GLOBAL JOURNAL OF GEOLOGICAL SCIENCES VOL. 6 NO. 2 2008: 95 - 104

STATISTICAL ANALYSIS OF TRACE ELEMENT CONCENTRATIONS IN SHALE – CARBONATE SEDIMENTS FROM NORTHEASTERN NIGERIA

E. E. NTEKIM, D. M. ORAZULIKE AND E.C. ASHANO

(Received 22 August, 2007; Revision Accepted 10 September, 2007)

ABSTRACT

Principal component and regression analysis of geochemical data in sampled shale – carbonate sediments in Guyuk, Northeastern Nigeria reveal enrichments of four predictor elements, Ni, Co, Cr and Cu to gypsum mineralisation. Ratios of their enrichments are Cu(10:1), Ni(8:1), Co(58:1) and Cr(30:1) The >70% intercorrelations between these elements plus >32% common factor loading and observed significant regression of Ca and Fe on Cu, Cr, Ni and Co depicts strong association between these trace elements and process of gypsum mineralisation.

KEYWORDS: intercorrelations, regression, factor analysis, predictor elements, gypsum, shale.

INTRODUCTION

Shale and carbonate rocks are common favourable sediments associated with sedimentary ores, including evaporites. This is principally due to the chemical nature of these sediments. Petrogenetically, carbonates and evaporites (commonly referred to as chemical precipitates) are closely related. These two, in turn, closely associate with shale due to progressive rhythmic carbonate sedimentation in regressive marine environments (Wilkinson, 1982; Boggs, 1987) and constituent clayey materials in the shale on which evaporites (especially gypsum) get adhered to. Repeated cyclic sequences of carbonate platforms are deposited during the quiet standstill phases and thick shale beds accumulation, occasioned by the pervasive low water energy conditions that follow periods of flooding during eustatic upheavals (Boggs, 1987). These "shorter-lived", fluctuations in sedimentation conditions is known to influence chemical sedimentation in evaporite basins through suspension mechanism, where thin gypsum laminations (of only few millimeters thickness) alternate with dark-gray laminae of carbonate and shaley rocks. Boggs (1987) suggests that the alternating gypsum (light) and lithologic (dark-gray) pairs of bands represent seasonal changes in water chemistry and temperature during the cyclic disturbances. These rhythmic sequences, which are observed in locations within the Upper Benue valley, Nigeria (Fig 1) reveals that the gypsum beds occur in shale strata adjoining limestone beds (Ntekim and Orazulike, 2003), especially at Dukul, Gudenyi, Lakoro, Gunda and Lamza. Vertical stratigraphic sequence examined along cuts on cliff slopes and stream courses in the study area is typical of carbonate sedimentation in marine environment (Boggs, 1987). The associated carbonate rocks (calcareous sandstones and limestone) with the shale attests to a carbonated environment, a necessary chemical condition for gypsum mineralisation (cf. Evans, 1978; Sonnenfeld, 1991; Uma, 1998). Probably the calcium carbonate minerals were altered in the adjoining limestone beds, and the Ca^{2+} ions were subsequently transported by the clay minerals into the shale where reaction with constituent free SO_4^{2-} ions produced the gypsum minerals.

Diagenesis of these typical marine chemical sediments (carbonates and evaporites), involve the breakdown and formation of various minerals and oxy-acid salts. Chemically the major cations in these rocks include Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, U^{2+}, Na^{+} and K^{+}, which are easily soluble in water. These, especially the major elements (Ca, Mg, Fe), participate in a wide range of geological processes during which isomorphic replacements between constituent cations take place. Such replacement is very pronounced in the various complicated sedimentation (both chemical and biochemical) processes during the formation of gypsum in enclosed sea basins (Milovsky and Kononov, 1985; Boggs, 1987). The relative concentrations of minor / trace elements, especially the base metals, are commonly used in geochemical exploratory studies to assess or delineate mineralisation, most especially ore bodies. Trace elements have great potential for use as mineralisation indicators or exploration pathfinders. They usually occur in trace amounts unless there is an anomaly hence; their determination can help detect abnormal chemical patterns, which may relate to mineralisation. In the present study, some major and trace element contents of the shale sediments were determined to examine their relationship to gypsum accumulation in the rock units.

E. E. Ntekim, Department of Geology, Federal University of Technology, Yola, Nigeria.
D. M. Orazulike, Geology Programme, Abubakar Tafawa Balewa University, Bauchi, Nigeria.
E. C. Ashano, Department of Geology and Mining, University of Jos, Nigeria.

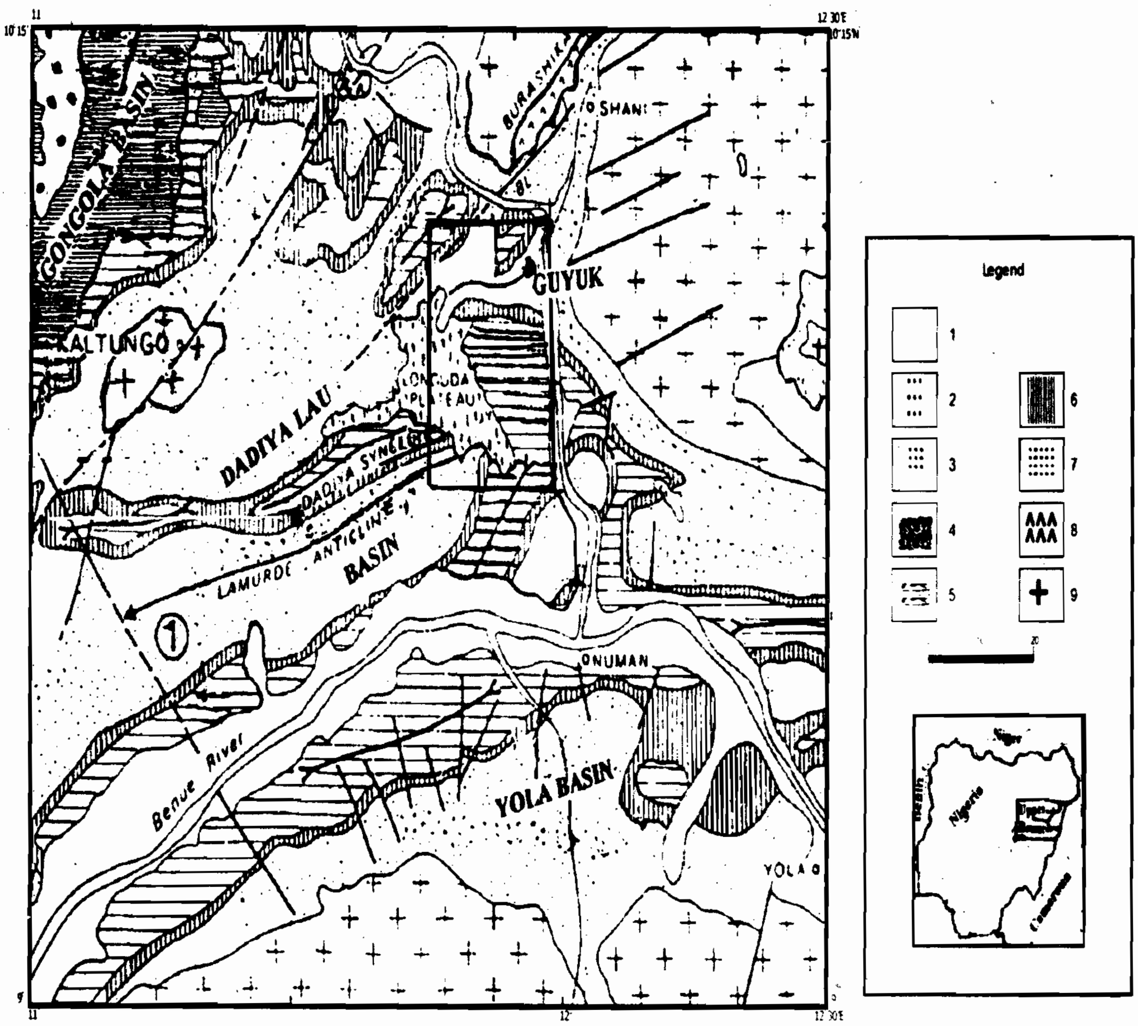


Fig. 1Location of Guyuk within the Upper Benue Valley
(Modified from Maurin et al, 1986)

1. Quaternary alluvium; 2. Tertiary to Recent volcanics; 3. Kerri Kerri Formation; 4. Gombe Formation.
5. Shale-limestone Formation; 6. Yolde Formation; 7. Bima Formation; 8. Burashika volcanics;
9. Undifferentiated Precambrian Basement. [Arean box is the Guyuk study area]

The purpose of this paper is to test statistically the abundance of trace elements in shale – carbonate rocks of Guyuk area in part of the lower Gongola basin of Nigeria and to develop a framework with which the likely gypsum mineralisation status of these rock types could be assessed on the basis of the distribution pattern of certain trace element contents.

Geology of the area

Several workers, including Opeloye (2002), Ntekim and Orazulike (2003) have studied the geology of Guyuk, the study area. Guyuk area (as part of the Upper Benue trough) has been affected by wrench faults and E – W trending submeridian normal faults, and has lithologic units that favour the formation of evaporites (Zaborski et al, 1997; Uma, 1998). The Late Cretaceous intense compressional earth movements, caused by deep-seated flexuring in the crystalline basement rocks determined the tectonic setting of the area (Carter et al, 1963; Benkhelil, 1986). Effects of these stresses produced narrow localised incipient basins, into which thick sedimentary sequences were later deposited. The sediments include detrital Bima sandstone, transitional Yolde, marine shale-limestone (Dukul, Jessu, Sekule and Numanha) units and partially continental Lamja sandstone, overlain by Tertiary Longuda basalts and a Quaternary river alluvium.

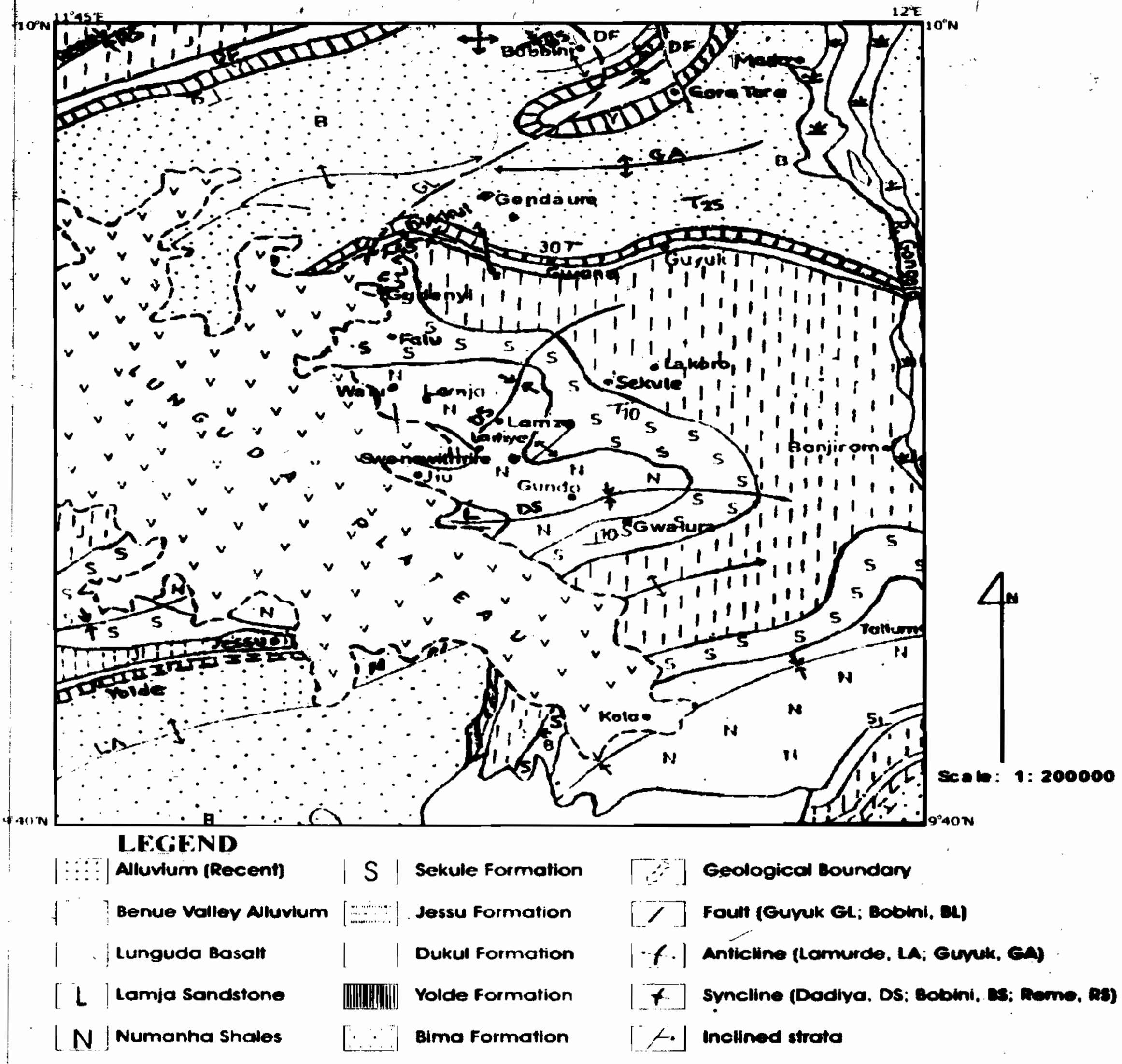


Fig. 2 Map of Guyuk Area showing Geology and Sample Locations (Modified from Carter et al, 1963)

The marine sediments consist of thick sequences of shale and fossiliferous limestone units and thin bands of siltstones and calcareous sandstone. The shale is black, carbonaceous and fossiliferous, and variously associated in the study locations. Encountered stratigraphic sections reveal shale – limestone – clay alternations at Gunda, Lamza, Walu, Dukul, Gudenyi, Bobini, Sukuliye and Lakoro; shale – mudstone alternations in Gwalura and Swenswithire; and sandy shale – clay alternations in Gwana. These associated stratigraphic sections reveal that Dukul, Sekule, Numanha and (lower parts of) Jessu Formations are enriched in gypsum in Guyuk area (cf. Braide, 1992).

METHOD

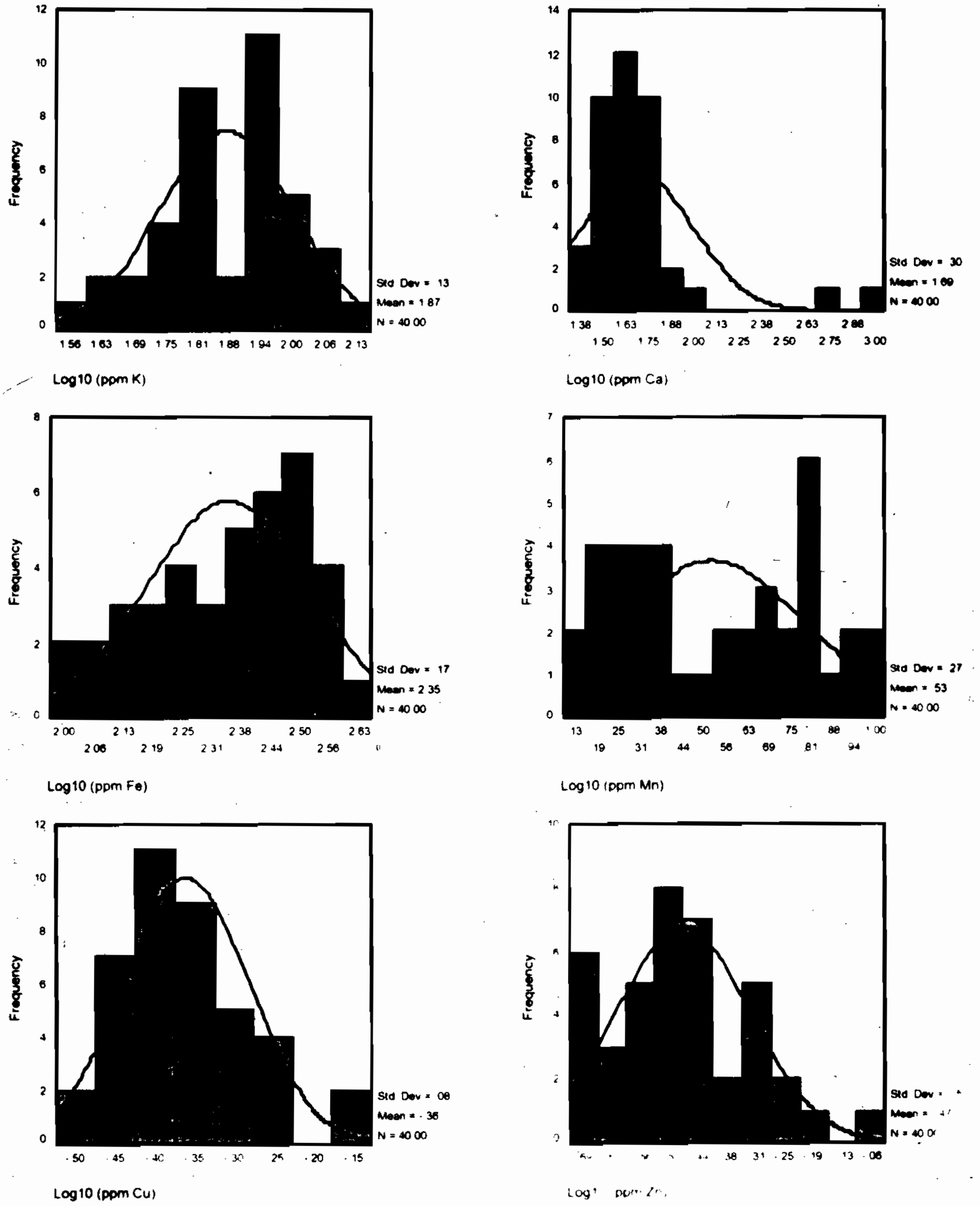
Principal component analysis (PCA) and regression statistical analyses were used to explore the data and establish statistical estimates of observed elemental distribution. Pearce (1976) suggests that statistical study of few analyses can be used to express the chemical variation in geological samples from particular sample locality. In this work, 40 shale samples and sixteen elements are used in the statistical analysis. The samples were selected after eliminating from the lists of collected samples, 10 outlier samples with much higher contents of the elements in relation to the rest of the samples. Concentration values used for the various analyses were log-transformed to reduce discrepancies between the values.

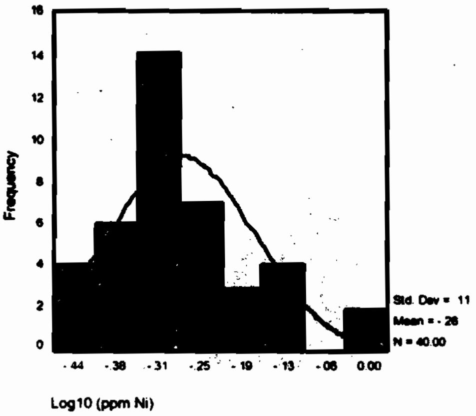
Beus and Grigorian (1975) submit that the ore producing (or mineralisation) potential in sedimentary formations can be assessed by various criteria, including abnormally high contents of principal metals, such as that make up the mineral deposit of interest, their association as well as increased variance in their distribution in rocks. In this work, the abundance and distribution variance of principal associated elements in shale and limestone samples collected from different localities in the study area were assessed. These include Ca, Fe, Mn, Cu, Zn, Ni, Co, Ba, Cr, As, Pb, Sr, Bi, Br, K and U.

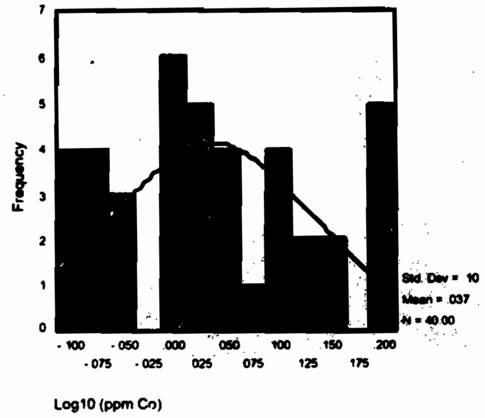
RESULTS

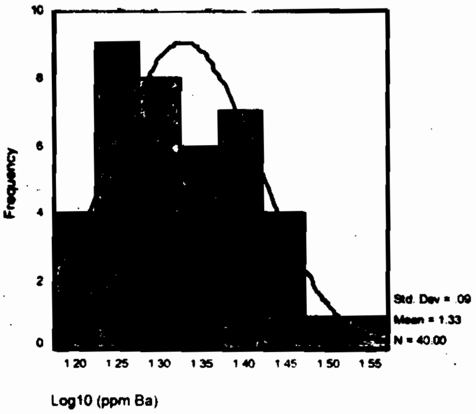
Table 1 shows the indicator elemental concentration levels in the analysed shale – carbonate rocks. The population distribution of the relevant elements obtained from histogram plots, the correlation matrix from multiple correlation, PCA factor loadings and multiple regression obtained from the data are displayed in Figure 3 and Tables 2, 3 and 4. Most shale samples have concentration between 42.5 – 52.5ppm Ca, Fe(262.5 – 287.5ppm), Mn(1.5 – 2.5ppm), Cu(0.27

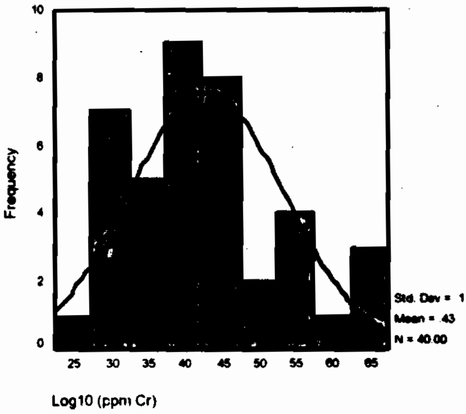
0.43ppm), Zn(0.22 - 0.28ppm), Ni(0.47 – 0.53ppm), Co(0.97 – 1.03ppm), Cr(2.38 – 2.62ppm), As(0.18 – 0.21ppm), Bi(0.13 – 0.16ppm). Average concentrations of the minor/trace elements vary within locations from 2610 – 8920 ppm Mn, Cu(300 – 670ppm), Zn(210 – 850ppm), Ni(380 – 1020ppm), Co(910 – 1590ppm), Cr(2250 – 4660ppm), As(160 – 300ppm), Pb(260 – 440ppm), Sr(790 – 3580ppm) and Ba(17750 – 31020ppm). In the limestone, mean concentrations of the minor/trace elements vary within the range Mn(6300 – 156030ppm), Cu(9820 – 29500ppm), Zn(310 – 1710ppm), Ni(630 – 1680ppm), Co(980 – 2560ppm), Ba(18440 – 61340ppm), Cr(2510 – 7150ppm), As(190 – 570ppm), Pb(300 – 860ppm) and Sr(720 – 4550ppm); and in clay samples, the average contents are Mn(1420 – 7580ppm), Cu(270 – 600ppm), Zn(180 – 690ppm), Ni(350 – 800ppm), Co(680 – 1450ppm), Ba(14720 – 33890ppm), Cr(1970 – 4460ppm), As(130 – 470ppm), Pb(180 – 710ppm) and Sr(1010 – 2680ppm). Generally, enhanced concentrations of the elements are observed at Lamza, Walu, Lakoro, Sukuliye, Gwalura and Gunda samples (Fig 4). The elements Ca, Fe, Mn, Sr, K and Ba are enriched in average shale and limestone rocks (Krauskopf, 1979; Mason and Moore, 1982) and Cr, Co, Cu, Ni, Zn, Pb, Bi, Br, U and As are normally in low concentrations in sediments, but are important constituents of both carbonate and clayey black shale that are concentrated in precipitating sulphide deposits (Milovsky and Kononov, 1985; Busek et al, 1991).

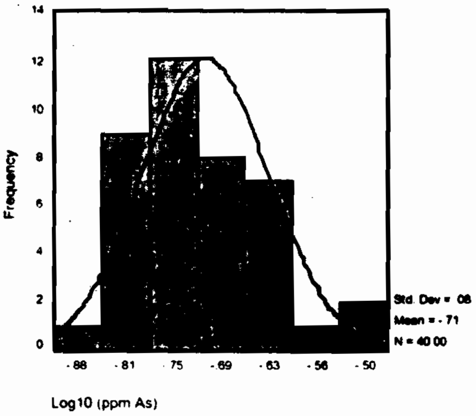


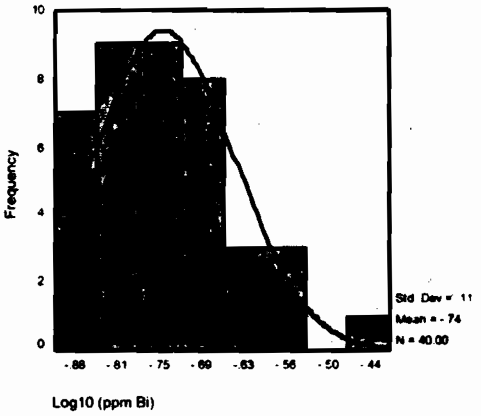

16
14
12
10
8
6
4
2
0
Frequency
Std. Dev = .11
Mean = -.28
N = 40.00
-.44
-.38
-.31
-.25
-.19
-.13
-.06
0.00
Log10 (ppm Ni)

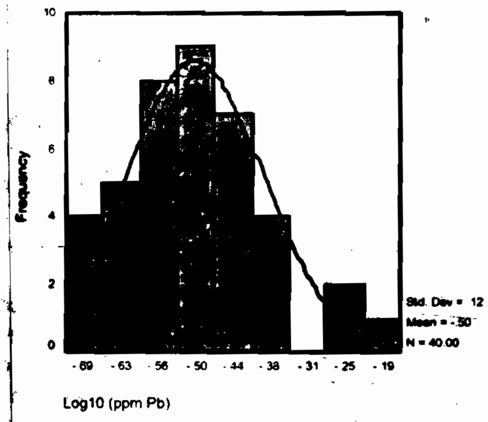

7
6
5
4
3
2
1
0
Frequency
Std. Dev = .10
Mean = .037
N = 40.00
-.100
-.050
.000
.050
.100
.150
.200
-.075
-.025
.025
.075
.125
.175
Log10 (ppm Co)

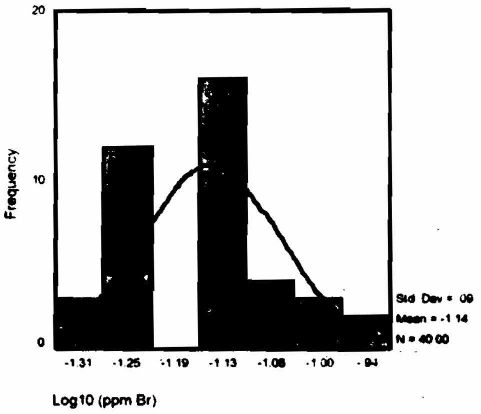

10
8
6
4
2
0
Frequency
Std. Dev = .09
Mean = 1.33
N = 40.00
1.20
1.25
1.30
1.35
1.40
1.45
1.50
1.55
Log10 (ppm Ba)


10
8
6
4
2
0
Frequency
Std. Dev = .11
Mean = .43
N = 40.00
.25
.30
.35
.40
.45
.50
.55
.60
.65
Log10 (ppm Cr)


14
12
10
8
6
4
2
0
Frequency
Std. Dev = .08
Mean = -.71
N = 40.00
-.88
-.81
-.75
-.69
-.63
-.56
-.50
Log10 (ppm As)


10
8
6
4
2
0
Frequency
Std. Dev = .11
Mean = -.74
N = 40.00
-.88
-.81
-.75
-.69
-.63
-.56
-.50
-.44
Log10 (ppm Bi)


10
8
6
4
2
0
Frequency
Std. Dev = .12
Mean = -.50
N = 40.00
-.69
-.63
-.56
-.50
-.44
-.38
-.31
-.25
-.19
Log10 (ppm Pb)


20
10
0
Frequency
Std. Dev = .09
Mean = -1.14
N = 40.00
-1.31
-1.25
-1.19
-1.13
-1.06
-1.00
-.94
Log10 (ppm Br)

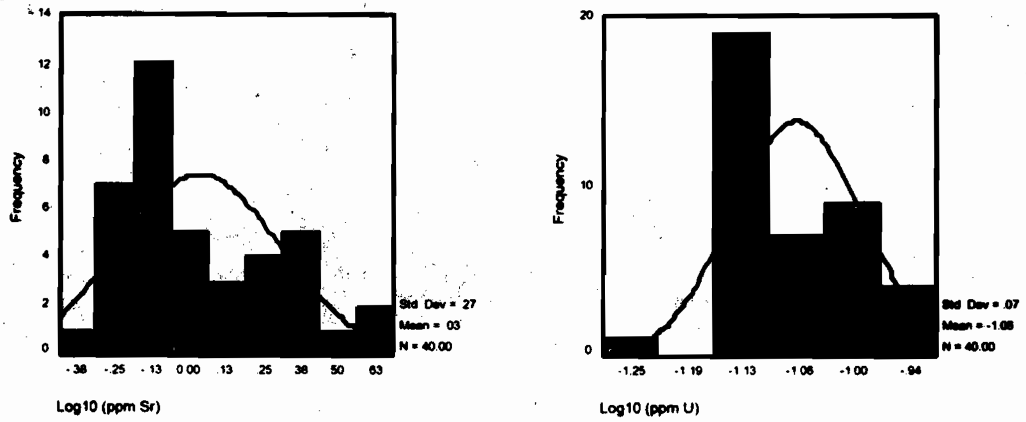


Fig. 3: Histogram plots of elemental concentrations in samples

Table 1: CONCENTRATION OF INDICATOR ELEMENTS IN SHALE SAMPLES (in x10^3ppm)

Element	STUDY LOCATION											A	Contrast
	1	2	3	4	5	6	7	8	9	10	Entire Area		
K	85.4	86.5	38.1	62.6	65.7	68.4	93.4	60.9	94.1	55.4	71.1		
Ca	45.4	43.8	41.6	400.0	50.5	39.7	57.1	488.2	75.6	357.9	159.9		
Fe	168.2	169.3	102.9	374.4	281.4	348.9	279.5	202.3	297.7	364.9	258.9		
Mn	2.61	4.70	1.59	11.66	3.72	14.40	3.60	9.70	6.99	15.70	7.50		
Ba	21.0	19.3	18.9	26.6	20.3	20.4	26.2	25.2	25.3	28.1	23.1		
Sr	1.02	1.02	0.79	1.86	0.95	0.83	1.87	2.98	2.43	1.98	1.60		
*Cu	0.41	0.40	0.37	0.52	0.36	0.45	0.55	0.53	0.61	0.76	0.49	0.046	11:1
*Zn	0.29	0.21	0.16	0.53	0.30	0.38	0.43	0.37	0.56	0.53	0.38	0.095	4:1
*Ni	0.48	0.44	0.35	0.77	0.45	0.63	0.52	0.65	0.71	0.87	0.59	0.072	8:1
*Co	0.90	0.98	0.65	1.23	0.99	1.24	1.31	1.27	1.41	1.46	1.14	0.019	60:1
*Cr	2.67	2.53	2.53	2.86	2.48	2.60	3.29	2.93	3.31	3.75	2.90	0.093	31:1
*As	0.19	0.17	0.13	0.23	0.16	0.19	0.22	0.22	0.26	0.28	0.21	0.012	18:1
*Pb	0.30	0.24	0.18	0.33	0.28	0.39	0.38	0.31	0.43	0.38	0.32	0.022	15:1
*Bi	0.17	0.16	0.13	0.21	0.14	0.18	0.21	0.22	0.25	0.27	0.19	0.005	38:1
*Br	0.07	0.06	0.05	0.08	0.06	0.07	0.09	0.09	0.10	0.10	0.08	0.045	1.8:1
*U	0.09	0.08	0.08	0.09	0.07	0.08	0.10	0.11	0.11	0.13	0.09	0.036	2.5:1

Key: 1 = Dukul; 2 = Gudenyi; 3 = Bobini; 4 = Lamza; 5 = Swenswithire; 6 = Walu;
7 = Lakoro; 8 = Sukuliye; 9 = Gwalura; 10 = Gunda.

A= Composite average in natural unmineralised shales (average of Krauskopf,1979; Rose et al,1979; Mason & Moore,1982 values)

* = Indicator elements

Contrast = Ratio of concentration in studied sediments to 'A' concentration.

DISCUSSIONS

Correlation coefficient of the data is determined to assess common intercorrelations between the constituent elements and principal component analysis is used to examine possible factors responsible for groupings of constituent elements. Correlation analysis of the analytical data confirmed this assertion. Table 2 shows significant correlation coefficients of the data set for shale samples. The analysis shows very high (>70%) intercorrelations between Ni, Bi, Cr, As, Cu, Br and U; and good (>50%) intercorrelation between other trace elements in the data set. Geochemically therefore, the environment is favourable for the simultaneous concentration of these elements. Principal component analysis of the data set shows that 72% of the proportion of variance for the 16 elements can be expressed in four R – mode factors (Table 3). Factor 1 has a high loading on Cu, Ni, Ba, As, Bi, Pb, Sr, Br, U, Co and Cr, and signifies the effect of gypsum mineralisation on the composition of the shale samples. These elements are closely associated with gypsum deposits (Boggs, 1987; Busek et al, 1991; Sonnenfeld, 1991). Factor 2 has a high loading on Fe, Cu, Zn, Ni, Co, Bi and Br, and represents the effect of petrogenetic late major and minor minerals (siderite, malachite, smithsonite, annabergite, erythrite, crocoite and associated alteration products rich in HBr and Bi_2O_3) that are commonly associated with the diagenetic alteration of carbonate rocks in oxidizing environments. Factor 3 has a high loading on K and negative loadings on the major petrogenetic and mineralisation indicator elements, signifying the effect of other minor minerals associated with gypsum e.g. polyhalite [$K_2Ca_2Mg(SO_4)_4$]. Factor 4 shows low factor loading on K, Mn, Cu and Pb, and negatively on all other elements in the data set, and can be interpreted to be other lithologic based geochemical signatures in the environment of deposition unrelated to gypsum mineralisation.

Table 2: Correlation Matrix For Elements in Shale Samples
(40 – sample size)

	K	Ca	Fe	Mn	Cu	Zn	Ni	Co	Ba	Cr	As	Bi	Pb	Br	Sr	U
K	1.0															
Ca	-	1.0														
Fe	-	-	1.0													
Mn	-	-	-	1.0												
Cu	-	-	-	-	1.0											
Zn	-	-	.512	-	.587	1.0										
Ni	-	-	-	-	.644	-	1.0									
Co	-	-	.572	-	.696	.587	-	1.0								
Ba	-	-	-	-	-	-	.616	-	1.0							
Cr	-	-	-	-	.606	-	.701	-	-	1.0						
As	-	-	-	-	-	-	.621	-	.561	.508	1.0					
Bi	-	-	-	-	.741	.585	.737	.629	-	.657	.746	1.0				
Pb	-	-	-	-	-	-	-	.528	-	-	.625	-	1.0			
Br	-	-	-	-	.755	-	.674	.626	.658	.602	.670	.731	.585	1.0		
Sr	-	-	-	-	-	-	-	-	-	-	-	-	-	.570	1.0	
U	-	-	-	-	.644	-	.609	.523	.570	.563	.840	.749	.568	.804	.595	1.0

Note: - = value below 0.5 significance level

Table 3: Principal Component Analysis of Correlation matrix of Shale data
(40 samples; samples 27, 36, 62, 81, 88, 92, 95, 96, 104, 105 omitted)

Element	Factors			
	1	2	3	4
K	0.264	-0.062	0.678	0.230
Ca	0.226	0.047	0.015	-0.901
Fe	-0.034	0.758	-0.413	-0.056
Mn	0.175	0.141	-0.845	0.185
Cu	0.559	0.630	-0.177	0.043
Zn	0 249	0.814	0.080	-0.089
Ni	0.604	0.402	-0.336	-0.379
Co	0.402	0.757	-0.044	-0.044
Ba	0.739	0.094	-0.335	-0.100
Cr	0.487	0.400	-0.201	-0.443
As	0.813	0.223	-0.009	-0.101
Bi	0.655	0 534	-0 074	-0.224
Pb	0.642	0 264	0 203	0.030
Br	0.819	0.363	-0.034	-0.164
Sr	0.640	-0.009	0.220	-0.290
U	0.876	0.255	0.149	-0.144
Cummulative %	32.4	19.8	11.1	9.1

Multiple regression analysis of the data is used to detect those samples in which element concentration is attributable to processes of mineralisation (Garrett, 1983; Howarth and Sinding-Larsen, 1983). Regression of the relevant major elements, Ca and Fe, against seven trace elements, Cu, Zn, Ni, Co, Cr, Pb and Sr reveals significant regression of Ca on Cu, Cr and Sr at 0.004, 0.033 and 0.048 values respectively; while Fe regressed on Ni, Co and Sr at 0.012, 0.001 and 0.021 values respectively. Other elements show values higher than the acceptable 0.05 significant levels (Table 4).

Table 4a **Shale Data: Regression of Ca on Cu, Zn, Ni, Co, Cr, Pb and Sr**
[Regression equation: Ca = 37.74 – 139.97Cu + 15.85Zn + 31.66Ni + 15.77Co + 10.20Cr – 16.06Pb + 5.57Sr]

Element	Coefficient	Std. Error	t ratio	Std. Coeff. Beta	Significance
Cu	-139.97	13.56	-3.08	-0.704	0.004
Zn	15.85	22.45	0.71	0.13	0.485
Ni	31.66	23.83	1.33	0.29	0.193
Co	15.97	15.59	1.01	0.22	0.319
Cr	10.19	4.57	2.23	0.44	0.033
Pb	-16.06	30.10	-0.0533	-0.09	0.597
Sr	5.57	2.71	2.06	0.32	0.048

F ratio for Cu, Zn, Ni, Co, Cr, Pb, Sr = 690.250/197.997 = 3.49

Table 4b: **Shale Data: Regression of Fe on Cu, Zn, Ni, Co, Cr, Pb and Sr**
[Regression equation: Fe = 28.94 – 272.72Cu + 133.76Zn + 283.77Ni + 249.49Co –16.42Cr – 189.16Pb – 29.35Sr]

Element	Coefficient	Std. Error	t ratio	Std. Coeff. Beta	Significance
Cu	-272.72	203.39	-1.341	-0.27	0.189
Zn	133.76	100.61	1.33	0.21	0.193
Ni	283.77	106.77	2.66	0.51	0.012
Co	249.49	69.85	3.57	0.69	0.001
Cr	-16.42	20.48	-0.80	-0.14	0.429
Pb	-189.16	134.91	-1.40	-0.21	0.170
Sr	-29.35	12.13	-2.42	-0.33	0.021

F ratio for Cu, Zn, Ni, Co, Cr, Pb, Sr = 23089.21/3976.08 = 5.81

From basic geochemical principles, the major probable indicator elements to gypsum mineralisation include Ca, Fe, Mn, Zn, Pb, Sr, Cu and Ba that participate in the various chemical processes during diagenesis of chemical precipitates (carbonates and evaporites) and Ni, Co, As and Cr, which are important constituents of both carbonate and clayey black shale that are notably concentrated in precipitating sulphide deposits (Keith and Degens, 1959; Milovsky and Kononov, 1985; Boggs, 1987; Busek et al, 1991). Considering the fact that major elements are not very indicative of environment of deposition (Ernst, 1970) and the petrogenesis of some of these elements, gypsum mineralisation indicators in this study area would include Ni, Co, As, Cr, Cu, Zn, Bi, Br, U and Pb. These indicator elements naturally occur in low concentrations in limestones and shale. When compared with research findings, their concentrations (Table 1) are several times more in studied sediments than in global natural unmineralised sediments, as obtained from Krauskopf (1979); Rose et al (1979); and Mason and Moore (1982).

Mean compositions of these indicator elements were examined in both the gypsum bearing and litho-beds that do not host gypsum bodies on the basis of obtained statistical data. Examination of the concentration levels using the standard (mean + 2 standard deviation) threshold mark reveal that about 4.6% of the samples contain anomalous concentrations of the elements. Using determined threshold value of each of the elements, about 2.9 – 8.6% of the gypsum-bearing shale samples are correctly identified as anomalous and about 91.4 – 97.1% are missed; and of the background values, 100% are correctly identified as non-gypsum bearing (Table 5). Of interest is that concentrations of K and Fe in all the samples were below the threshold mark and concentrations of Cu, Co and Cr statistically identified one Lakoro sample (no.31) to be gypsum bearing, against its non-gypsum bearing status in the field. The Cu, Co and Cr elements are therefore, probably closely related to gypsum hosted in the sediments (hence, are good predictor elements), and the Lakoro sample could possibly be mineralised at other unexposed sections of the location. On the other hand, K and Fe elements are not very necessary indicators of gypsum occurrence.

Table 5: Measure of Concentration levels of Elements

Element	Sample Size	Prime range (ppm)	m + 2d value (ppm)	A %	B %
K	40	85.0 – 95.0	122.66	0	2.9
Ca	40	42.5 – 52.5	80.23	8.6	0
Fe	40	262.5 – 287.5	412.23	0	0
Mn	40	1.5 – 2.5	9.10	5.7	0
Cu	40	0.27 – 0.43	0.61	2.9	2.9
Zn	40	0.22 - 0.28	0.63	5.7	0
Ni	40	0.47 – 0.53	0.86	5.7	0
Co	40	0.97 – 1.03	1.58	2.9	2.9
Ba	40	17.0 – 19.0	31.21	2.9	0
Cr	40	2.38 – 2.62	4.23	5.7	2.9
As	40	0.18 – 0.21	0.28	5.7	0
Bi	40	0.13 – 0.16	0.29	2.9	0
Pb	40	0.22 – 0.28	0.52	8.6	0
Br	40	0.06 – 0.08	0.11	5.7	0
Sr	40	0.5 – 0.75	3.27	8.6	0
U	40	0.06 – 0.08	0.12	8.6	0

Note: A% = anomalous samples correctly identified;
B% = background values mistakenly identified as anomalous

On the basis of the regression equation (Table 4), concentration of a negligible -139.97ppm of Cu, 10.2ppmCr and 5.57ppm of Sr could be used to predict the presence of Ca in gypsum mineralised region; and about 283.77ppm of Ni, 249.49ppm of Co and -29.35ppm of Sr would serve to predict for Fe content. However, on simple linear regression of Ca on individual predictive element, Ni, Bi, U and Br (with 0.010, 0.042, 0.034 and 0.019 values respectively) could be good predictors for Ca content in the environment. From the analysis therefore, Cu, Cr, Ni, Co and Sr elements are good predictors (at 0.05 significance level) for Ca and Fe in gypsum – rich areas. Ca is the major cation in gypsum deposit and Fe is usually mobilised under reducing and precipitated under oxidizing conditions; and show strong presence and influence in early sulphide (pyrite) and carbonates (siderite) and secondary sulphates (melanterite) during the diagenetic process of gypsum formation. Elements that can predict enrichments of these two major cations are seen as geochemical tracers or pathfinder elements. Hence Cu, Cr, Ni and Co are good pathfinder elements to gypsum mineralisation. Under normal conditions, these trace elements would be mobile in the strongly acidic solutions during the oxidation of pyrites and other sulphide ores. However, the diffusion of the organic waters through organic – rich and unconsolidated sediments rich in Fe possibly generated Fe(OH)$_3$, which provide a good adsorptive surface (scavenger) for these elements (Maynard, 1983). Also, interaction between the diffused water (which are low in oxygen) with oxygenated surface water (common in environment of gypsum formation) would trap these elements (Beus and Grigorian, 1975), and incorporate them into the gypsum precipitated during interaction of the sulphate and carbonate – rich waters during the diagenetic processes. These geochemical processes must have worked simultaneously to produce the distribution and dispersion patterns of the elements in the Guyuk area as illustrated in Figure 4.

The observed high intercorrelations between the identified seven trace elements (Ni, Bi, Cr, As, Cu, Br and U) and their collective intercorrelation with Fe signifies their close affinity to the processes involving Fe. Iron is seen as a vital element in the various geochemical processes namely sedimentation, diagenetic alteration and adsorption within the environment of gypsum formation and accumulation.

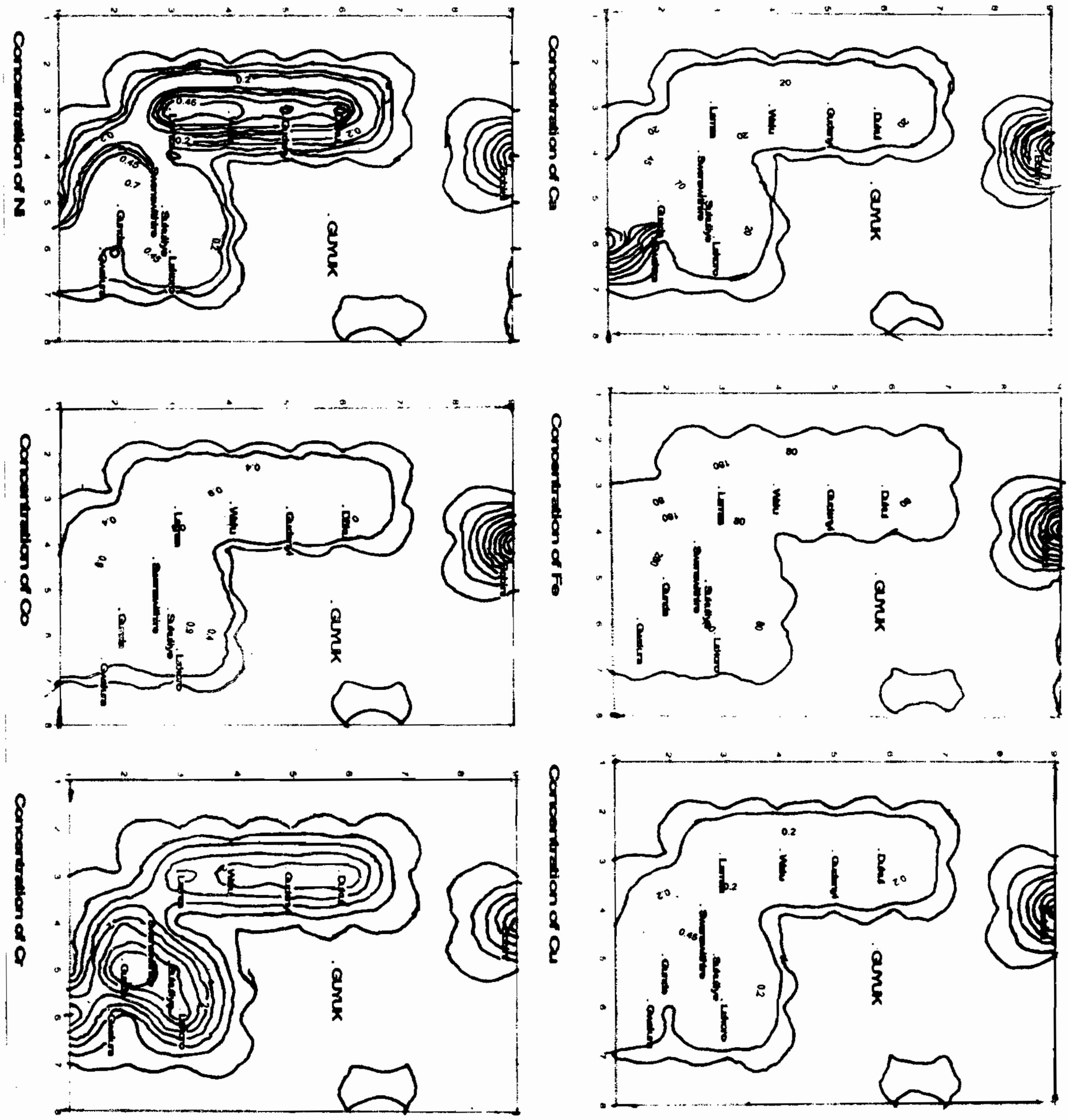


Fig. 4 Contours of some elemental contents in shale samples

CONCLUSIONS

Study of the geochemical pattern in sampled sediments identifies and distinguishes enrichments of four predictor elements, Ni, Co, Cr and Cu to be related to gypsum mineralisation. The ratios of the enrichments of these elements to gypsum in the studied shale sediments are Cu(11:1), Ni(8:1), Co(60:1) and Cr(31:1). These concentrations are anomalously higher relative to natural unmineralised shale materials and are well above the 2:1 contrast value recommended by Hawkes (1959) as useful anomaly. Similarly, the high (>32%) loading of a single factor on a group of mineralisation indicator elements including these four (Cu, Cr, Ni and Co) and the observed significant regression of Ca and Fe on them depicts the strong bond between these trace elements to process of gypsum mineralization. Hence their common trend of variance marks mineralisation of gypsum in the study area.

ACKNOWLEDGEMENTS

The authors acknowledge the critical comments of colleagues during the course of this work, and that of the anonymous reviewers.

REFERENCES

Benkhelil, J., 1986. Structure and geodynamic evolution of the intracontinental Benue Trough, Nigeria. Elf Nig. Ltd., Nigeria. Bull. Centres Rech. Explor. Prod. Elf- Aquitaine (BCREDP), 12: 29 – 128.

Beus, A. A. and Grigorian, S. V., 1975. Geochemical Exploration Methods for Mineral Deposits. Applied Publishing Co., Wilmette, 287p.

Boggs, S., (Jnr), 1987. Principles of Sedimentology and Stratigraphy. Macmillan Publishing Company, New York, 784p.

Braide, S. P., 1992. Studies on the sedimentary and tectonics of the Yola Arm of the Benue Trough: Facies Architecture and their tectonic significance. J. Min. Geol., 28: 23-31.

Busek, F., Cerny, J. and Sramek, J., 1991. Sulphur isotope studies of atmospheric S and the corrosion of monuments in Prayne, Czechoslovakia. In: Krouse, H.R. and Grinenko, V.A. (Eds.), Stable Isotopes – Natural and Anthropogenic Sulphur in the Environment. John Wiley & Sons, England, pp 399 – 408.

Carter, J. D, Barber, W., Tait, E. A. and Jones, J. P., 1963. The Geology of parts of Adamawa, Bauchi and Bornu provinces of Nigeria. Geol. Surv. Nig. (GSN) Bull., 30: 1- 109.

Ernst, W., 1970. Geochemical Facies Analysis. Elsevier, Amsterdam, 152p.

Evans, R., 1978. Origin and significance of the Evaporites in basins around Atlantic margin. Bull. Assoc. Amer. Petrol. Geologists (AAPG), 62: 223 - 234.

Garrett, R. G., 1983. Mathematical and Statistical activity in North America, In: Howarth, R.J. (Ed.), Statistics and Data Analysis in Geochemical Prospecting. Elsevier Scientific Publishing Co., Amsterdam, pp341 – 350.

Hawkes, H. E., 1959. Geochemical Prospecting, In: Abelson, P.H. (Ed.), Researches in Geochemistry. John Wiley, New York, 2: 62 – 78.

Howarth, R. J. and Sinding-Larsen, R., 1983. Multivariate Analysis, In: Howarth, R.J. (Ed.), Statistics and Data Analysis in Geochemical Prospecting. Elsevier Scientific Publishing Co., Amsterdam, pp207 – 283.

Keith, M. I. and Degens, E. T., 1959. Geochemical indicators of marine and freshwater sediments. In: Abelson, P.H. (Ed.), Researches in Geochemistry. John Wiley, New York, 2, pp 38 – 61.

Krauskopf, K. B., 1979. Introduction to Geochemistry (2^{nd} ed.). McGraw-Hill Kogakasha Ltd., London, 617p.

Mason, B. and Moore, C.B., 1982. Principles of Geochemistry (4^{th} ed.). John Wiley & Sons Inc., NewYork, 344p.

Maynard, J. B., 1983. Geochemistry of Sedimentary ore Deposits. Springer-Verlag, New York, 305p.

Milovsky, A. V. and Kononov, O. V., 1985. Mineralogy. Mir Publishers, Moscow, 320p.

Ntekim, E. E. and Orazulike, D. M., 2003. Structural and Lithologic characteristics of Lamurde – Lau area in Upper Benue Trough, N.E. Nigeria: A strategy for Gypsum Prospecting. Nig. J. Pure & Appl. Sci., 19: 1692 – 1697.

Opeloye, S. A., 2002. Some Aspects of Facies Architecture, Geochemistry and Paleoenvironments of Senonian Formations in Yola Arm, Upper Benue Trough (Nigeria). Unpl. Ph.D. Thesis, Abubakar Tafawa Balewa University, Bauchi, Nigeria, 160p.

Pearce, J.A., 1976. Statistical Analysis of major element patterns in Basalts. J. of Petrology, 17(1): 15 – 43.

Rose, A.W., Hawkes, H.E. and Webbs, J.S., 1979. Geochemistry in Mineral Exploration (2^{nd} ed.). Academic Press Ic. (London) Ltd., London, 657p.

Sonnenfeld, P., 1991. Evaporite Basin Analysis. Reviews in Economic Geology, 5: 159-168.

Uma, K.O., 1998. The brine fields of the Benue Trough, Nigeria: A comparative study of geomorphic, tectonic and hydrochemical properties. J. Afri. Earth Sc., 26(2): 261-275.

Wilkinson, B. R., 1982. Cyclic Cratonic Carbonates and Phanerozoic Calcite Sea. J. Geol. Education, 30: 189 – 203.

Zaborski,P., Ugodulunwa,F.,Idornigie,A . Nnabo,P. and Ibe, K., 1997. Stratigraphy and Structure of the Cretaceous Gongola basin, Northeast Nigeria. Elf Nig. Ltd., Bull. Centres Rech. Explor. Prod. Elf-Aquitaine (BCREDP), 21 153 – 185.