

MINERALOGICAL, GEOCHEMICAL AND ENVIRONMENTAL DEPOSITION OF CLAY IN ESNA SHALE AT EL-BURUK – EL-HASSANA AND EL-HIMMAH – BAGHDAD AREAS NORTH SINAI, EGYPT.

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ABSTRACT

This paper deals with the study of the Mineralogical, Geochemical and Environmental deposition of Clays in Esna Shale at El-Buruk- El-Hassana and El- Himmah Baghdad areas, North Central Sinai, Egypt.

The present work is based on the field and laboratory work carried out by present authors.

sixty stratigraphic sections representing Esna shale unit in the study area were studied, measured and sampled.

The laboratory work comprise 17 samples for XRD analysis to study the mineral constituents of the clay and argillaceous rocks and 36 samples for chemical analysis using XRF method to detect the major oxides SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, TiO₂, MnO, Na₂O, K₂O, SO₃--, Cl-, P₂O₅ and L.O.I. and ten samples for the trace constituents, F, Ba, Cr, Cu, Li, Ni, Zn, As, B, Ga, Se, Y, V, Co, Rb, Sr, Nb, Mo, Sn, Sb, La, Yb, Hf, Ta, Pb, Zr and Ce.

Montmorillonite and kaolinite are the main constituents of clays. The other associated minerals are quartz, gypsum, halite and dolomite.

Geochemical speaking, SiO₂, Al₂O₃, K₂O and Na₂O are controlled by the amount of montmorillonite, kaolinite and illite while CaO and MgO contents are controlled by calcite and dolomite which occur as minor constituents.

The high and low contents of Fe₂O₃ and MnO respectively are attributed to the low oxidation potential that prevailed during the deposition of clay causing precipitation of Fe+2 keeping Mn+2 in soluble state.

Esna Shale of the study areas are deposited in deposition environments changes from very shallow inner neritic zone to outer neritic zone.

INTRODUCTION

The study area is located at the north Sinai Governorate, Egypt. The study area lies between latitudes 30° 00' 00" ' - 30° 45' 00" N and longitudes 33° 30' 00" – 34° 00' 00" E (Fig.1), covering about 4000 km². The northern part of the study area is located 40 km south of El Arish city. It is easily accessible through the Ismailia-El-Arish asphaltic road. The sedimentary sequence ranges in age from Jurassic to Eocene. The lithostratigraphic investigation allowed to subdivided this succession into nine rock units namely, from oldest to youngest, Safa, Malha, Halal, Wata, Matulla, Duwi, Sudr, Esna Shale, and Thebes formations and finally covered with Quaternary deposits in parts.

The present work deals with the Geochemical, Mineralogical and Environmental deposition of clays in the Esna Shale occur in two area namely El-Hammah- Baghdad and El-Hassana - El-Buruk area north Sinai, Egypt.

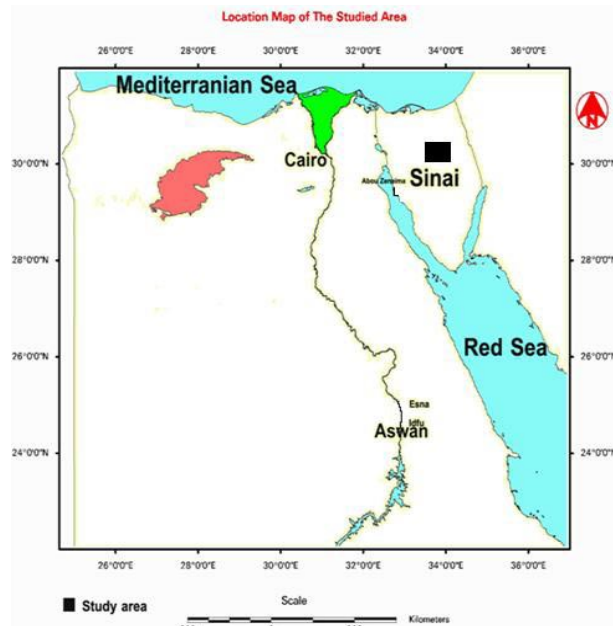


Fig. 1: Location Map of The Study Area.

GEOLOGIC SETTING

The sedimentary sequence ranges in age from Jurassic to Eocene. The lithostratigraphic

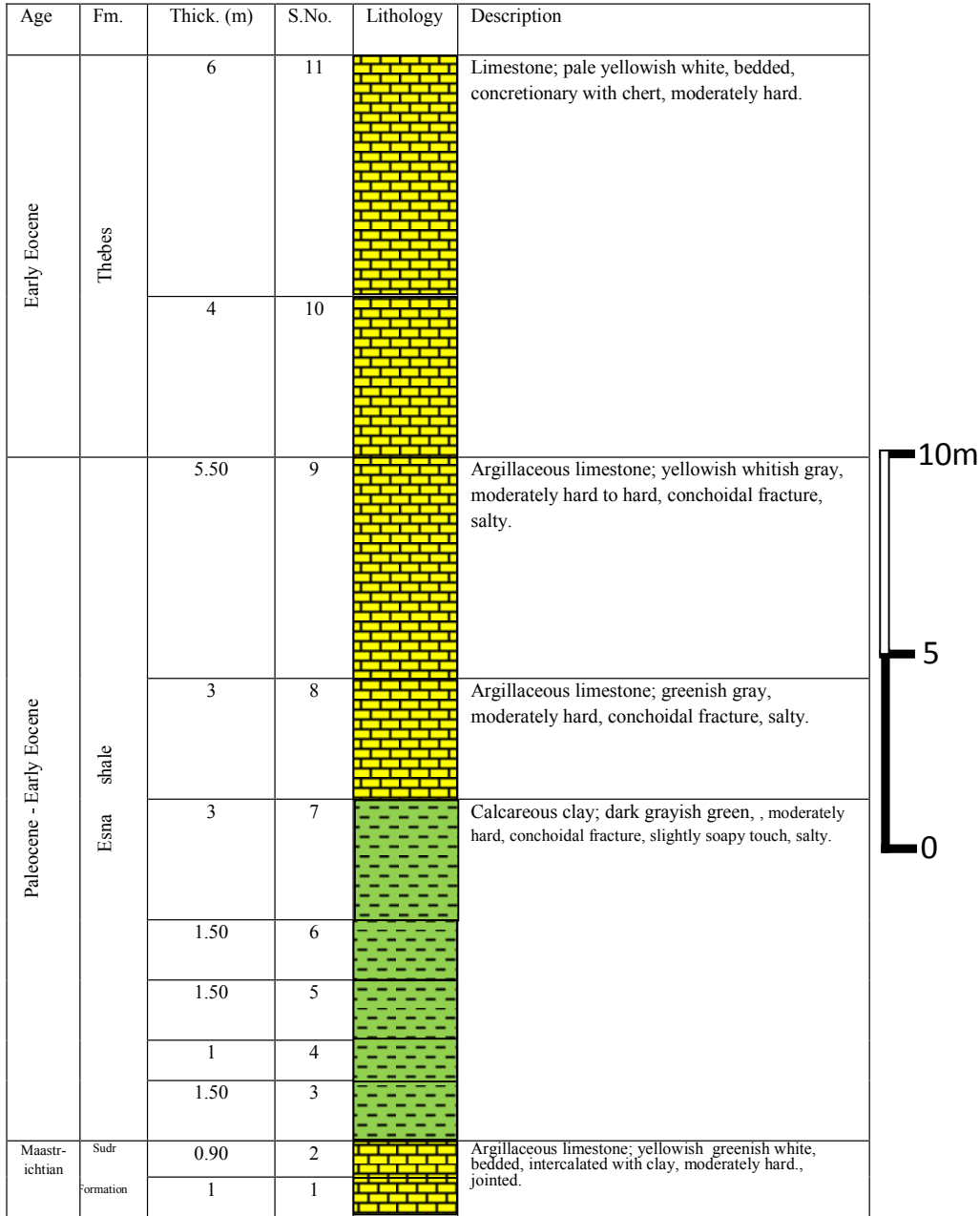


Fig. 3: Lithostratigraphic columnar section of Esna Shale at EL-Buruk-El-Hassana area.

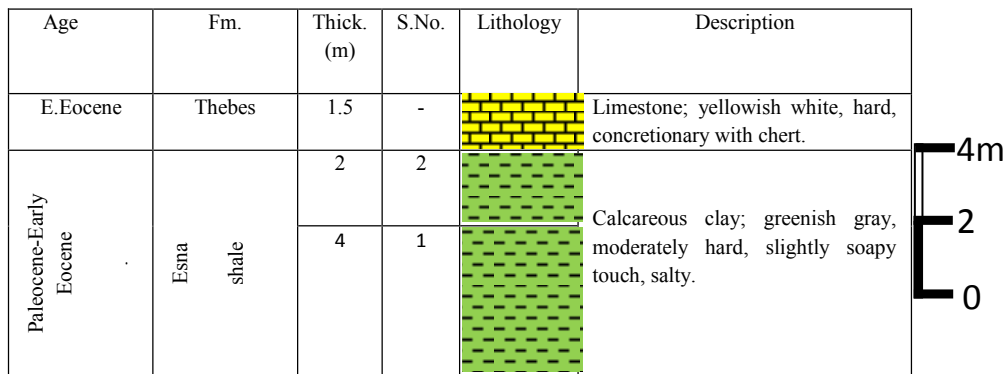

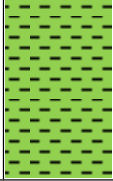
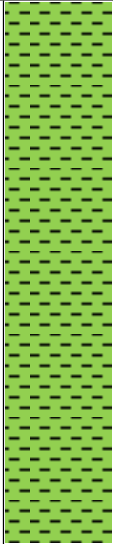


Fig. 4: Lithostratigraphic columnar section of Esna Shale at EL-Buruk-El-Hassana area.

Age	Fm.	Thick. (m)	S.No.	Lithology	Description
Quaternary	Wadi deposits	1	--		Wadi deposits, consist of gravel and sand.
Paleocene-Early Eocene	Esna shale	5	2		clay; olive gray, soapy touch.
		+15	1		

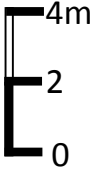


Fig. 5: Lithostratigraphic columnar section of Esna Shale at EL-Himmah-Baghdad area.

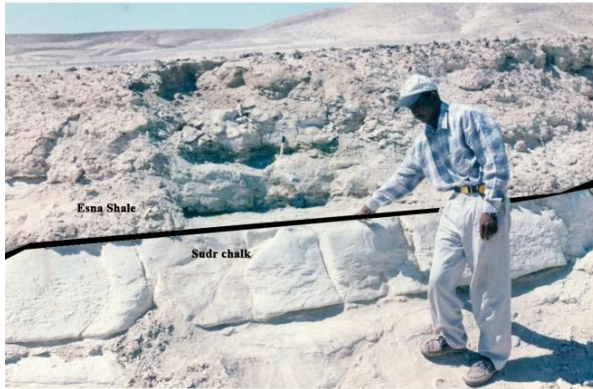


Fig. 6: Photograph showing the contact between Sudr Formation and Esna Shale .

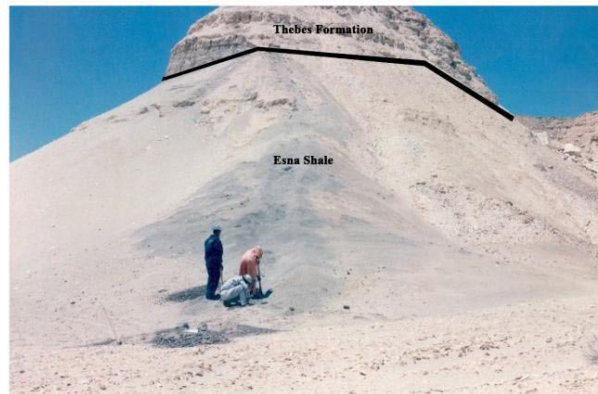


Fig. 7: Photograph showing stratigraphic sequence of Esna Shale capped with Thebes Formation.

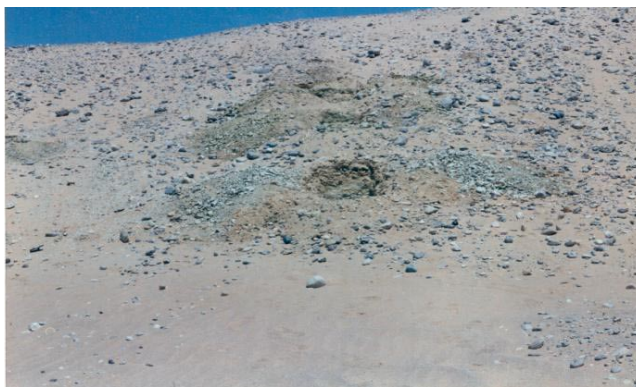


Fig. 8: Photograph showing excavated bit of clay at the middle part of Wadi El-Himmah area.

Mineralogy

In the present study X- ray diffraction analysis was carried out of 17 representative clay samples to identify the different clay minerals .

1- X-Ray diffraction analysis:

Aphilips X- ray diffraction equipment model PW/1710 with monochromator, Cu- radiation ($\lambda = 1.542 \text{ \AA}$ at 40 Kv, 30 MA and scanning speed 0.02o/ sec. were used. The reflection peaks between $2\theta = 2\theta$ and 60θ , corresponding spacing (d, \AA) and relative intensities (I/I^o) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files.

- The procedure proposed by Jackson (1969) and Carver (1971) was used to prepare a clay fraction for mineralogical study taking in consideration that clay minerals remain unchanged.

2-RESULTS:

X- ray diffraction analysis revealed that the samples is composed of the following minerals in a decreasing order of their abundance as shown in table No.(1).

Table (1) showing the mineral composition of the analysed samples of Esna shale sediments.

FM.	Section No.	Sample No.	Major Const.	Minor Const.	Trace Const.
Esna Shale	1	5	Montmorillonite and Calcite	Quartz	Kaolinite
	1	6	Montmorillonite and Calcite	Quartz	Kaolinite
	1	7	Montmorillonite and Calcite	Quartz	Kaolinite
	1	8	Calcite	Montmorillonite Quartz and	Quartz
	1	9	Calcite	Montmorillonite Fluorapatite and Quartz	Kaolinite
	3	6	Calcite	Quartz	Kaolinite and Illite
	3	12	Calcite	Montmorillonite and Quartz	Dolomite
	4	4	Calcite	Quartz	Halite, Dolomite, Illite and Barite
	5	5	Calcite	Quartz	Montmorillonite, Kaolinite, Dolomite, Halite and Barite
	5	6	Calcite	Quartz	Kaolinite, Montmorillonite, Halite and Barite
	6	1	Calcite	Quartz	Montmorillonite, Kaolinite, Halite, Barite, Dolomite and Gypsum
	7	1	Calcite	Halite	Quartz, Montmorillonite, Kaolinite, Gypsum, Bassanite and Barite
	8	1	Calcite	Quartz Gypsum,	Halite, Illite and Dolomite
	10	1	Calcite	montmorillonite and Quartz	Kaolinite, Halite and Bassanite
11	1	Montmorillonite and Kaolinite	Quartz and Calcite	Halite	
12	1	Montmorillonite and Kaolinite	Quartz	Feldspar	
14	1	Montmorillonite and Kaolinite	Calcite and Quartz	Gypsum and Halite	

Montmorillonite, kaolinite, illite are recorded in the studied 10 samples at AL-Hammah-Baghdad and El-Hassana- EL-Buruk area are relatively different from major constituents, minor constituents or trace constituents.

Table No. (1) show that The Esna shale of northern area is represented by montmorillonite and kaolinite as main mineral with calcite and quartz as minor amount while at the southern area Esna shale deposits consists of calcite as main mineral with quartz and montmorillonite as minor amount; occasionally in some location calcite and montmorillonite is the main mineral while quartz is a minor amount.

From table No. (1), it is observed that kaolinite is encountered with appreciable amount in the studied samples revealed that the environment of depositon is strong leaching environment, an acid reaction medium and presence of aluminosilicates according to Weaver (1985b).

x-ray diffraction charts given in Fig. (9,10,11). From the X.RD charts the following mineral constituents are recorded.

1- Montmorillonite

Montmorillonite occur as a dominant mineral in some of the studied samples and occurs as minor and trace constituents in other samples. The characteristic diffraction lines of montmorillonite according to ICDD card are 15 Å, 5.01Å, 2.58 Å, 2.50 Å, 1.88 Å and 1.70 Å.

2-Kaolinite

Kaolinite is the dominant mineral with montmorillonite in some of the studied samples and occurs as trace constituents in other samples. The characteristic diffraction lines of Kaolinite according to ICDD card are 7.17 Å, 3.847 Å, 3.579 Å, 3.420 Å, 2.754 Å, 2.566 Å, 2.495 Å, 2.237 Å, 2.197, 2.093 Å, 2.080 Å, 1.997 Å, 1.939 Å, 1.870 Å, 1.689 Å and 1.669 Å.

3-Calcite

Calcite also occur as a dominant mineral in some of the studied samples and occurs as trace constituents in other samples. Its characteristic diffraction lines according to ICDD card are 3.852 Å, 3.030Å, 3.02Å, 2.834Å, 2.495 Å, 2.284Å, 2.094 Å, 1.9261 Å, 1.9071 Å, 1.8726 Å, 1.6259 Å, 1.604Å, and 1.5821 Å.

4- Illite

Illite is present in a few samples in very small amount as trace constituents. Its characteristic diffraction lines according to ICDD card are 10 Å, 4.95 Å, 4.48 Å, 3.17 Å, 2.87 Å, 2.61Å, 2.51 Å, 2.42Å, 1.98Å and 1.82Å.

5- Quartz

Quartz is present in many samples in small amount as minor and trace constituents. Its characteristic diffraction lines according ICDD card are 4.257 Å, 3.342Å, 2.457, 2.282 Å, 2.127 Å, 1.8179 Å, and 1.6719 Å.

6- Dolomite

Dolomite is present in many samples in very small amount as trace constituents. Its characteristic diffraction lines according ICDD card are 2.899 Å.

7- Illite- Montmorillonite

Illite- Montmorillonite is present in a few samples in very small amount as trace constitu-

ents. Its characteristic diffraction lines according ICDD card are 9.5 Å, 5.17 Å and 4.46 Å.

8- Fluorapatite

Fluorapatite is present in a few samples in very small amount as trace constituents. Its characteristic diffraction lines according to ICDD card are 2.814Å.

From the X-ray diffraction analysis for 17 representative sampl it can be concluded that The northern area (El-Himmah-Baghdad area) is represented by clay deposits consists of montmorillonite and kaolinite as main mineral with calcite and quartz in minor amount while the southern area (El-Bruk-El-Hassanah area) is represented by Esna shale deposits consists of calcite as main mineral with quartz and montmorillonite in minor amount; occasionally in some location calcite and montmorillonite is the main mineral with quartz in minor amount.

Geochemistry:

Thirty six samples of Esna shale are prepared for chemical analysis using XRF method to detect the major oxides SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, TiO₂, MnO, Na₂O, K₂O, SO₃--, Cl-, P₂O₅ and L.O.I. and ten samples for the trace constituents, F, Ba, Cr, Cu, Li, Ni, Zn, As, B, Ga, Se, Y, V, Co, Rb, Sr, Nb, Mo, Sn, Sb, La, Yb, Hf, Ta, Pb, Zr and Ce. The results are given in table (2,3,4).

Major Oxides:

From the results of the chemical analysis of the major constituents the following can be concluded:

1- SiO₂, Al₂O₃ and Fe₂O₃:-

The SiO₂ and Al₂O₃ contents in the study area vary from 8.65% to 63.32% with an average 29.90% and from 0.9% to 18.96% with an average 6.71 respectively. The high SiO₂ and Al₂O₃ values can be attributed to the high content of free quartz with the clay minerals. The average contents of Fe₂O₃ in the studied samples are 7.35, 1.91 and 0.91 % for clay, calcareous clay and argillaceous limestone respectively. The abundance of iron oxide may be also due to the the iron contained in the lattice structure of the clay minerals and reflecting their ferruginous

Table (1) showing the mineral composition of the analysed samples of Esna shale sediments.

FM.	Section No.	Sample No.	Major Const.	Minor Const.	Trace Const.
Esna Shale	1	5	Montmorillonite and Calcite	Quartz	Kaolinite
	1	6	Montmorillonite and Calcite	Quartz	Kaolinite
	1	7	Montmorillonite and Calcite	Quartz	Kaolinite
	1	8	Calcite	Montmorillonite	Quartz
	1	9	Calcite	Quartz and Montmorillonite	Kaolinite
	3	6	Calcite	Fluorapatite and Quartz	Kaolinite and Illite
	3	12	Calcite	Montmorillonite and Quartz	Dolomite
	4	4	Calcite	Quartz	Halite, Dolomite, Illite and Barite
	5	5	Calcite	Quartz	Montmorillonite, Kaolinite, Dolomite, Halite and Barite
	5	6	Calcite	Quartz	Kaolinite, Montmorillonite, Halite and Barite
	6	1	Calcite	Quartz	Montmorillonite, Kaolinite, Halite, Barite, Dolomite and Gypsum
	7	1	Calcite	Halite	Quartz, Montmorillonite, Kaolinite, Gypsum, Bassanite and Barite
	8	1	Calcite	Quartz	Halite, Illite and Dolomite
	10	1	Calcite	Gypsum, montmorillonite and Quartz	Kaolinite, Halite and Bassanite
	11	1	Montmorillonite and Kaolinite	Quartz and Calcite	Halite
	12	1	Montmorillonite and Kaolinite	Quartz	Feldspar
14	1	Montmorillonite and Kaolinite	Calcite and Quartz	Gypsum and Halite	

character. Fe₂O₃ occurs in a free state as pigment (hydrolysate). During diagenesis iron has a great tendency to re-enter silicate structure and this silication of the iron oxide results in the formation of glauconite in marine deposits .

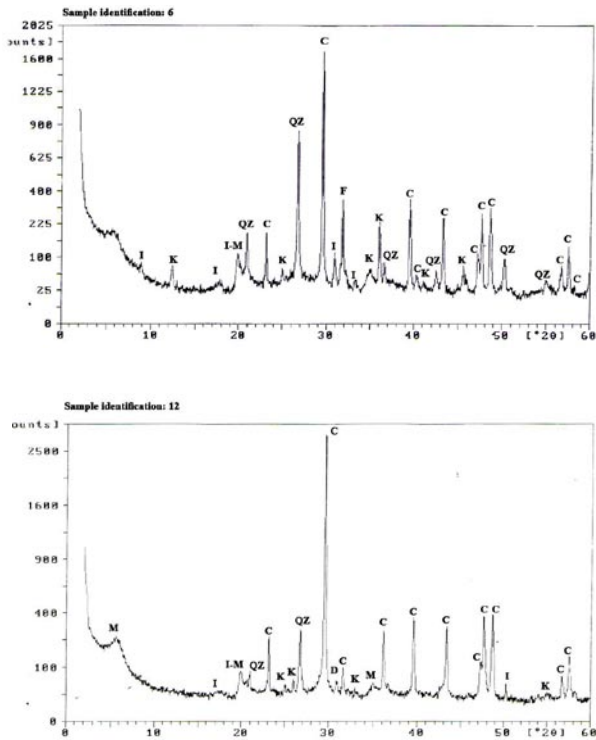
2- CaO, MgO and L.O.I.:

The average content of CaO in the studied samples are 1.01, 28.52 and 39.19 % where as the average content of MgO are 0.02, 1.89 and 1.26 % for clay, calcareous clay and argillaceous limestone respectively.

The abundance of CaO is due to the presence

of calcite and gypsiferous material material in the clays. The MgO content may be related to the minor amount of dolomite detected by the mineral analysis or to their incorporation within the clay mineral lattice.

The L.O.I. average contents are 9.85, 27.04 and 34.43 % for clay, calcareous clay and argillaceous limestone respectively. The high content of L.O.I. in carbonates and shales, in part due to the presence of appreciable amounts of organic matter and involving of carbon dioxide (CO₂). Also the L.O.I. may be related to the water release.



M= Montmorillonite K= Kaolinite I=Illite
 I-M= Illite-Montmorillonite
 QZ= Quartz C= Calcite D= Dolomite
 F=Fluorite

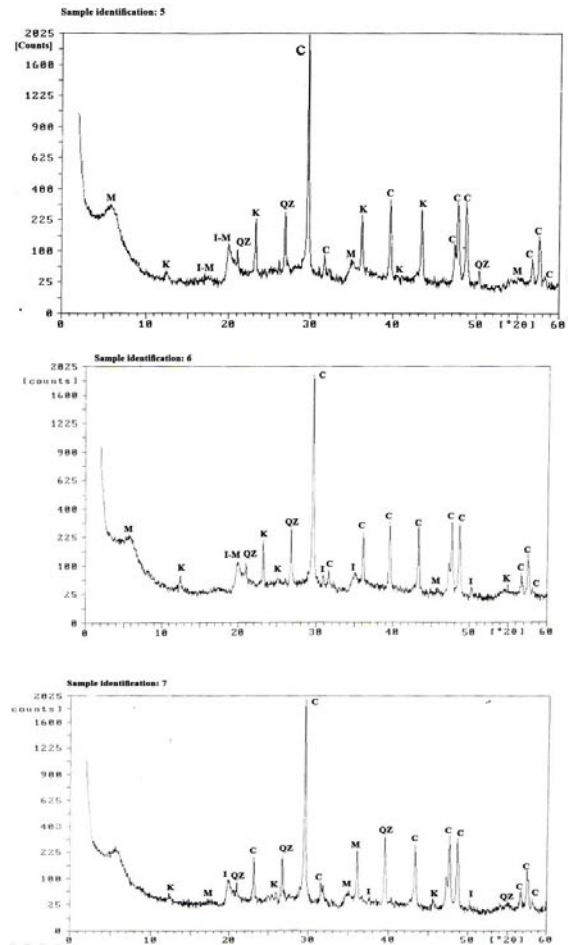
Fig. 9: selected X. Ray Diffraction pattern of samples 6, 12 in section no.3
 3-The Na₂O and K₂O:

Sodium oxide content ranges from 0.8% to 2.75% with an average 1.54 in Al-Hammah-Baghdad area and range between 0.17% and 3.23% with an average 1% in Al-Bruk-Al-Hasanah area. Potassium oxide (K₂O) concentration in the studied Esna shale samples ranges between 0.24% and 5.01%.

According to Millot (1970), the clay could preferentially adsorb the high content of Na₂O and K₂O. Consequently the high contents of Na₂O and K₂O are related to the clay minerals of montmorillonite, kaolinite and illite. The content of K₂O is higher in the illite rich clay than kaolinite rich one, and Na₂O content is related to the minor amount of halite detected by the mineral analysis.

4-MnO

The MnO content ranges between 0.02 and 0.04 %, < 0.01 and 0.15 % and between <0.01 and 0.06 % in clay, calcareous clay and argil-



M= Montmorillonite K= Kaolinite I=Illite I-M= Illite-Montmorillonite QZ= Quartz
 C= Calcite

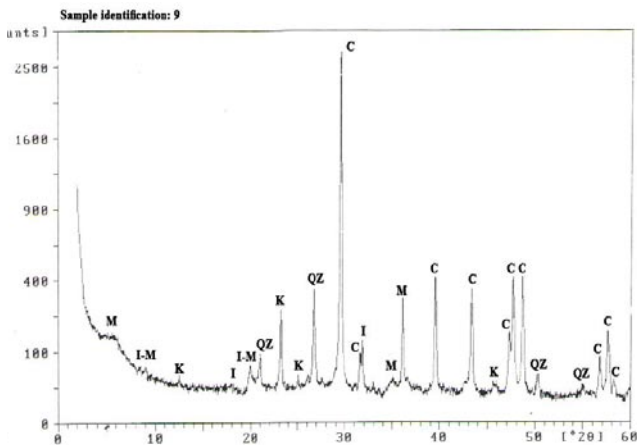
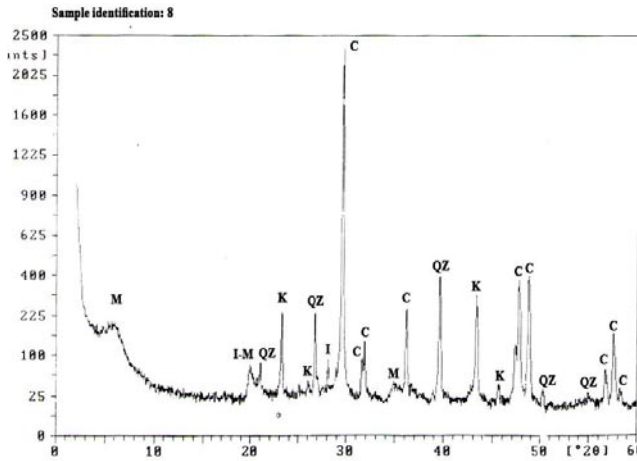
Fig. 10: selected X-Ray Diffraction pattern of samples 5, 6, 7 in section no1

laceous limestone respectively. According to Nicholla et al (1962) the low content of MnO can be attributed to its mobility in the reducing environment than that under oxidizing environment.

5- SO₃ and Cl:

The average content of SO₃ are 0.71, 0.98 and 0.32 % while the average content of Cl - are 1.27, 1.73 and 1.18 % in the clay, calcareous clay and argillaceous limestone respectively. The high contents of SO₃ are due to the reducing medium of deposition. The high contents of Cl- (up to 2.92%) is partially present as salt (halite) as indicated by the high Na₂O (up to 2.07%) as detected mineralogically.

The clay minerals montmorillonite, kaolinite and illite indicated by mineral analysis control



M= Montmorillonite K= Kaolinite I=Illite I-M= Illite-Montmorillonite Qz= Quartz C= Calcite

Fig. 11: selected X-Ray Diffraction pattern of samples 8, 9 in section no.1

SiO₂, Al₂O₃, K₂O and Na₂O. The CaO and MgO are controlled by the presence of calcite and dolomite which occur as minor minerals.

The high and low content of Fe₂O₃ and MnO respectively is attributed to the low oxidation potential which prevailed during deposition causing the precipitation of Fe (a goethite) in various forms, keeping Mn in solution.

Trace Elements:

From the results of the chemical analysis of the trace constituents the following can be concluded:

-Boron (B):

Boron content ranges in the studied samples

between 4.6 and 112ppm in Al-Bruk-Al-Hasanah area. Boron is a minor element regarded as an indicator of the salinity of the environment of deposition (Goldschmidt and Peters 1932 a&b). Tourtelot (1964) found that the offshore marine shales contain larger median amounts of B than their near-shore equivalent.

-Strontium (Sr):

Strontium content in the analysed samples ranges from 564 to 821ppm. Barber(1974) stated that Sr is allocated to carbonate fraction of the shales and sandstones and it may be incorporated in the clay minerals by the cation exchange capacity. Chiling et al. (1967) mentioned that “strontium increases towards shore, where warm waters”. Kukul (1971) suggested that “the strontium content affected mainly by the aragonite content and strontium content in carbonate sediments appears to be a reliable indicator for the salinity and temperature”.

-Copper (Cu):

Copper content ranges in the studied samples between 23 and 223ppm. The association of Cu with organic matter was given by Vine and Tourtelot (1970), where as Spear and Amin (1981) related Cu to the detrital fraction.

-Chromium:

Chromium content ranges in the analyses samples between 23.8 and 88.1ppm with an average 51.19ppm. Mackenzie (1966) reported that most of Cr in sediments is concentrated in mica and clay minerals. The association of Cr with organic matter was given by Vine and Tourtelot (1970), whereas Spear and Amin (1981) related Cr to the detrital fraction. The chromium content can be attributed to the presence of clays in the form of montmorillonite which in turn favours an alkaline environment of deposition.

-Cobalt (Co):

Co content ranges in the analysed samples between 1 and 16ppm in section no.1 with an average 8.4ppm. According to Landergren and Joensuu (1965) the contribution of both Co and Ni is due to adsorption reactions in the sea and biological processes.

-Nickel (Ni):

Nickel content ranges in the analysed samples between 24 and 202.1ppm Vine and Tour-

Esna Shale

Table (2), showing major element contents and average of the studied Esna shale samples

FM.	Section N.o.	S.No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	MnO	Na ₂ O	K ₂ O	SO ₃ ²⁻	Cl ⁻	P ₂ O ₅	L.O.I	CaO+MgO	Description	
Esna Shale	1	3	24.59	4.76	2.06	31.15	1.67	0.17	0.1	1.32	1.16	3.1	1.05	0.64	28	32.82	Calcareous Clay	
		4	22.05	3.25	1.02	35.45	1.27	0.12	0.02	1.13	0.8	0.35	1.25	0.51	32.28	36.72		
		5	26.35	9.01	2.62	30.5	2.22	0.23	0.04	0.83	0.39	0.61	1.62	0.61	24.08	32.72		
	2	6	25.36	8.6	2.81	29.5	2.37	0.26	0.03	0.32	0.78	0.27	2.45	0.53	26.34	31.87	Calcareous Clay	
		7	21.15	7.27	2.13	34.05	1.88	0.21	0.03	0.77	0.83	0.4	1.93	0.55	28.4	35.93		
	3	1	25.65	6.92	2.12	28.65	2.15	0.2	0.03	0.03	0.17	1.04	0.52	2.75	0.43	28.27	30.8	Calcareous Clay
		1	27.45	4.77	1.82	30.28	1.87	0.19	0.02	0.88	1.14	0.24	1.28	0.55	28.75	29.87		
		6	32.6	6.55	3.49	20.6	4.39	0.42			-1.25	0.62	N.D	-	1.12	26.24	25	
	4	8	24.98	4.26	1.95	30.28	2.19	0.35	0.11	0.07	1.13	0.33	0.04	1.58	0.36	32.54	32.47	Calcareous Clay
		9	36.16	3.16	1.79	27.89	0.65	0.25	0.04	0.59	0.24	0.16	0.16	0.67	0.39	25.97	28.54	
	Esna Shale	5	10	25.31	4.58	1.7	29.71	2.11	0.4		0.38	0.27	0.22	1.33	0.34	31.77	31.82	Calcareous Clay
			3	27.15	3.77	0.86	32.25	1.35	0.12	0.05	1.6	0.7	0.23	2.03	0.52	29	33.6	
		4	35.2	5.3	1.58	25.3	1.9	0.19	0.07	0.83	0.07	0.52	0.83	0.56	0.53	26.4	27.2	Calcareous Clay
		5	33.5	5.79	2.3	21.8	1.98	0.24	0.07	1.15	2.12	2.67	0.95	3.01	0.56	24.7	23.78	
		6	6	24.2	5.63	1.55	27.4	2.07	0.17	0.15	0.15	1.95	2.39	0.87	2.85	0.33	30.5	29.47
1			29.1	5.91	1.78	27.7	2.18	0.19	0.14	0.14	1.01	1.23	0.7	1.21	0.35	28.6	29.88	
7		1	15.1	4.4	1.36	23.2	1.95	0.15	0.1	0.1	3.23	5.01	3.58	4.62	0.42	36.5	25.15	Calcareous Clay
		2	27.5	2.43	0.65	33.25	0.91	0.08	0.02	0.81	0.35	0.29	0.29	0.9	0.35	31.49	37.5	
8		1	25.3	3.6	1.66	33.1	1.44	0.15	0.02	0.02	1.02	1.03	0.29	1.32	0.4	30.1	34.54	Calcareous Clay
		10	33.54	7.71	3.16	19.88	2.86	0.36	0.01	0.8	0.61	0.61	7.8	1.5	0.15	21	22.74	
15	1	31.02	4.06	1.5	30.52	0.92	0.24	<0.01	<0.01	1.24	0.69	0.18	2.01	0.25	27.33	31.44	Calcareous Clay	
	2	37.02	5.17	2.28	25.05	1.46	0.32	<0.01	<0.01	1.45	0.78	0.17	2.23	0.25	23.74	26.51		
Esna Shale	average	27.74	5.31	1.91	28.52	1.89	0.22	0.04	0.03	1.01	1.1	0.98	1.73	0.46	27.04	31.44	Argillaceous Limestone	
		15.65	4.99	1.3	39.5	1.36	0.13	0.03	0.03	0.85	0.85	0.4	1.63	0.43	32.47	40.86		
	1	16.65	2.93	0.9	40.15	0.83	0.1	0.03	0.03	0.83	0.58	0.33	1.53	0.33	34.47	40.98	Argillaceous Limestone	
	2	20.15	3.48	1.16	36.2	1.3	0.11	0.02	0.44	0.85	0.85	0.053	2.15	0.41	32.62	37.5		
	3	3	8.65	1.27	0.24	44.95	1.25	0.04	<0.01	<0.01	1.32	0.27	0.32	1.06	0.3	39.69	76.48	Argillaceous Limestone
		12	17.56	4.17	2.19	34.49	3.58	0.37	0.03	0.03	0.18	0.26	0.36	-	0.25	33.73	38.07	
	4	1	21.51	0.9	0.29	39.41	0.43	0.05	0.06	0.06	0.69	0.24	0.2	1	0.3	34.56	39.84	Argillaceous Limestone
		2	25.03	1.41	0.68	36.35	0.46	0.06	0.06	0.06	0.96	0.41	0.68	1.35	0.3	31.95	36.81	
	8	2	15.45	1.57	0.53	42.49	0.92	0.08	0.01	0.01	0.56	0.44	0.24	0.75	0.22	36	43.41	Argillaceous Limestone
		2	17.58	2.59	0.91	39.19	1.26	0.11	0.02	0.02	0.11	0.47	0.32	1.18	0.31	34.43	43.41	

Table (3), showing major element contents and average of the studied Esna shale samples

Section N.o.	S.No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	MnO	Na ₂ O	K ₂ O	SO ₃ ²⁻	Cl ⁻	P ₂ O ₅	L.O.I	CaO+ MgO	Description
11	1	49.52	18.18	9.21	2.47	3.01	1.11	0.03	1.09	1.2	0.35	2.15	0.1	11.14	5.48	Clay
12	1	55.4	18.96	7.48	0.64	3.46	1.15	0.04	0.97	1.08	0.3	1.05	0.09	8.93	4.1	
13	1	47.78	17.9	8.36	4.22	1.44	0.91	0.02	2.75	1.02	1.75	1.5	0.14	11.56	5.66	
14	1	48.37	16.17	7.09	5.7	3.46	0.81	0.02	1.17	0.91	1.02	1.75	0.13	12.98	9.16	
16	1	61.23	16.71	6.15	1.35	1.25	1.04	0.02	2.05	0.84	0.18	0.55	0.13	7.96	2.6	
16	2	63.32	16.09	5.84	0.74	1.18	1.07	0.03	2.35	0.83	0.67	0.65	0.12	6.53	1.92	
Average		54.27	17.33	7.35	2.52	2.3	1.01	0.02	1.73	0.98	0.71	1.27	0.11	9.85		

telot (1970) found that the average value of Ni in marine black shale is 50ppm; higher amount of this element can be probably attributed to hydrothermal activities or other environment. Potter et al. (1963) reported that Ga and Ni elements are significantly more abundant in marine than in non –marine argillaceous sediments.

-Vanadium (V):

Vanadium content in the analysed samples ranges between 35 and 69ppm in section no1 with an average 55.8ppm. Shales and calcareous shales have higher average (ppm) of V than both ferruginous and marly limestone samples (Hirst, 1962). Distribution of Vanadium is controlled by the presence of organic matter. Vanadium deposits may be formed by various reactions with organic matter or by precipitation after the formation of sedimentary rocks as result of reducing conditions caused by organic matter (Krauskopf, 1979).

-Zirconium (Zr):

Zirconium content ranges in the analysed samples between 75 and 90ppm with an average 82.4ppm. Habib et al. (1986) concluded that Zr is moderately correlated with Al₂O₃ and might be partly incorporated in the clays. Vine and Tourtolet (1970) stated that Zr is related to the detrital fraction. Zohny (1977) reported that Zr remains largely in the resistates which usually contain considerably more Zirconium than do the hydrolyzates.

-Barium (Ba):

Barium content ranges in the analysed samples between 71.1 and 2619 ppm with an average 1507.56ppm. Kukul (1971) stated that “strontium and barium this pair of elements and their relation to salinity has been much discussed. It is generally believed that the Ba²⁺/Sr²⁺ ration increases with salinity”. According to Kukul

Table (4) Concentration of the trace constituents in the studied area

Section. No.	3					1				
Sample No.	6	8	9	10	12	5	6	7	8	9
F%	0.5	0.3	0.25	0.25	0.3					
Ba	84.5	71.1	299.8	2358.1	1479.1	1945	1821	2619	2389	2009
Cr	88.1	49.2	23.8	36.3	26.5	56	66	83	44	39
Cu	67	41	25	35	23	98	40	223	47	139
Li		9.3	13.7	8.7						
Ni	137	114.5	252.1	156	135.3	65	58	36	27	24
Zn	87.5	49.9	78.7	106.5	86.5	95	107	77	50	31
As	ND	ND	ND	12	ND					
B	112	26.4	39	4.6	40.4					
Ga	61.8	46.9	41.1	53	51.1					
Se	ND	ND	ND	ND	ND					
Y	252	139	96.2	106	84.7	29	26	35	25	24
V						62	67	69	46	35
Co						11	16	8	6	1
Rb						21	22	21	16	13
Sr						564	677	747	695	821
Nb						10	10	10	8	7
Mo						2	2	2	2	2
Sn						2	3	3	0	0
Sb						1	0	1	1	0
La						109	72	103	72	72
Yb						6	7	5	5	5
Hf						4	4	3	5	3
Ta						5	5	4	6	5
Pb						<1	0	<1	<1	<1
Zr						79	95	88	75	80
Ce						30	32	28	35	10

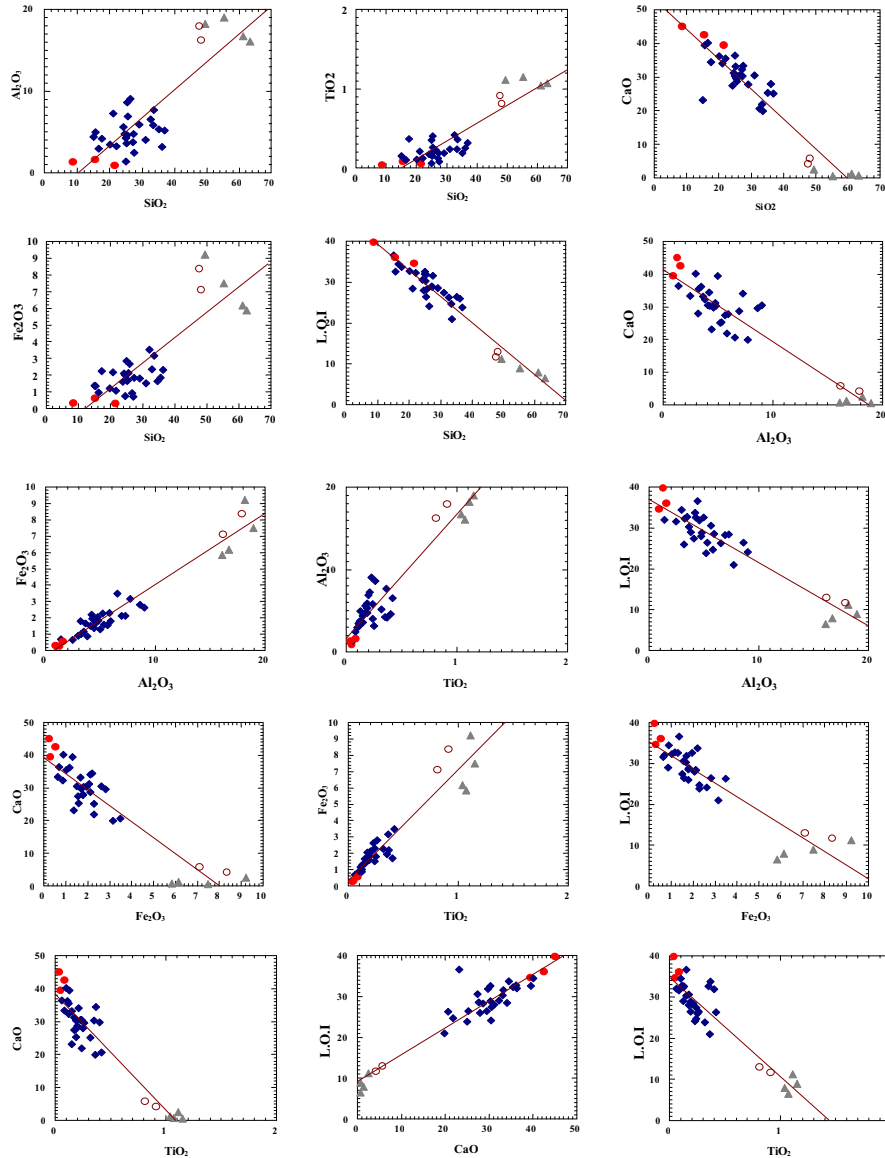


Fig. 12: show Interelement correlation

(1971) the increasing of salinity in AL-Bruk-Al-Hasanah clay samples attributed to the high content of Barium as shown above.

-Rubidium (Rb):

Wedepohl (1971) concluded that Rb is a marine element built it is incorporated in the clay minerals during deposition or early diagenesis. Rb content ranges in the analysed samples between 13 and 22ppm. The occurrence of rubidium element in the study samples indicate that the clay of Esna shale are deposited in the marine environment.

-Lithium (Li):

Lithium content ranges in the analysed samples between 8.7 and 13.7ppm. low values of

Lithium can be attributed to the environment of deposition which was slightly alkaline, reducing environment where the Eh was very low.

-Lead:

Lead content in the analysed samples is <1 in all analysed samples and absent in samples no.6 in section no.1. The detected lead content shows lower values than that given by Turekian and Wedepohl (20ppm) (1961). The low detected values of lead than that given by Turekian and Wedepohl (1961) can be attributed to the environment of deposition which was slightly alkaline, reducing environment where the Eh was very low (Krauskopf, 1979).

-Zinc (Zn):

Rankama and Sahama (1950) concluded

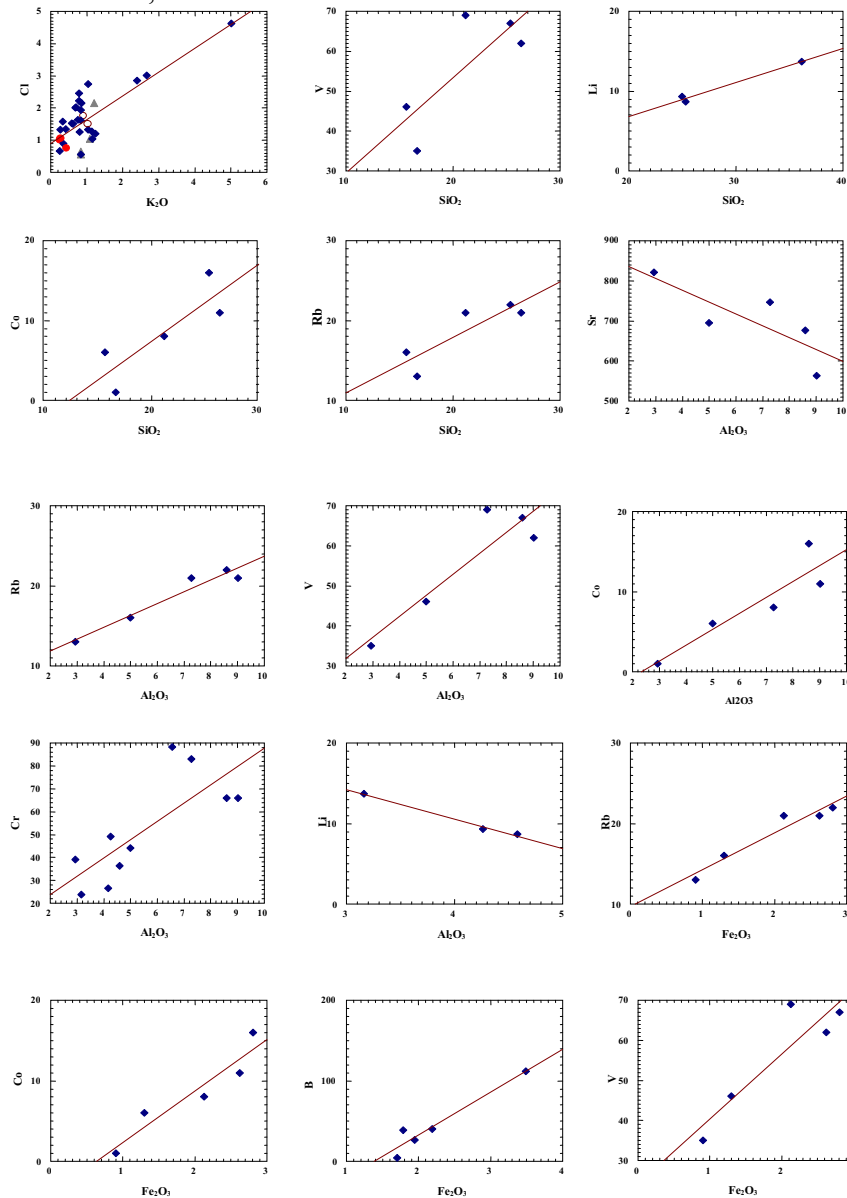


Fig. 13: show Interelement correlation

that Zn +2 ion is very mobile; Zn goes readily into solution during weathering as Sulphates or chloride which could be transported in surface and ground waters in a manner that it may be enriched by redeposition as sulphide, oxide, carbonate or silicate. It might also be enriched in the hydrolyzates, oxidates as well as in shales containing organic remains, where H₂S production is rather weak. Zn content ranges in the analysed samples between 31 and 107ppm with an average 76.36ppm. this result accordance with that stated by Rankama and Sahama (1950).

Silica (SiO₂):

SiO₂ has a strong positive correlation with the major constituent Al₂O₃, TiO₂, Fe₂O₃ and a positive correlation with Na₂O, MgO and

with SO₃ where SiO₂ increase with increase of Al₂O₃, TiO₂, Fe₂O₃, Na₂O, MgO and SO₃--. Al₂O₃ content versus SiO₂ correlation diagram shows dependent relationship. This may be due to the presence of silica in the form of clay minerals and/or free silica (quartz) as detected by X-ray investigation. Sodium which is recorded may be present in the form of water soluble salts (mainly halite) and / or as a constituent in the clay minerals. SiO₂ in the Esna shale sediments has a strong negative correlation with the major constituent K₂O, CaO, Cl-, P₂O₅ and L.O.I. where SiO₂ decrease with increase of L.O.I., CaO, K₂O, Cl and P₂O₅. This indicate that Silica is found in the form of clay minerals and/or free quartz as detected by X-ray investigation.

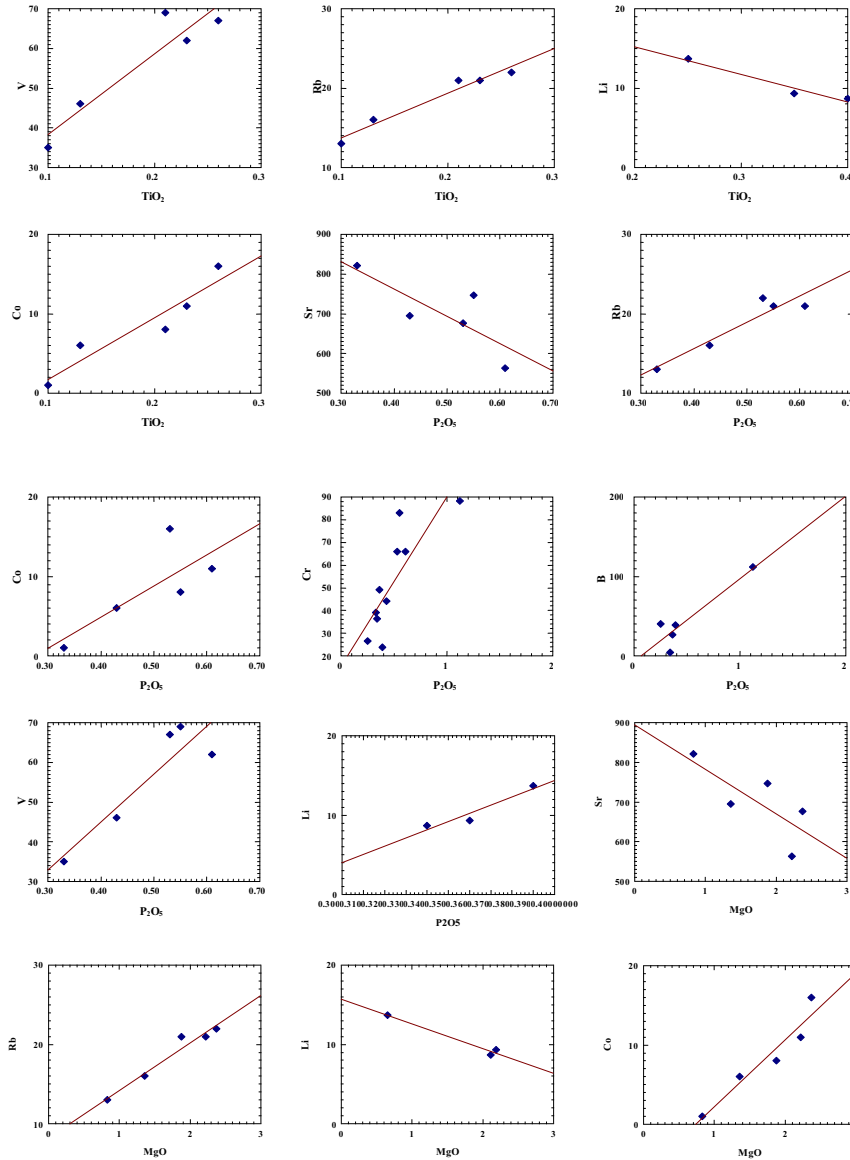


Fig. 14: show Interelement correlation

SiO₂ in the studied samples has a strong positive correlation with the trace element Li , Rb , Co , V , Ni , Zr and a positive correlation with B , Zn and Cr , while it has a strong negative correlation with the trace element Sr , MnO , Cu , Ba and Pb.

Alumina (Al₂O₃):

Al₂O₃ in the studied samples has a positive correlation with the major constituent Fe₂O₃, TiO₂, K₂O, MgO, SO₃⁻⁻ and Na₂O where Al₂O₃ increases with increasing of K₂O, MgO, SO₃⁻⁻, Na₂O and Fe₂O₃. A consistent relationship has been found between Al₂O₃ and Fe₂O₃ in most of the studied samples. A positive correlation has been found between Al₂O₃ and K₂O this due to that Potassium is preferentially

adsorbed by clays (Millot,1970).Al₂O₃ versus TiO₂ correlation diagram . Show dependent relationship, so is the titanium is rich in clays. Al₂O₃ has a negative correlation with CaO, L.O.I., Cl⁻ and P₂O₅ where Al₂O₃ decreases with increasing of CaO, L.O.I., Cl and P₂O₅ . Al₂O₃ in the studied samples has a strong positive correlation with the trace element Rb, Co, V, Cr, B, Zr, Zn and a positive correlation with Cu and Ba. Machenzie (1966) reported that most of Cr in sediments is concentrated in mica and clay mineral consequently, there is an intimate geochemical correlation between Al₂O₃ and Cr . Dependent relationship was observed between Cr, Co and Al₂O₃ this due to that the Clays carry cobalt and chromium in crystal lattices as well

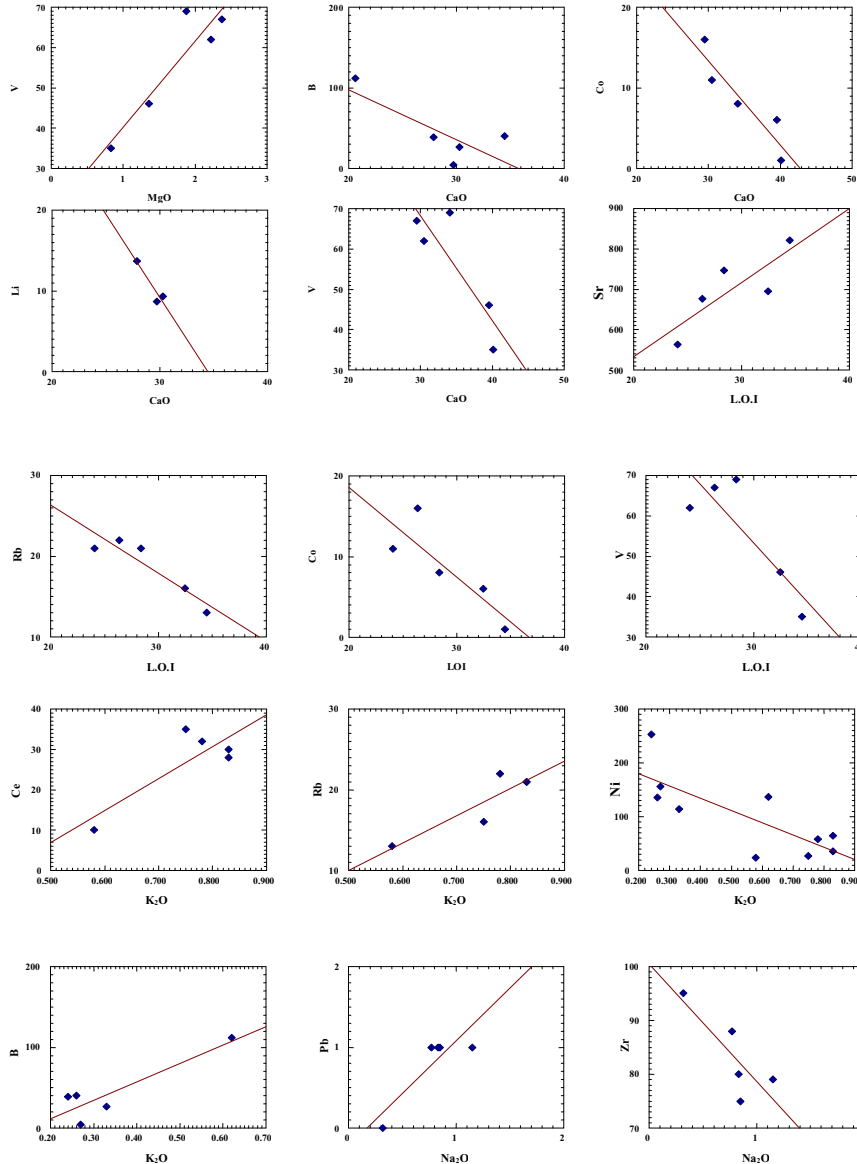


Fig. 15: show Interelement correlation

as in association. Dependent relationship was observed between V and Al₂O₃ also the same relationship was found between V and Fe₂O₃ this due to the distribution of Vanadium is controlled by the presence of organic matter or by precipitation after the formation of sedimentary rocks as result of reducing conditions caused by organic matter (Krauskopf,1979). Al₂O₃ in the Esna shale sediments has a strong negative correlation with the trace elements Li, Sr, and a negative correlation with MnO, Pb and Ni .

Iron oxide (Fe₂O₃):

Fe₂O₃ in the studied samples has a positive correlation with TiO₂, SO₃²⁻, Na₂O K₂O and MgO where Fe₂O₃ increases with increasing of SO₃²⁻, Na₂O, K₂O and MgO. MgO versus

Fe₂O₃ Show generally positive dependent relationship. It may indicate that the iron are consistent mainly with that of dolomite. This perhaps indicate that also Fe₂O₃ has been formed diagenetically with Mgo (dolomite), while it has a negative correlation with L.O.I., P₂O₅, Cl⁻ and CaO Where Fe₂O₃ decreases with increasing of L.O.I, P₂O₅, Cl⁻ and CaO .

Fe₂O₃ in the studied samples has a strong positive correlation with the trace element Rb, Co, V, B, Cr, Zr, Zn and a positive correlation with Ni , while it has a negative correlation with the trace element Sr, Li, MnO, Pb and Cu and Ba. A strong positive correlation between Cr and Fe due to that Cr and Fe favour precipitation as hydroxide.

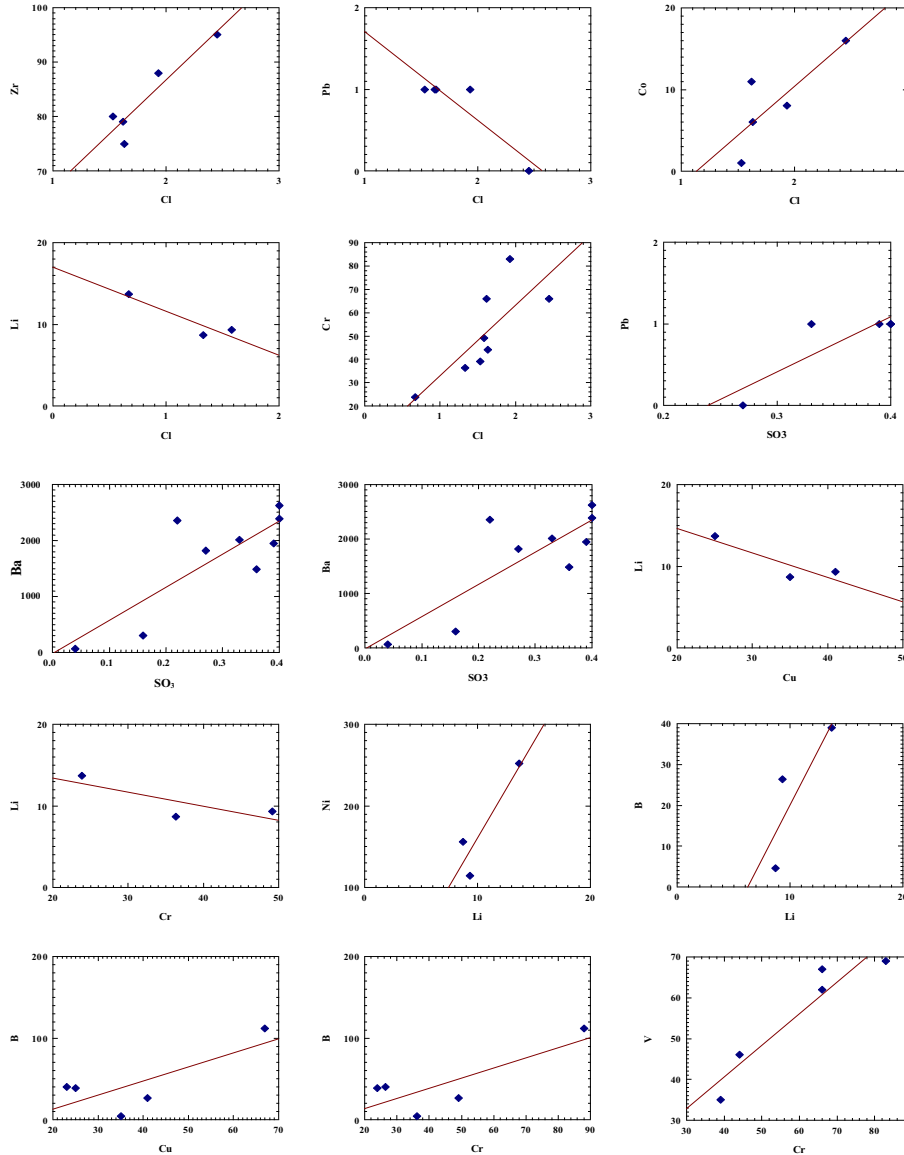


Fig. 16: show Interelement correlation

Calcium (CaO):

CaO has a strong positive correlation with L.O.I. and has positive correlation with P₂O₅ and Cl⁻. Where CaO increases with increasing L.O.I., P₂O₅ and Cl⁻, while it has a negative correlation with TiO₂, SO₃²⁻, Na₂O and K₂O. Where CaO increases with decreasing of SO₃²⁻, Na₂O, and K₂O.

CaO has a positive correlation with the trace element Sr, MnO, Pb, Cu and Ba, and a strong negative correlation with the trace element Li, Rb, Co, V, B, Zn, Zr, Ni, and Cr. CaO behaves reversibly to those of MgO content, MgO content increases in the expense of CaO (calcite). This may support the presence of dolomite as detected by X-ray investigation.

Magnesium (MgO):

MgO in the studied samples has a positive correlation with P₂O₅, Cl⁻, SO₃ and K₂O, and a negative correlation with L.O.I., Na₂O and CaO. Where MgO increases with increasing P₂O₅, Cl⁻, SO₃ and K₂O and with decreasing of L.O.I., Na₂O, and CaO.

MgO has a strong positive correlation with the trace element Rb, Co, V, B and a positive correlation with Zr, Zn, MnO and Ni, while it has a negative correlation with the trace element Li, Sr, Pb and Cu and Ba.

Sodium (Na₂O):

Na₂O in the studied samples has a positive correlation with Cl⁻ and SO₃²⁻. Where Na₂O increases with increasing of Cl⁻ and SO₃²⁻, and

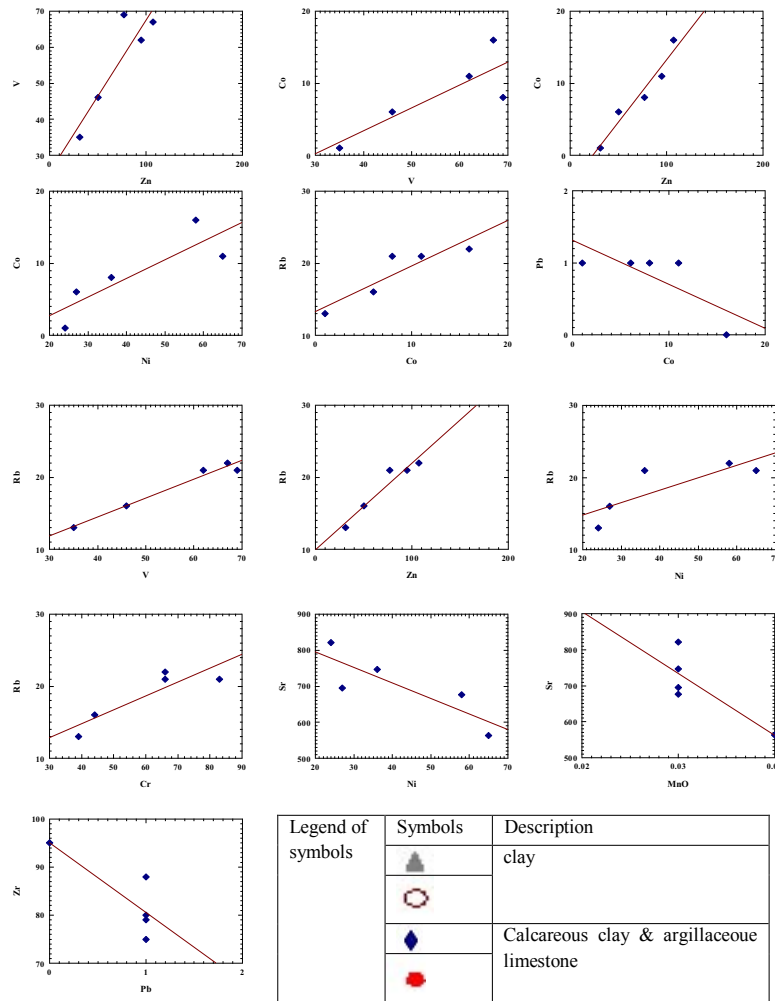


Fig. 17: show Interelement correlation

has a negative correlation with L.O.I. and P2O5, hence Na2O increases with decreasing of L.O.I. and P2O5.

Na2O has a positive correlation with the trace element Pb, B, Cr, and Cu, and a strong negative correlation with the trace element Zr, Sr, Co, Zn, Ba, V, Rb, Ni and Li .

Potassium (K2O):

K2O in the studied samples has a positive correlation with L.O.I., P2O5, Cl-, SO3-- and Na2O, and a strong positive correlation with the trace element Rb, V, B, Cr, Co and a positive correlation with Cu, MnO, Ba, Zr and Zn, while it has a negative correlation with the trace element Ni, Sr, Li and Pb. hence K2O increases with increasing L.O.I., P2O5, K2O, SO3--and Na2O .

Loss on ignition (L.O.I.):

L.O.I. in the studied samples has a positive correlation with MnO, CaO, K2O, Cl- and P2O5,

and a negative correlation with SiO2, TiO2, Al2O3, Fe2O3, MgO and Na2O. hence L.O.I. increases with increasing MnO, CaO, K2O, Cl- and P2O5.

L.O.I. has a strong positive correlation with the trace element Sr, Pb, Ba and MnO, and a negative correlation with the trace element Li, Rb, V, Co, B, Zn, Cr, Zr, Ni, and Cu .

SO3--:

SO3-- in the studied samples has a positive correlation with Cl-,and it has a negative correlation with L.O.I. and P2O5, hence SO3-- increases with decreasing L.O.I. and P2O5. hence SO3-- increases with increasing Cl-, this due to high content of SO3--, Cl- indicates evaporational effect enhancing deposition of sediments in semi restricted environment, while SO3-- has a strong positive correlation with the trace element Pb, Ba, Cu, Cr, B, Mno, Li and Zn and a negative correlation with the trace element Zr, Ni, Co, V, Sr and Rb.

Cl-:

Cl- in the studied samples has a positive correlation with L.O.I. and P2O5, and a strong positive correlation with the trace element Zr, Co, Cr, Rb, V, and a positive correlation with Ba, MnO, Cu and Zn. Hence Cl- increases with increasing L.O.I. and P2O5, while it has a negative correlation with the trace element Li, Pb, Ni, B, and Sr.

P2O5:

P2O5 in the studied samples has a positive correlation with L.O.I., and a strong positive correlation with the trace element Li, Rb, V, B, Cr, Co and a positive correlation with Zr, MnO, Zn and Cu, while it has a negative correlation with the trace element Sr, Ba, Pb and Ni.

TiO2:

TiO2 has a positive correlation with SO3--, Na2O, MgO, Fe2O3, and Al2O3, and a negative correlation with L.O.I. and P2O5, Cl- and MnO. Hence TiO2 increases with increasing SO3--, Na2O, and TiO2 increases with decreasing L.O.I., P2O5, Cl-, CaO and MnO.

TiO2 has a strong positive correlation with the trace element Rb, V, Co, Zr, Ni and a positive correlation with Zn, Cr, and B, while it has a negative correlation with the trace element Li, Sr, Pb, Ba, Cu and MnO.

MnO:

MnO has a positive correlation with L.O.I., P2O5, Cl, SO3, Na2O, K2O, CaO and MgO, hence MnO increases with increasing L.O.I., P2O5, Cl, SO3--, Na2O, K2O, CaO and MgO, while it has a negative correlation with Fe2O3 and Al2O3, hence MnO increases with decreasing Fe2O3 and Al2O3.

MnO has a strong positive correlation with the trace element Ni, Zn, Rb and a positive correlation with Co, Pb, Cr and V, where it has a negative correlation with the trace element Sr, Ba, Zr, Cu and MnO.

Li:

Li in the studied samples has a positive correlation with the trace element Ni and B and a negative correlation with the trace element Zn, Cu and Cr.

Co:

Co has a positive correlation with the trace element Rb, V, Ni, Zn and Zr and a negative correlation

relation with the trace element Pb.

Rb:

Rb has a positive correlation with the trace element Zr, V, Ni, Zn, Cr, and a negative correlation with the trace element Pb.

B:

B has a strong positive correlation with the trace element Cr and Cu, and a strong negative correlation with the trace element Ba, Ni and Zn.

V:

V has a positive correlation with the trace element Co, Cr, Zn and Zr, while it has a negative correlation with the trace element Pb.

Sr:

Sr has a strong positive correlation with the trace element Zn, Cu, Ba, Pb and Zr, while it has a strong negative correlation with the trace element Ni, Cr. Sr versus SiO2 shows independent relationship while Sr versus CaO shows general dependent relationship and Sr versus MgO diagrams show independent relationship, from the previously mentioned illustrations, it can be noted that strontium depends on CaO in its presence and it escapes during dolomitization.

Pb:

Pb has a negative correlation with the trace element Zr.

Cu:

Cu in the Esna shale sediments has a positive correlation with the trace element Cr, Ba, Pb, Sr, V and Zr, and a strong negative correlation with the trace element Li, Ni, Co and Zn.

Ba:

Ba has a positive correlation with the trace element Pb, Sr, V, Zn, and a positive correlation with the trace element Co, Zr, and Zn, while it has a strong negative correlation with the trace element Li, Ni, Sr, and Pb.

Ni:

Ni has a positive correlation with the trace element V, Zr and Zn, and a negative correlation with the trace element Sr and Pb.

Zn:

Zn has a positive correlation with the trace element Zr.

Depositional environment:

Abdel-Hameed et al (1999) concluded that

Esna Shale of El-Bruk area are deposited in open marine environment.

Ibrahim (1992) in his work mentioned that the constant composition of a common montmorillonite with common kaolinite, as well as un common illite or its complete absence indicate prevailing open marine conditions through the deposition of shale during which illite is completely transformed to montmorillonite.

Montmorillonite can be formed under different climatic conditions and from different source rocks (Weaver (1989).

The correlation between K_2O/Al_2O_3 and MgO/Al_2O_3 can be used to discriminate between marine and non marine clay (Roaldest, 1978). according to this correlation the present study samples of Esna Shale (Fig. 18) are deposited in marine environment.

Garrels and Christ (1965) and Weaver(1967), K/Na and K/Mg ratios are equally important (low ratios favour the formation of montmorillonite and chloritic materials and high ratios favour the formation of illite) and high values are more likely to occur in continental than marine environments. According to above the most of the study samples shown low value of K/Na and K/Mg ratio, this indicate that these sediments deposited in marine environment.

According to above mineralogical study (by using XRD) revealed that the predominant of montmorillonite in some sample of the two study areas, It is suggested that montmorillonite has been formed on the exposure of illite. These

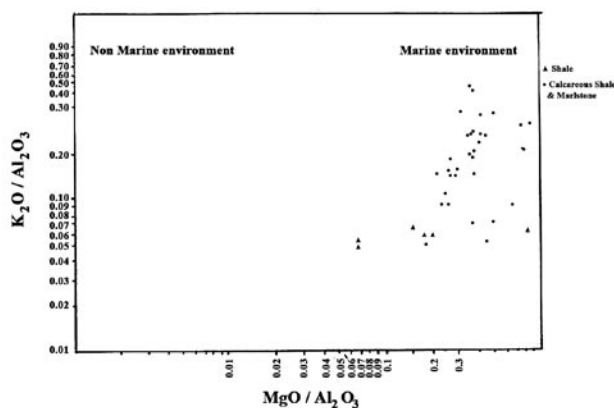


Fig. 18: Correlation between K_2O/Al_2O_3 and MgO/Al_2O_3 of studied samples.

changes could be occurred as a result of ion-exchange in marine condition.

Chilingar et al. (1967) stated that in as much as , shallow near shore waters are systematically warmer as a rule than deep off shore waters, the gross of Ca/Mg ratio of a mixed detrital carbonate sediments reflects temperature, depth, distance from shore relationships". He confirmed Chave (1954) observation that is an inverse relationship between the Ca/Mg ratio and the environmental temperature. Chave (1954) concluded that there is an increase in Mg content with increase of temperature. According to above it can be concluded that the shale of the study area are deposited in shallow near shore warm waters while calcareous shale and argillaceous limestone are deposited in deep off shore waters with low temperature.

El-Sabrouty, M. (2003) distinguish the paleoenvironmental conditions as an open marine deposition under a warm humid climate at the time of the Esna shale sedimentation in the North- Central Sinai.

Hassan et al. (1993) studied the variation of CaO / MgO in relation to the variation of the microfacies of the Eocene carbonates in the Nile valley and the Eastern Desert and concluded environmental changes with the change of CaO / MgO ratio as follows:-

- 1- The CaO / MgO ratio less than 10 reflects deposition in very shallow inner neritic zone.
- 2- The CaO / MgO ratio range from 10 – 50 reflects deposition in shallow inner neritic zone.
- 3- The CaO / MgO ratio range from 50 – 100 reflect deposition in deep water inner neritic.
- 4- The CaO / MgO ratio more than 100 reflects deposition in an outer neritic.

According to above the clays and argillaceous rocks of Esna shale of the study areas are deposited in depositional environments changes from very shallow inner neritic zone to outer neritic zone.

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