090	-.106	-.043	-.024
Co	.817	-.624	.004	-.039	.072
Cu	-.374	-.057	.211	-.708	.211
Ni	.018	-1.027	-.050	-.181	-.048

Primary Factor Pattern Matrix for group IV (Cont'd)

Factor	1	2	3	4	5
Pb	.812	-.175	.641	.222	.129
Sc	.087	-.151	-.160	.427	-.730
V	-.342	.038	-.001	.816	-.410
Y	.907	.237	-.107	.204	-.309
Zn	-.386	-.559	-.498	.128	.215
Zr	.948	.082	.012	-.162	-.173
Se	.834	-.698	.131	-.032	-.342
As	.979	-.055	-.082	-.019	.005
B	-.356	-.083	.172	-.060	.908
Co_2	-.273	-.166	-.966	-.222	-.267
C	.413	.292	-.776	.116	-.150
S	.584	-.863	-.033	-.100	.008