5 Geochemistry

The geochemistry is concerned primarily with quantitative analysis, which measures the concentration of elements, compounds, isotopes or chemical species (e.g. Fe^{2+} as distinct from Fe^{3+}). In dealing with rocks, sediments and minerals, it is useful to distinguish between major elements (those present at concentrations exceeding 1 % by mass, making up the main minerals of the rock), minor elements (concentrations between 0.1 % and 1.0 %) and trace elements (concentrations less than 0.1 %). In drawing these distinctions, one should recognise that the same element may be a major element in one type of sample, e.g. sulphur in an ore concentrate, but a trace element in another, e.g. sulphur in fresh basalt (Gill 1997).

The occurrence of characteristic fossils and gross lithologic aspects of a sediment have been and still are the principal methods of environmental interpretation. However, the geochemical distribution of certain major, minor and trace elements may provide direct information on the depositional environment of the host sediments. It is emphasized, however, that it may be misleading to attempt to use the absolute abundance values of a single element as an indicator of the environment (Degens et al. 1957). Indications of the depositional environment can be revealed by elements adsorbed on organic or inorganic materials from the surrounding waters. The indicators can be incorporated into primary minerals or into organic substances forming in these waters, or they can be incorporated into authigenic minerals growing within the sediments during or shortly after their deposition (Cody 1971).

According to Degens et al. (1957) a good environmental indicator for marine or non-marine sediments should be: 1) markedly affected by salinity changes; 2) relatively widespread; 3) abundant enough to be detected and measured with a reasonable degree of precision;
4) formed or concentrated in the rock in which it is formed; and 5) relatively unaffected by post-depositional changes. There is an abundance of literature with respect to trace elements, whole rock composition, isotope ratios, exchangable cations and other methods used in determining the environment of deposition. So far no technique has proved to be an "ideal" indicator of paleosalinity (Walters et al. 1987).

The studied samples consists mainly of carbonaceous shale and associated phosphate, limestone and marl sediments. The geochemical investigations were performed to investigate mainly shale samples. Other associated sediments are represented in small numbers.

5.1 Major and trace elements

Major and trace elements on whole rock of 48 carbonaceous shale samples and seven samples of the associated phosphate from the studied five locations were analysed by XRF. The results of the XRF analysis of the samples is presented in Appendix (Table 4 & 5). The abundance of major elements for all analysed samples are presented graphically in figure10.
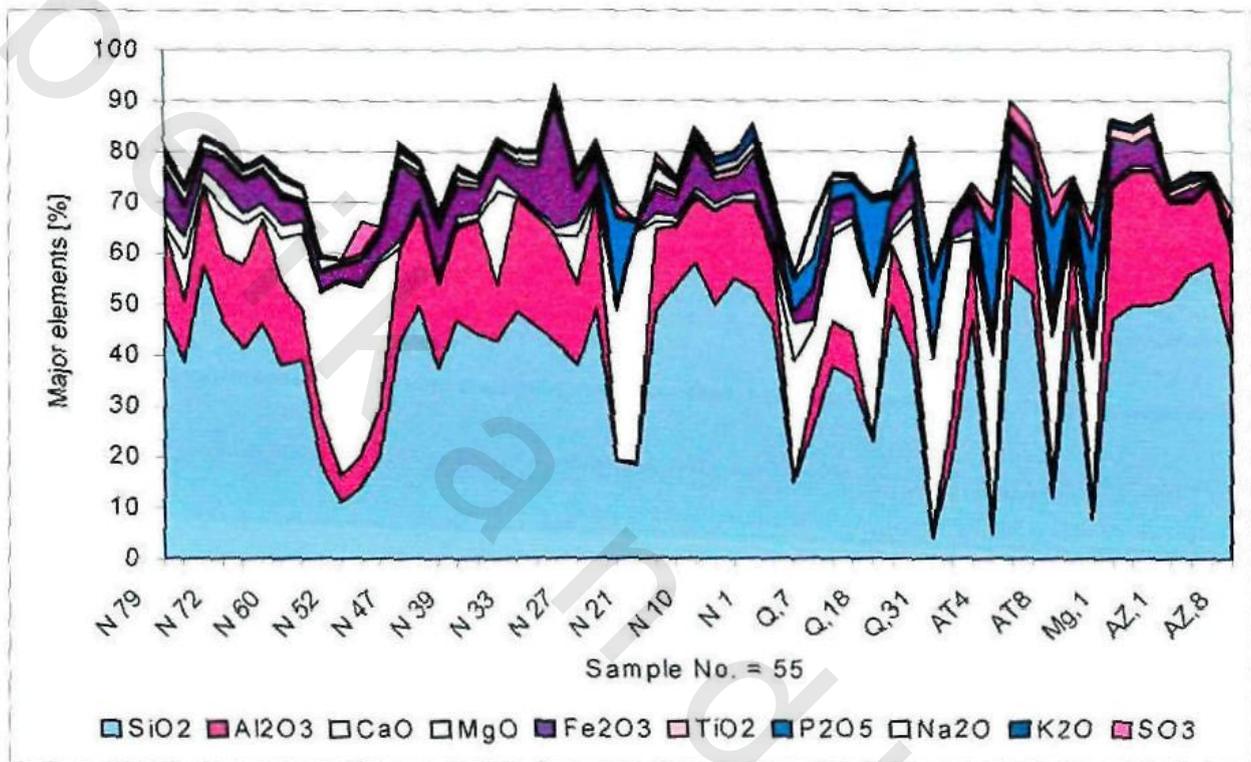
The major constituents are SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, P_2O_5, Na_2O, K_2O, SO_3.

AZ = Abu Zinema area (Carboniferous).

Mg = Al Maghara coal mine(Jurassic).

AT = Abu Tartur phosphate mine (Cretaceous).

Q = Quseir phosphate mines (Cretaceous).

N = Nile Valley section (Cretaceous –Eocene).

Fig. 10: Major elements variation of the studied samples including 7 phosphate samples.

The major and trace elements composition of the carbonaceous shales in this study is compared to published average shales in Table 2. In general, the bulk compositions of the carbonaceous shales in the present study compares quite closely with the published average shale compositions.

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Table 2: Comparison of chemical composition of the studied shales with published average shales (1 to 4) and regional average composition (5 to 8).

	present study n =48	1	2	3	4	5	6	7	8
SiO_2 %	45.80	64.82	58.10	58.50	n.a.	8.50	6.92	35.44	52.50
Al_2O_3 %	16.80	17.05	15.40	15.00	13.22	2.90	1.98	9.82	15.41
TiO_2 %	1.04	0.80	n.a.	0.77	0.33	0.10	0.15	0.43	0.71
Fe_2O %	4.80	5.70	4.02	4.72	2.86	1.20	1.12	3.97	7.04
MgO %	1.40.	2.83	2.44	2.50	1.77	0.60	0.99	3.56	3.99
CaO %	5.12	3.51	3.11	3.10	2.10	32.30	40.70	18.30	4.36
Na_2O %	0.75	1.13	1.30	1.30	0.94	n.a.	0.04	0.66	1.48
K_2O %	0.84	3.97	3.24	3.10	2.41	n.a.	0.04	0.70	0.15
P_2O_5 %	0.62	0.15	n.a.	0.16	n.a.	1.80	1.89	3.34	1.48
Sr ppm	252	142	n.a.	300	200	940	1117	466	333
Ba ppm	99	636	n.a.	580	300	99	n.a.	143	116
V ppm	155	130	n.a.	130	150	78	78	639	205
Ni ppm	47	58	n.a.	68	50	136	594	124	57
Cr ppm	148	125	n.a.	90	100	256	305	277	136
Zn ppm	84	n.a.	n.a.	95	300	271	322	578	169
Cu ppm	25	n.a.	n.a.	45	70	83	60	56	42
Zr ppm	167	200	n.a.	160	n.a.	n.a.	n.a.	47	126

1= NASC (Gromet et al. 1984); 2= Average shale (Pettijohn 1975); 3= Average shales (Turekian and Wedepohl 1961); 4= Average black shales (Vine and Tourtelot 1970); 5= Average Israelian black shales (Ahmed 1997); 6= Average Jordanian black (oil) shales (Abed and Amireh 1983); 7= Average Quseir and Safaga (Eastern Desert, Egypt) black shales (Ismael 1996); 8= Average Abu Tartur (Western Desert, Egypt) black shales (Ahmed 1997). n.a. = not available

The average of major and trace elements for the studied formations is shown in Table 3. The major constituents are SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, P_2O_5, Na_2O, K_2O and SO_3 The trace elements measured are Sr, Ba, V, Ni, Cr, Zn, Cu, Zr, Rb, Cl and F.

The Dakhla Shale in Quseir mines shows the highest values for the trace elementsV, Ni, Cr, Zn and Cu (1357, 71, 344, 757 and 116 ppm respectively) due to oxidation of the organic matter in the in the Quseir mines (see chapter 5.2).

Table 3: The major and trace elements average of formations at the studied locations

Location	Nile Valley Section					Quseir Mines	Abu Tartur Mine	Al Maghara Mine	Abu Zinema area
	Esna Shale	Tarawan Chalk	Dakhla Shale	Duwi Fm.	Varigated Shale	Dakhla Shale	Duwi Fm.	Safa Fm.	Ataqa Fm.
SiO_2 %	41.52	12.53	42.29	44.70	52.53	36.20	51.10	48.86	51.58
Al_2O_3 %	14.51	5.77	18.20	10.20	17.00	10.00	15.83	26.21	17.03
CaO %	8.35	35.61	4.86	12.10	0.18	14.80	1.62	0.35	0.42
MgO %	2.61	0.63	1.54	1.10	1.32	1.70	2.70	0.78	0.30
Fe_2O_3 %	5.18	3.43	8.32	4.35	5.02	4.77	5.61	6.42	0.79
TiO_2 %	0.66	0.30	0.82	0.70	1.29	0.50	0.80	2.12	0.95
P_2O_5 %	0.18	0.17	0.13	0.42	0.24	2.52	0.62	0.09	0.05
Na_2O %	1.85	0.71	1.33	1.56	1.52	1.55	0.10	0.11	0.50
K_2O %	0.82	0.26	0.61	0.80	2.03	0.70	1.10	0.93	0.69
SO_3 %	0.26	3.15	0.34	0.50	0.26	0.50	2.10	0.47	1.21
Sr ppm	353	846	211	344	781	479	257	109	47
Ba ppm	145	53	81	201	163	90	84	87	108
V ppm	168	80	187	101	136	1357	175	158	128
Ni ppm	57	34	49	27	24	71	33	71	15
Cr ppm	171	149	183	100	105	344	115	196	75
Zn ppm	142	41	102	71	48	757	51	91	76
Cu ppm	22	12	21	26	31	116	23	25	25
Zr ppm	97	42	96	193	275	105	121	561	243
Rb ppm	44	12	25	26	61	30	27	40	27
Cl ppm	3006	720	2458	3123	2234	7217	63	109	2886
F ppm	1076	800	426	881	858	3292	472	36	800

On the following a discription and detailed discussion of the important and affective major and trace elements in the geochemistry of the studied carbonaceous shale and associated phosphate samples.

5.1.1 Silica (SiO$_2$)

Silica is the dominant constituent of all studied shale samples. The average content of silica in the samples is 45.80%. With exception of carbonate and phosphate samples, the silica averages are 51.58%, 48.86 %, 51.10 %, 36.20 % and 45.30 % in Abu Zinema, Al Maghara, Abu Tartur, Quseir and Nile Valley samples respectively.

Considerably higher average SiO$_2$ contents exist in NASC and average shales of Pettijohn (1975) is 64.82% and 58.50% respectively. The black shales of the neighbouring countries contain much less SiO$_2$ compared to the studied shales. In the Jordanian black shales the average SiO$_2$ is 6.92% (Abed and Amireh 1983) and 8.5% in the Israelian oil shales. Both Jordanian and Israelian oil shales are also markedly depleted in Al$_2$O$_3$ and TiO$_2$. This may indicate a black argillaceous limestone rather than a proper black shale (Ahmed 1997). The lower content of SiO$_2$ in the studied shales from Quseir confirms the previous study by Ismael (1996). This may be attributed to their enrichment in carbonate minerals. Silica tends to decrease with the increase of carbonates. Therefore, a positive relation between silica and argillaceous sediments on the one hand, a negative relation on the other hand can be expected denoting the different environmental conditions of siliceous and calcareous sediments (Abdou 1989).

According to the Pearsons correlation coefficient (r) Appendix (Table 6a), the SiO$_2$ is positively correlated with Al$_2$O$_3$, TiO$_2$ and K$_2$O (r=0.59, 0.57 and 0.52 respectively). Therefore SiO$_2$ is considered to be dominantly terrigenous in origin which is shown in a scatterplot of SiO$_2$ with Al$_2$O$_3$, TiO$_2$, Zr and K$_2$O (Fig. 11). A part of the silica may be attributed to a biogenic origin by silica secreting organisms, such as radiolaria or diatoms, thus the SiO$_2$ contents in Nile Valley and Quseir samples should be based on a biogenic origin. Silica may also be precipitated as cement filling cavities. The SiO$_2$ may occur as quartz disseminated with kaolinite, or deposited with the tiny flakes of the clay minerals (Bain and Smith 1987; Moore and Reynolds 1997).

Pettijohn (1975) stated that silica is present in shales as a part of the clay minerals, as undecomposed detrital silicates and as free silica, both detrital quartz and biochemically precipitated silica such as opal of radiolarians, diatoms, and spicules. The SiO$_2$ content in the studied shales correlates positively with Al$_2$O$_3$. This indicates that SiO$_2$ is mainly present in the studied shales as a part of the clay minerals and detrital silicates.

The SiO_2/Al_2O_3 ratio of the studied samples is listed in Appendix (Table 4). Felix (1977) reported that the SiO_2/Al_2O_3 ratio for pure montmorillonite ranges from 2.80 to 3.31 while for pure kaolinite it is about 1.18. With exception of the Al Maghara shale samples which recorded SiO_2/Al_2O_3 ratios somewhat similar to that of kaolinite (1.82, 1.88 and 1.89 for sample Mg1, Mg3, and Mg5 respectively), this is confirmed by the XRD results. The SiO_2/Al_2O_3 ratio for samples from other locations varies between (1.93 and 5.33) higher than that for pure kaolinite and also higher than that for pure montmorillonite. This may be indicate that the clay mineralogy of these locations (Abu Tartur, Nile Valley and Quseir) consists mainly of smectite and/or a mixture of smectite and kaolinite or chlorite. This has also been confirmed by XRD. The abundance of Si, Al, Ti and K in shales may be perturbed from parent material by weathering, transport and depositional processes (Nesbitt et al. 1980).

5.1.2 Alumina (Al$_2$O$_3$)

High alumina contents are recorded in the argillaceous and clayey sediments. The average content of alumina in the studied shales of the different localities (16.80%) is similar to that of average shales of Pettijohn (1975) and NASC (15.40% and 17.05 % respectively), slightly higher than that of the average black shales (13.22%) of Vine and Tourtelot (1970) but much higher than the argillaceous black sediments of Jordanian (1.98%) and Israelian shales (2.90 %) (Ahmed 1997). With the exception of carbonate and phosphate samples, its averages are 17.03%, 26.21%, 15.83%, 10.00% and 15.00 % in Abu Zinema, Al Maghara, Abu Tartur, and Quseir and Nile Valley samples respectively.

The Al_2O_3 concentration is thought to be a good measure of detrital influx. The positive correlation between Al_2O_3 and both SiO_2, TiO_2, and Zr (r=0.59, 0.79 and 0.54 respectively) and the positive trend in scatterplot of Al_2O_3 with both SiO_2 and TiO_2 (Fig.11) can be explained by a terrigenous origin. This may be due to the presence of a considerable amount of detrital clays. Generally the studied shales show coherence between silica and alumina Appendix (Table 4) indicating that both molecules are carried mainly in the clay minerals.

5.1.3 Calcium (CaO)

The average content of CaO in the studied mere shale samples is 5.12 %. With the exception of carbonate and phosphate samples, its averages are 0.42%, 0.35%, 1.61%, 14.80 % and 6.38 % in Abu Zinema, Al Maghara, Abu Tartur, Quseir and Nile Valley respectively.
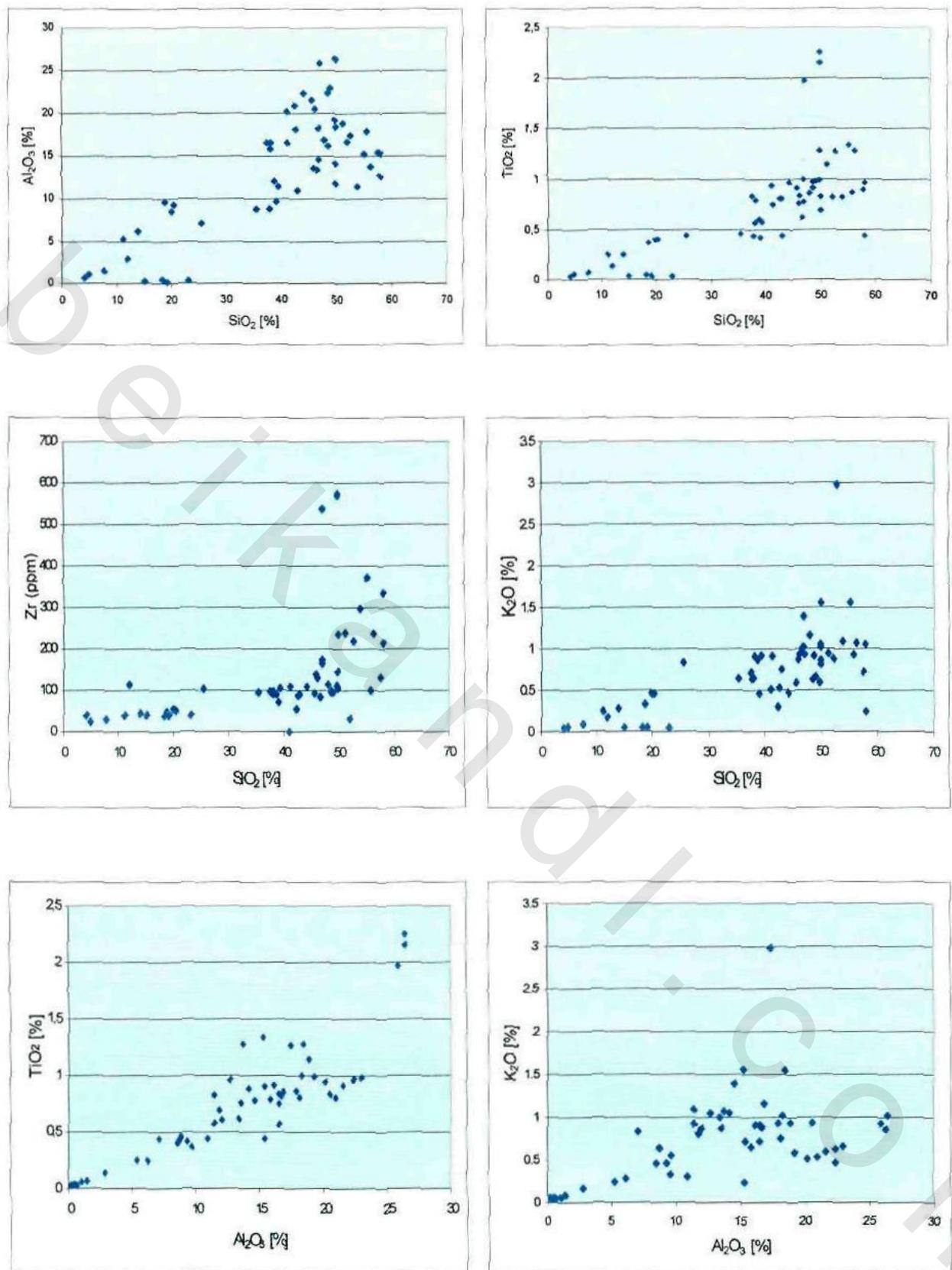
Fig. 11 : The relationships between SiO_2 with Al_2O_3, TiO_2, Zr & K_2O and Al_2O_3 with TiO_2 & K_2O for the studied samples

The mean value of CaO in the studied shales at Abu Zinema, Al Maghara and Abu Tartur is relatively lower than that of average black shales 2.1 % of Vine and Tourtelot (1970) and average shales 3.15 % of Pettijohn (1975), while the mean value of Nile Valley samples being closely similar to NASC (3.56 %). The average content of CaO in Quseir shale samples in the present study is 14.80 %, slightly similar to a value of 18.3 % by (Ismael 1996) in Quseir.

Jordanian and Israelian oil shales are more calcareous (40.7 % and 32.3 % CaO respectively, Ahmed 1997). CaO shows a negative correlation with SiO_2, Al_2O_3, TiO_2 and K_2O (r = -0.89, -0.77, -0.63 and -0.50 respectively) (Fig.12). This reflects a different source of CaO and these elements. CaO is considered to be dominantly of biochemical origin, while SiO_2, Al_2O_3, TiO_2 and K_2O are of terrigenous origin. CaO may be used as marine indicator because, marine shales often have considerably more calcium than non-marine ones (Refaat 1993). The obtained data show that the shales at Abu Zinema, Al Maghara and the lower part of Nile Valley section, which are considered as non-marine shales, have an average CaO lower than those of the shales which are considered as the marine shales of Abu Tartur, Quseir and Nile Valley Appendix (Table 4).

5.1.4 Magnesium (MgO)

The average content of MgO in the studied shales samples is 1.40 %. Its averages are 0.30 %, 0.78 %, 2.70 %, 1.70 % and 1.70 % in Abu Zinema, Al Maghara, Abu Tartur, Quseir and Nile Valley respectively. It is closely similar to those of average black shales Vine and Tourtelot (1970), average shales of Pettijohn (1975), NASC shales, shales of Jordanian and Israelian oil shales (1.17%, 2.5%, 2.85 %, 0.99 % and 0.6 % respectively).

MgO may be present as:
1- Octahedral and interlayer cation in the clay lattices. Mg^{2+} and Ca^{2+} substitute Al^{3+} in the octahedral sites of smectite or illite for not more than 2.7 % (Weaver and Pollard 1973). Na^+ and Mg^{2+} ions are the major exchange cations in marine smectite.
2- Mg^{2+} may substitute Ca^{2+} in early formed calcite in the form of dolomite and ferroan dolomite. MgO shows a weak negative correlation with CaO (r = -0.15; see Fig.12) and Appendix (Table 6a). This reflects a different source of both of the elements. The study of thin sections indicates that Ca is of biogenic source and Mg of diagenetic origin by dolomitization.
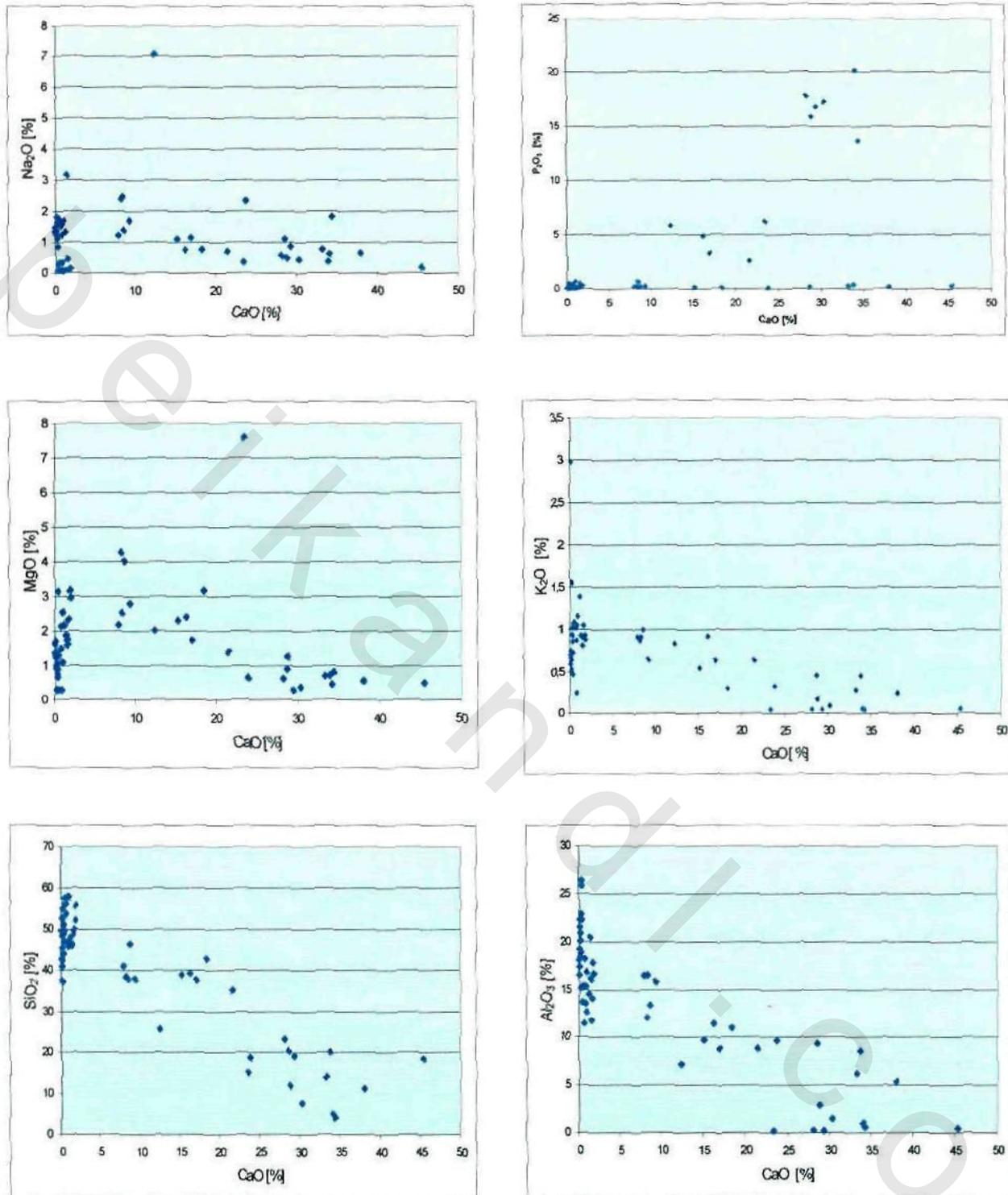
Fig. 12: The relationship between CaO with Na₂O, P₂O₅, MgO, K₂O, SiO₂ & Al₂O₃ for the studied samples.

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5.1.5 Iron Oxide (Fe$_2$O$_3$)

The average content of Fe$_2$O$_3$ in the studied shales samples is 4.80 %. Its averages are 0.79 %, 6.42 %, 5.61 %, 4.77 % and 5.72 % in Abu Zinema, Al Maghara, Abu Tartur, Quseir and Nile valley respectively. With the exception of Abu Zenima shales, the recorded averages are higher than those of average black shales of Vine and Tourtelot (1970), average shales of Pettijohn (1975), Jordanian and Israelian oil shales (2.86 %, 4.72 %, 1.12 % and 1.20 % respectively), and close to that of NASC (5.70 %).

Iron is present either in the structure of clay minerals and/or as an independent Fe-mineral such as goethite. Sharma (1979) stated that in the marine environment, the hydroxides of iron are carried as particles and colloids in suspension and therefore, tend to aggregate in the fine fraction of sediments. The enrichment of Fe$_2$O$_3$ in the studied shales may be attributed to their formation under more reducing conditions with a high input of non-reactive iron to the basin (Ahmed 1997). There is a weak positive correlation between Fe$_2$O$_3$ and the SiO2, Al$_2$O$_3$, MgO, TiO$_2$, Na$_2$O Appendix (Table 6a) and positive correlation between Fe$_2$O$_3$ and Ni. This may be due to the association of Fe^{3+} with clay minerals.

5.1.6 Titanium (TiO$_2$)

The average titanium oxide content of the studied shale samples is 1.04 %, slightly higher than that of average crustal shales of Turekian and Wedepohl (1961) and NASC (0.77 % and 0.78 %) and higher than the average black shales of Vine and Tourtelot (1970) (0.33 %). The TiO$_2$ content of the studied samples is much higher than those of Jordanian and Israelian oil shales (0.15 % and 0.1 % respectively).

The strong positive correlation of TiO$_2$ with Al$_2$O$_3$ and Zr (r=0.79 and 0.87) Appendix (Table 6a) and (Fig.13). This may suggest that Ti is essentially associated with clays and reflecting its terrigenous origin. TiO$_2$ is usually disseminated within the clays as discrete minerals, e.g. rutile and anatase (Degens 1965). TiO$_2$ shows a strong negative correlation with the marine indicators or constituents e.g CaO and P$_2$O$_5$ (-0.63, -0.20) and weak negative correlation with MgO and SO$_3$ Appendix (Table 6a). This reflects the different sources of TiO$_2$ and these elements, and is indicating the detrital origin of TiO$_2$.
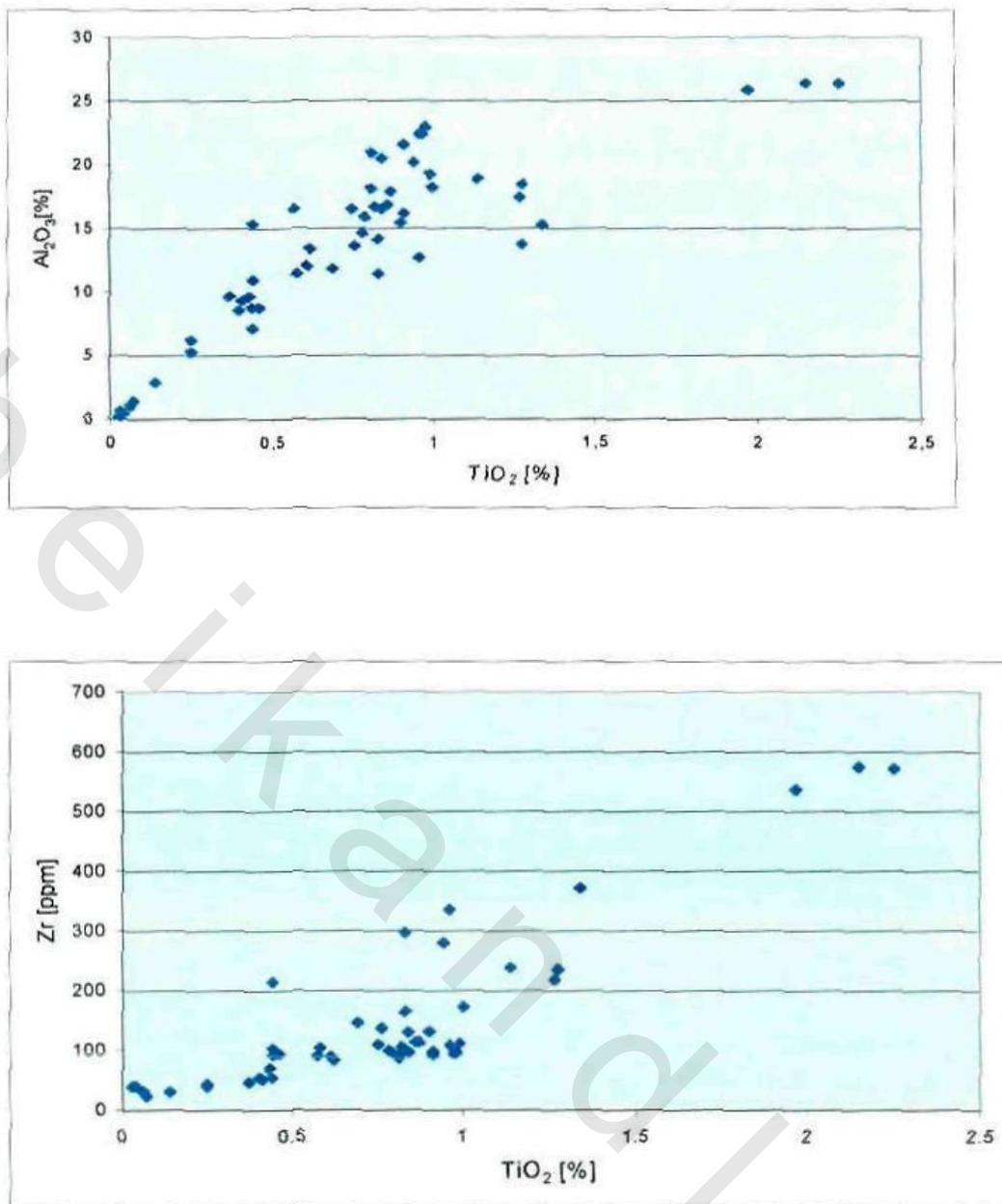
Fig. 13: The relationship between TiO₂ with Al₂O₃, and Zr for the studied samples.

5.1.7 Phosphorus (P₂O₅)

The studied shales show a wide range of phosphorus content. High amounts of phosphorus are due to the presence of apatite or collophane. The mean value of P_2O_5 in the studied shales is 0.62 %. This is higher than those of the average shales of Turekian and Wedepohl (1961) and NASC (0.16 % and 0.11%) and lower than those of the Jordanian and Israelian oil shale (1.89 % and 1.80 %). Shales samples collected from the phosphate mines have higher P_2O_5 content than those collected from the other locations.

5.1.8 Sodium (Na₂O)

The mean value of Na_2O (0.75%) is slightly similar to that of average black shales 0.94 %of Vine and Tourtelot (1970) and lower than those of average shales of Turekian and Wedepohl (1961) and NASC (1.30 % and 1.15 % respectively), while it is higher than those of Jordanian and Israelian oil shales (0.043 %). Na_2O shows a negative correlation with SiO_2, Al_2O_3, and CaO. This may be due to the presence of Na_2O in the form of water soluble salts (mainly halite). Halite was detected by XRD analysis in some of the studied shale samples.

5.1.9 Potassium (K₂O)

The average content of potassium in the studied shales (0.84 %) is lower than those of the average black shales of Vine and Tourtelot (1970), the average shales of Turekian and Wedepohl (1961) and the NASC shales (2.41 %, 3.10 % and 3.99 % respectively). This may be due to the enrichment of clays in those shales mixed-layer, different to the studied shales, where smectite clays dominate. The mean value of K_2O is higher than those of Jordanian and Israelian oil shales (0.042 % and 0.04 %). K_2O shows a positive correlation with SiO_2, Al_2O_3, TiO_2, Zr, Cu and Rb (r = 0.52, 0.28, 0.48, 0.35, 0.57 and 0.82 respectively). This indicates the association of K_2O with aluminosilicate phases.

The K_2O content is in agreement with the results of the clay mineral investigations, because the low content reflects the absence of or the low content of illite minerals (see chapter 4). The weak negative correlation of K_2O with SO_3 (r = -0.11) in samples with less illite content can be interpreted that potassium is preferentially adsorbed by clays (Millot 1970).

5.10 Sulphate (SO₃)

The average content of SO_3 in the studied shales (0.62 %) is higher than the content in average shales (0.60 %) of Turekian and Wedepohl (1961). The high value of SO_3 in the black shale of Abu Tartur Phosphate mine may be due to the fact that SO_3 primarily occurs in pyrite and also may occur in gypsum. This corresponds to the results of the XRD and SEM analyses. XRD shows pyrite in the Duwi Formation in Abu Tartur and gypsum in Dakhla and Esna Shale. SEM study shows pyrite framboids in the Duwi Formation in Abu Tartur.

5.2 Distribution of significant trace elements

5.2.1 Vanadium

In the studied shales, vanadium attains an average concentration of 155 ppm and varies from 20 ppm to 3151 ppm. The average vanadium content in the studied samples is higher than those of average shale (130 ppm) of Turekian and Wedepohl (1961) and also higher than vanadium in average black shale (150 ppm) of Vine and Tourtelot (1970). It has been suggested that some V may be complexed within the kerogene molecule. The high concentrations of V in the inorganic fraction may be the result of oxidation and weathering of the organic matter and the subsequent mobilization and concentration in host rocks (Riley and Saxby 1983).

Vanadium shows a positive correlation with some of the other trace elements, such as Ni, and Cr (r=0.46 and 0.52) Appendix (Table 6a) and (Fig.14). This association is considered to be typically of organic matter (Krauskopf 1956; Gulbrandsen 1966; Cook 1972). Vanadium shows positive correlation with Al_2O_3, TiO_2, the clay fraction and also a positive correlation with TOC (Fig.14). This indicates that vanadium is considered to be typically of organic matter association rather hosted by detrital silicate minerals (Stow and Atkin1987).

In the calcitic samples, the vanadium content is lower than in the dolomitic ones. This is mainly attributed to differences in the clay mineral content and not to the type of carbonates. The highest value of vanadium in the present study was recorded in the calcareous shale samples of Quseir mines at 3150 ppm. This is due to the oxidation and weathering of organic matter in these samples and subsequent mobilization and concentration of vandium.

5.2.2 Nickel

The average Ni content in the studied samples is 47 ppm, lower than Ni in average shale 68 ppm of Turekian and Wedepohl (1961) and also slightly lower than Ni in average black shale (50 ppm) of Vine and Tourtelot (1970). Nickel shows strong positive correlation with Cr and Zn (r = 0.61and 0.64) Appendix (Table 6a). Nickel shows also positive correlation with TOC and slightly positive correlation with Al_2O_3, TiO_2 and clay fraction (Fig.14). This indicates an association of these elements mainly with the organic matter and clay.
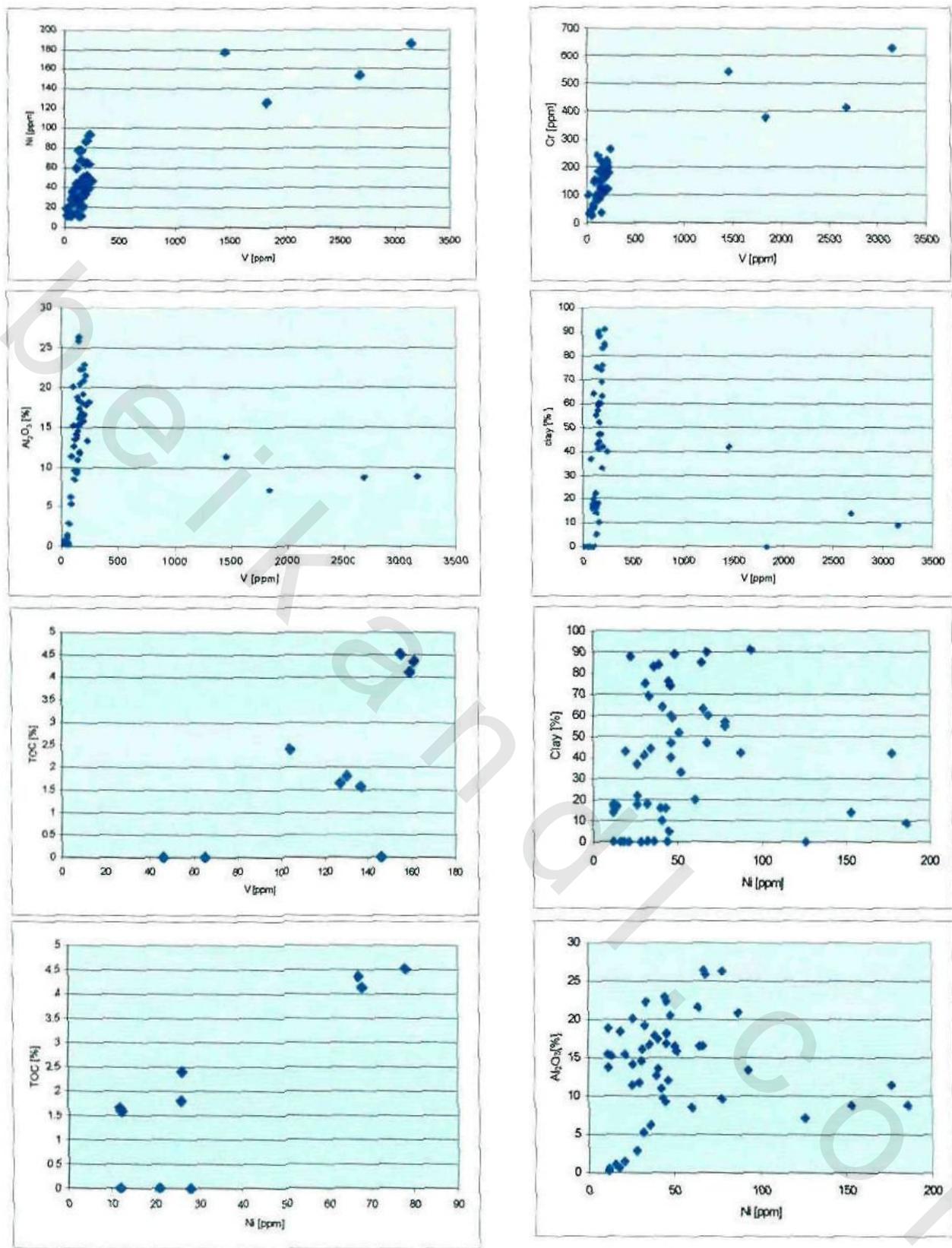
48

Fig. 14: The relationships between V with Ni, Cr, Al₂O₃, clay & TOC and Ni with clay,
TOC & Al₂O₃ for the studied samples.

Nickel, when present in significant quantities, originates from ultrabasic and basic rocks (Shapiro and Breger 1968). Weathering of such rocks and mobilization by humic acids may contribute to the high concentration of Ni in seawater. Turekian (1978) stated that, Ni is abundant in deep marine sediments (up to 300 ppm) but much less so in coastal sediments (39 ppm). Average contents of Ni are also less than 100 ppm in shales, 50 ppm in the black shales of the United States, 41 ppm in marine clays, 13 ppm in oil and only a few ppm in limestones. Phosphate rocks have an average content of 50 ppm similar to those of black shales, but a higher content than those of most other types of sediment. Nevertheless, Ni concentration in sea water is the order of 0.5 to 2 ppm, follows the trend of that of the nutrients P and Si and like the concentration of Zn, generally the Ni content is higher in reduced sulphidic areas compared to oxygenated areas. Moreover, Ni is concentrated in trace amounts in all organisms.

Brumsack (1980) found that the elements Ni, Cu, Zn and Fe are almost always associated with sulphides and hence concluded that normal seawater is sufficient to account for the high metal concentration in black shales: he further considered that despite of a definite correlation of the metal organic carbon, the organic matter is not regarded to be responsible for heavy metal concentrations.In the present study the low Ni content indicate that it associated with organic matter.

5.2.3 Chromium

The average chromium content of the studied samples is 148 ppm. This is higher than the Cr content in average shale (90 ppm) of Turekian and Wedepohl (1961) and also higher than Cr in average black shale (100 ppm) of Vine and Tourtelot (1970). Cr shows a weak positive correlation with Al_2O which may be due to the adsorption of Cr on the surface of clays or due to the replacement of Al_2O_3 by Cr in clays. However, Cr may be adsorbed on iron and manganese oxides, clays, apatites and organic matter (Prevot 1990).

Cr, V, Zn and Cu are always strongly intercorrelated (Fig. 15). There is a positive correlation between Cr, V and Ni (r = 0.52, and 0.61) Appendix (Table 6a). This association indicate that these elements are incorporated in organic matter and clay minerals. Cr shows also a positive correlation with TOC and a slightly positive correlation with Al_2O_3 and the clay fraction (Fig.15). This indicates an association of these elements mainly with the organic matter and the incorporation into the clays fraction. Cr was presumably derived from a source dominated
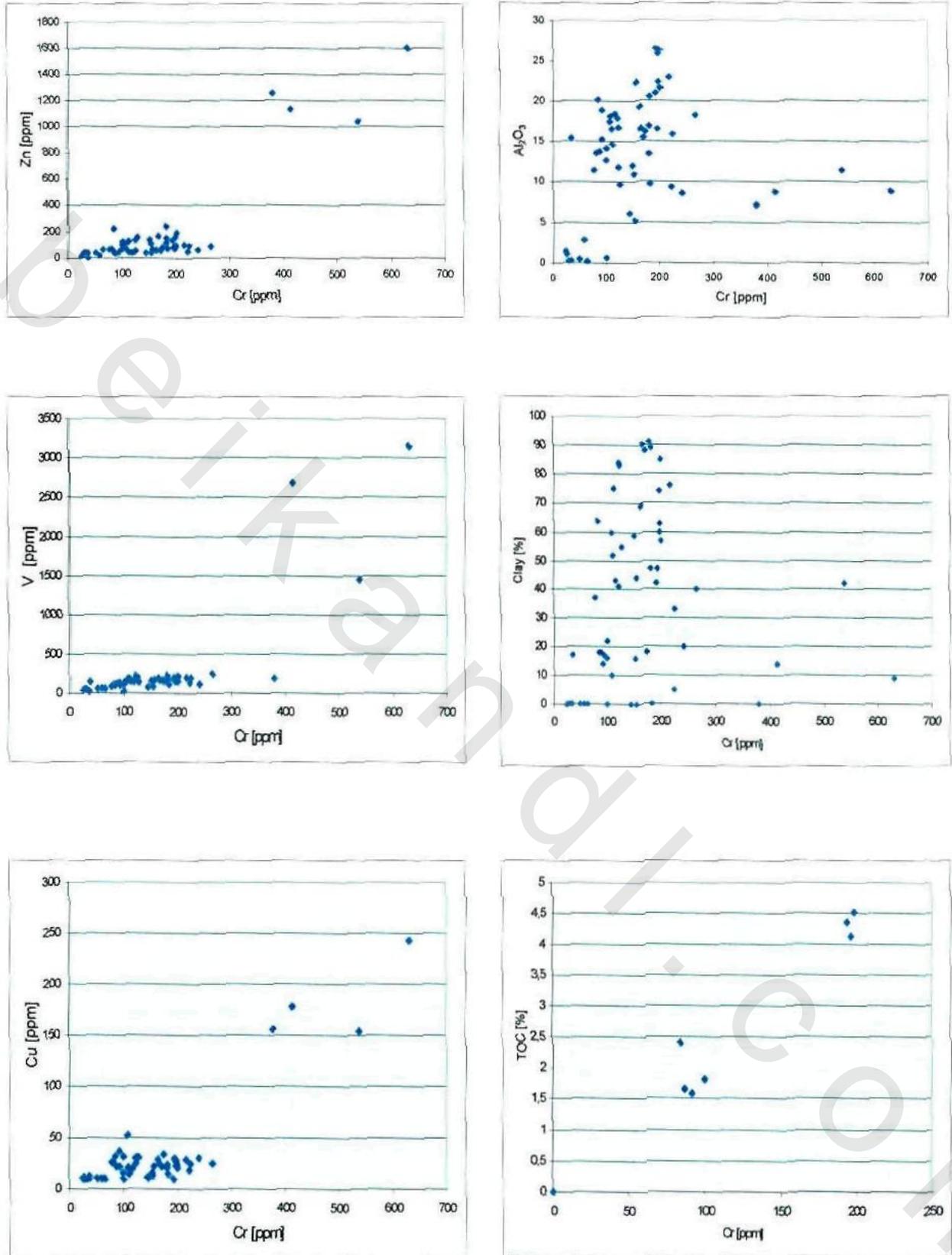
Fig. 15: The relationship between Cr with Zn, Al₂O₃, V, clay, Cu and TOC for the studied samples.

by mafic volcanic rocks (Gill 1981). High Cr and Ni concentrations and the positive correlation between the two elements have been used as an indicator of mafic and ultramafic provenance for the sedimentary origin. The concentration of Cr and Ni in shales further reflects the incorporation of Cr and Ni ions into clay particles during the weathering of ultramafic rocks containing chromite and other Cr and Ni-bearing minerals (Garver et al 1994). The enrichment in Cr and Ni in the studied shales may indicate that mafic to ultramafic components were among the basement complex, the sediments were derived from.

5.2.4 Cobalt

The studied samples show Co contents less than 10 ppm, with the exception of Al Maghara samples which recorded high values of Co (sample No. mg1, mg3 and mg5 with 29, 25 and 36 ppm respectively) and also a few samples from the Nile Valley section. The cobalt content in the studied samples is lower than Co in average black shale (10 ppm) of Vine and Tourtelot (1970). This indicates that cobalt is not significantly adsorbed nor incorporated into the clay minerals or the organic matter admixed with the samples (Ismael 1996).

5.2.5 Strontium

Strontium is abundant in the studied shale samples. It ranges between 17 ppm and 1703 ppm with an average of 252 ppm. This average is higher than the Sr content in the average black shale (200 ppm) of Vine and Tourtelot (1970) and lower than the Sr content in both the average shale (300 ppm) of Turekian and Wedepohl (1961) and the average Israelian black shales (940 ppm) of Ahmed (1997) and the average Jordanian black shale (1117 ppm) of Abed and Amireh (1983). Sr may be concentrated by non-calcareous plankton (Knauer and Martin 1973), and especially aragonitic materials and shells, as well as by primary apatite in bones and teeth of vertebrates. In the present study, with the exception of black shale of Carboniferous and Jurassic age from Abu Zinema and Al Maghara, the studied shales show high strontium values. This related to the association of Sr with CaO and organic matter.

5.2.6 Zinc

The average zinc content in the studied samples is 84 ppm. This average is lower than Zn in average shale (95 ppm) of Turekian and Wedepohl (1961) and lowers than Zn in average black shale (300 ppm) of Vine and Tourtelot (1970).

Like chromium, zinc shows a positive correlation with the Ni element (r =0.64) which may be explained as related to organic matter. With its ionic radius of 0.83 Å, Zn is liable to replace bivalent cations, such as Ca, Mg and Fe. Zn is reported to induce aragonite formation (Angus et al. 1979), but 20 to 140 ppm of Zn could also coprecipitate with calcite (Pomerol 1984). Zn is adsorbed on clay minerals and iron manganese oxides.

5.2.7 Copper

Copper is one of the elements which is indispensable to living organisms, however it becomes very highly toxic at high concentrations. This explains its association with organic matter in organic sediments but always in very moderate amounts. Black shales and bituminous clays are rich in Cu with a content of about 90 ppm (Prevot 1990). The black shale of Abu Tartur area contains moderate contents of Cu (23 ppm). This value is intermediate between those reported for bituminous clays and shallow marine sediments (Ahmed 1997). Ismael (1996) indicates that copper is somewhat enriched in the <2μm fraction of Quseir shales, thus revealing its adsorption or incorporation into the clay minerals.

In the present study the average copper content is 25 ppm. This is lower than copper in the average shale (45 ppm) of Turekian and Wedepohl (1961) and in the average blacke shale (100 ppm) of Vine and Tourtelot (1970). Copper shows a positive correlation with Rb(r = 0.52). This indicates that copper is associated with organic matter and clay minerals..

5.2.8 Zirconium

Zirconium in the studied shale samples shows an average of 97 ppm. This average is lower than the zirconium content in the average shale (160 ppm) of Turekian and Wedepohl (1961) and higher than Zr in the average black shale (70 ppm) of Vine and Tourtelot (1970). It shows high values in Abu Zinema, Al Maghara and Abu Tartur black shale samples (243 ppm, 561ppm and 121 ppm respectively). This indicates that Zr may be incorporated into organic matter or adsorbed by clay minerals. Zirconium shows positive correlation with Al_2O_3 and TiO_2 (r=0.54 and 0.87 respectively). This is the result of the close association between these elements and clays, and therefore reflects their terrigenous origin.

5.3 Discussion of chemical effects

Elemental concentrations in sediments result from the competing influences of provenance, weathering, sorting, and sediment diagenesis (Quinby-Hunt et al., 1991). When comparing the chemical composition of the classic shale composites, the studied shales show generally enrichment of elements that are chemically immobile and are associated with terrigenous influx, such as Al, Ti and Zr. Al and Ti which can survive throughout intensive chemical weathering and diagenesis (Cullers 2000). Their concentration in sediments is used as a measure of detrital input. The major constituents of the studied shale samples do not vary greatly from one location to another. The SiO_2, Al_2O_3 and TiO_2 tent to form together the main constituents of the studied shales and are normally related to clays. SiO_2, Al_2O_3 and TiO_2 are well correlated in all samples. This indicates that the major constituents SiO_2, Al_2O_3 and TiO_2 of the studied shale samples are dominantly terrigenous in origin.

In the Gulf of Maxico, shales have K_2O contents that increase systematically with depth from 2 to 4 wt % in the Paleocene-Eocene Wilcox Formation and from 2 to 5 wt% in the Oligocene–Miocene Frio Anahnace succession (Bloch et al. 1998). Potter et al. (1980) has shown the geochemical properties of shales change with time. Abdul Almanan (2002) stated a significantly higher content of K_2O in early Paleozoic shales, than in younger shales.

In the present study K_2O varies only slightly from Paleozoic shales to Eocene shales, e.g. between 0.26 for Tarawan Chalk to 2.03 for the Variegated Shale in Nile Valley. This is due to the enrichment of smectite and kaolinite in the studied shales and therefore strictly related to the mineralogy of the samples. Further it is noticed that K_2O decreases with increasing of carbonate content.

The black shales at Abu Zinema area of Carboniferous age and at Al Maghara coal mine of Jurassic age are enriched in SiO_2, Al_2O_3, TiO_2, and Zr and depleted in the marine indicators CaO and MgO. This seems to indicate that the shales at Abu Zinema area and Al Maghara coal mine have been deposited under reducing conditions with non–calcareous planktons input or under continental conditions. This is confirmed by their association with coal and detrital kaolinite.

In the contrary the shales from the Abu Tartur phosphate mine, the Quseir phosphate mines and the Nile Valley section were deposited in a marine environment, as given evidence for by

foraminifera, smectite, pyrite and their association with phosphate. The Abu Tartur and the lower part of the Nile Valley samples are more argillaceous and depleted in CaO than those of Quseir and Dakhla and Esna Shale at the Nile Valley, which might have been deposited in a shallow marine environment with a high productivity of calcareous organic matter.

Numerous of investigators have used several trace elements, including B, Ga, V, Li, Ni, Rb, as paleosalinity indicators for sediments especially of shales (Goldschmidt and Peters 1932; Potter et al. 1963; Ohrdorf 1968; Dominik 1985; Schreier 1988). These studies showed that Ba, Rb, Mg, Fe, and Ca are higher in marine shales, whereas Zr, Ti, Al, Ga, Li and Cr are terrestrial indicators. Schultz et al. (1980) observed that Cr, Ni, Zn, Fe and P are significantly more abundant in marine strata of Pierre Shale (Cretaceous) of the northern Great Plains. Walters et al. (1987) observed a pattern of trace elements in the shale of the Dakota Sandstone similar to pattern of terrestrial indicators described above.

In the present study the shale samples at Abu Tartur phosphate mine, Quseir phosphate mines and Nile Valley section show higher contents of the trace elements Sr, Ba, V, Ni, Cr, Zn, Rb than shale samples at Abu Zinema and Al Maghara. This indicates that the shale samples at Abu Tartur phosphate mine, Quseir phosphate mines and Nile Valley section were deposited in a marine environment.

5.4 Weathering effects

The chemical index of alteration (CIA) defined as CIA = 100 x Al_2O_3/ (Al_2O_3 + CaO + Na_2O + K_2O) have been established as a general indicator of the degree of weathering in any provenance regions (Nesbitt and Young 1982). High values (i.e, 76-100) indicate intensive chemical weathering in the source area whereas low values (i.e., 50 or less) indicate unweathered source areas.

The CIA values for the studied shales Appendix (Table 4) indicate that the shale samples of Ataqa Formation of the Carboniferous in Abu Zinema and of Safa Formation in Al Maghara have experienced strong chemical weathering (CIA >90) at the source area. Further, the depletion of Na and Ca reflects an intense chemical weathering of the source rocks. As Al_2O_3, CaO, Na_2O and K_2O are related with (CIA) they exhibit variations between the investigated samples reflecting variable climatic zones or rates of tectonic uplift in source areas. This corresponds with the results of Ghandour et al. (2003) in Safa Formation and also with the

observations of Nyakairu and Koeberl (2001) who recorded high CIA values (87 to 96) and low contents of alkali elements from kaolinitic rich sediments in Central Uganda.

For the calcite-enriched samples the CIA was not applied. The calcite-free samples of the Duwi Formation, the Dakhla Shale and the Esna Shale in Abu Tartur, the Nile Valley and Quseir show high CIA values (>76). This indicates moderate to intensive chemical weathering in the source area. This is also confirmed by the dominance of smectite in these formations. This proves the assumption that the area was located near the palaeoequator and had experienced warm, wet, and tropical to subtropical conditions characterized by low seasonality contrasts and predominantly chemical weathering, as also described by Tantawy et al. (2001).

Also Rb/Sr ratios of sediments are a monitor of the degree of source-rock weathering (McLennan et al. 1993). The studied shale samples of Upper Cretaceous-Lower Tertiary in Quseir, Abu Tartur and Nile Valley have an average Rb/Sr ratio of 0.16. This value is lower than that of the average upper continental crust of 0.32 and the average post-Achean Australian shale of 0.8 (McLennan et al. 1983). This suggests that the degree of source area weathering was moderate. On the other hand the studied shales of Carboniferous and Jurassic age in Abu Zinema and Al Maghara have average Rb/Sr ratios of 0.49, indicate that the degree of source area weathering was more intense compared to the younger sediments of Cretaceous and Tertiary age.

5.5 Provenance analysis for sedimentary rocks

Cr and Ni High levels of Cr and Ni and strong positive correlations between the two elements have been used by various authors (e.g., Hiscott 1984; Wrafter and Graham 1989 and Garver et al. 1994, 1996) to infer a mafic to ultramafic provenance of the sedimentary rocks. The concentration of Cr and Ni in shales is further reflecting the incorporation of Cr and Ni ions to clay particles during the weathering of ultramafic rocks containing chromite and other Cr and Ni-bearing minerals (Garver et al.1996). The level of Cr enrichment in the studied shales (weight average 148 ppm), its strong positive correlation with Ni (r = 0.61) and the high Cr/Ni ratios of about 3.7 indicate that mafic to ultramafic components were the main components among the basement complex source rocks.

Vanadium Stow and Atkin (1987) stated that V is enriched in organic rich shales deposited under reducing conditions and might also be hosted by detrital silicate minerals.

The V/Cr ratio has been used as a paleo-oxygenation indicator in a number of studies. Values of V/Cr >2 are thought to represent anoxic depositional conditions, whereas values below 2 are indicative of more oxidizing conditions (Dill et al. 1988). The studied shales of Egypt have V/Cr values below 2 Appendix (Table 5), which may indicate that all of the studied sediments were deposited under relatively oxidizing conditions with exception of the Duwi Formation in Abu Tartur, which was deposited in a reducing environment.

TiO_2/Al_2O_3 Brooks (1973, Spears and Kanaris (1976) found that the Carboniferous sediments in England have high TiO_2/Al_2O_3 ratios reflecting a strong correlation to the ratios in the parent basalt. Amajor (1987) utilized the TiO_2 versus Al_2O_3 binary plot to distinguish between granitic and basaltic source rocks. In figure 16 the TiO_2 versus Al_2O_3 binary diagram for the studied samples, it is demonstrated that the provenance material varies from predominantely granitic to mixed granitic basaltic rocks.
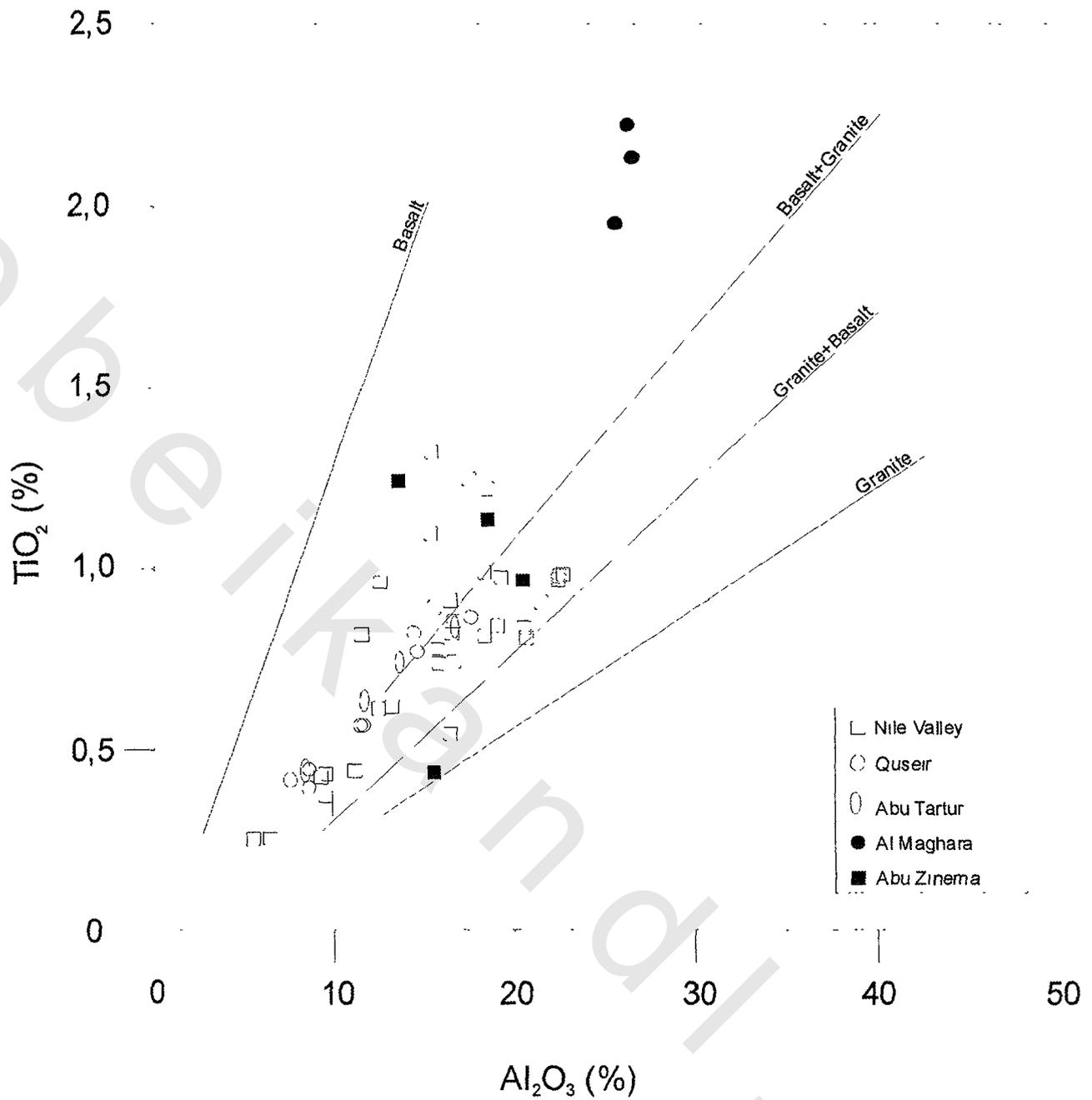
Fig. 16: TiO₂ /Al₂O₃ binary plot of the studied shale samples.

(provenance field from Amajor, 1987)

5.6 Distribution of major and trace elements in phosphate rocks

5.6 Distribution of major and trace elements in phosphate rocks

The studied phosphate samples show P_2O_5 values ranging between 6.20 % in the cherty phosphate in Quseir mine to 20 % in Abu Tartur mine and average 15.40 % (Fig. 17). In Egypt, phosphate bearing strata of economic importance and associated shales of the Duwi Formation are stretching from the Red Sea coast in Quseir over the Nile Valley into the Western Desert in Abu Tartur. They belong to a marine transgressive sequence which started on the top of predominantly fluvial Nubia Sandstone and grades into a sequence of an open marine environment(Germann et al. 1987). The Campanian to Maastrichtian Duwi Formation of a shallow marine origin (El-Ayyat and Kassab 2004) is overlain by shales, marls and limestones of the Maastrichtian to Paleocene Dakhla Formation, the sediments reflecting deposition under inner neritic to outer shelf conditions and repeated sea level changes (Hendriks 1985; Tantawy et al. 2001).
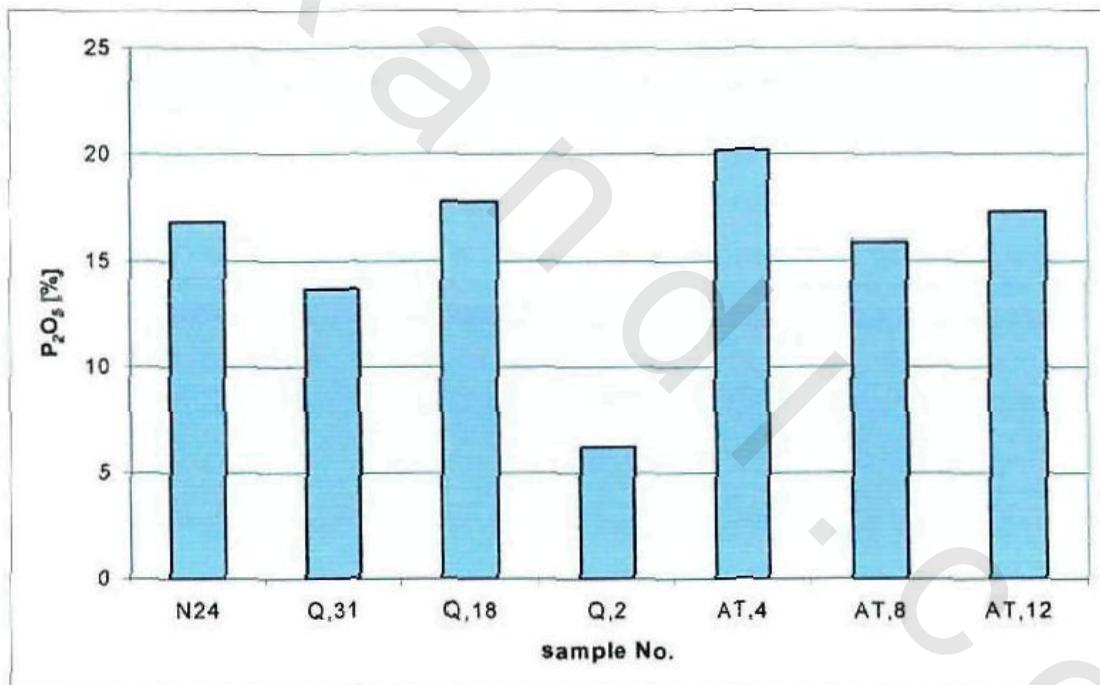

Fig 17: Distribution of P_2O_5 in the studied phosphate samples.

Phosphorus in sediments exists mainly in three forms, authigenic minerals (Ruttenberg and Berner 1993; Schuffert et al. 1994, 1998), in an organic form (Filipek and Owen 1981) and adsorbed on sediment particles (Sundby et al. 1992; Jensen et al. 1995). Inorganic phosphorus, which is synthesized authigenically in pore water, generally accounts for around 70 % of the total reactive phosphorus in marine sediments (Filippelli, 1997). Phosphorus in

organic matter accounts for 10-40 % of total phosphorus in coastal marine sediment (Kamatani and Maeda 1989) but is preferentially was released during decomposition of the organic matter (Ingall and Van Cappellen 1990). Dissolved reactive phosphate which is released to pore water can be adsorbed on sediment particles; it is easily desorbed and dissolved into pore water under anoxic conditions (Watanabe and Tsunogai 1984). Thus, authigenic phosphorus minerals in sediments are the main sinks for phosphorus from the ocean (Filippelli, 1997; Louchouarn et al.1997).

Marine phosphatogenesis and its characteristically P-C-Si-enriched sedimentary products are intimately related to upwelling phenomena (Cook 1984; Slansky 1986). Upwelling of nutrient-rich waters stimulates biomass productivity, and thus, biological preconcentration of phosphorus, silica and carbon is affected. Analysis of regional and stratigraphical distribution of phosphate and black-shale facies, and their sedimentological and geochemical properties has led to the general description of a phosphatogenetic model based mainly on an upwelling conception (Ganz 1984; Schröter 1986). The periods of particularly intensive and world-wide phosphate enrichment, as e.g. the Upper Cretaceous-Lower Tertiary Span, coincide with periods of warm-humid climatic conditions and related intensive chemical weathering (Valeton 1983; Prasad 1983; Riggs 1984).

The strong positive correlation of P_2O_5 with CaO, Sr and F ($r= 0.66$, 0.93 and 0.95 respectively Appendix (Table 6b) and (Fig. 18) is interpreted to be due to the substitution of both, the Sr and CaO within the carbonate-fluorapatite phase (Gulbrandsen 1966, 1970; Bliskovsky et al.1967; Tooms et al.1969; Mcconnell 1973)

The high silica content in the cherty phosphate samples from both of Quseir and Nile Valley, with average 14.11 % and 19.21% is indicating of biogenic origin, by diatoms (Germann et al. 1987). The vertebrate fauna of the Egyptian phosphorites (Dominik & Schaal 1984) is characterized by the simultaneous occurrence of marine (mainly sharks and mosaaurs) and freshwater inhabitants (e.g.Ceratodontides and other fish species). Germann et al. (1987) stated that, from the paleoecological point of view, the depositional situation of the Late Cretaceous phosphorites in Egypt is characterized by marginal marine conditions more or less influenced by freshwater influx.

The trace elements V, Ni, Cr, Zn and Rb in the phosphate show averages of 43, 17, 48, 46 and 8 ppm lower than these of the overlain black shales. This indicates leaching processes

outgoing from the overlain black shales. The low average content of detrital terrigenous influx Al_2O_3, TiO_2 and Rb (Fig.18) and the association of the phosphate bed with oyster limestone and diatom enrichment in Quseir and in the Nile Valley is indicating the marine origin of the phosphates in the Eastern part of Egypt.
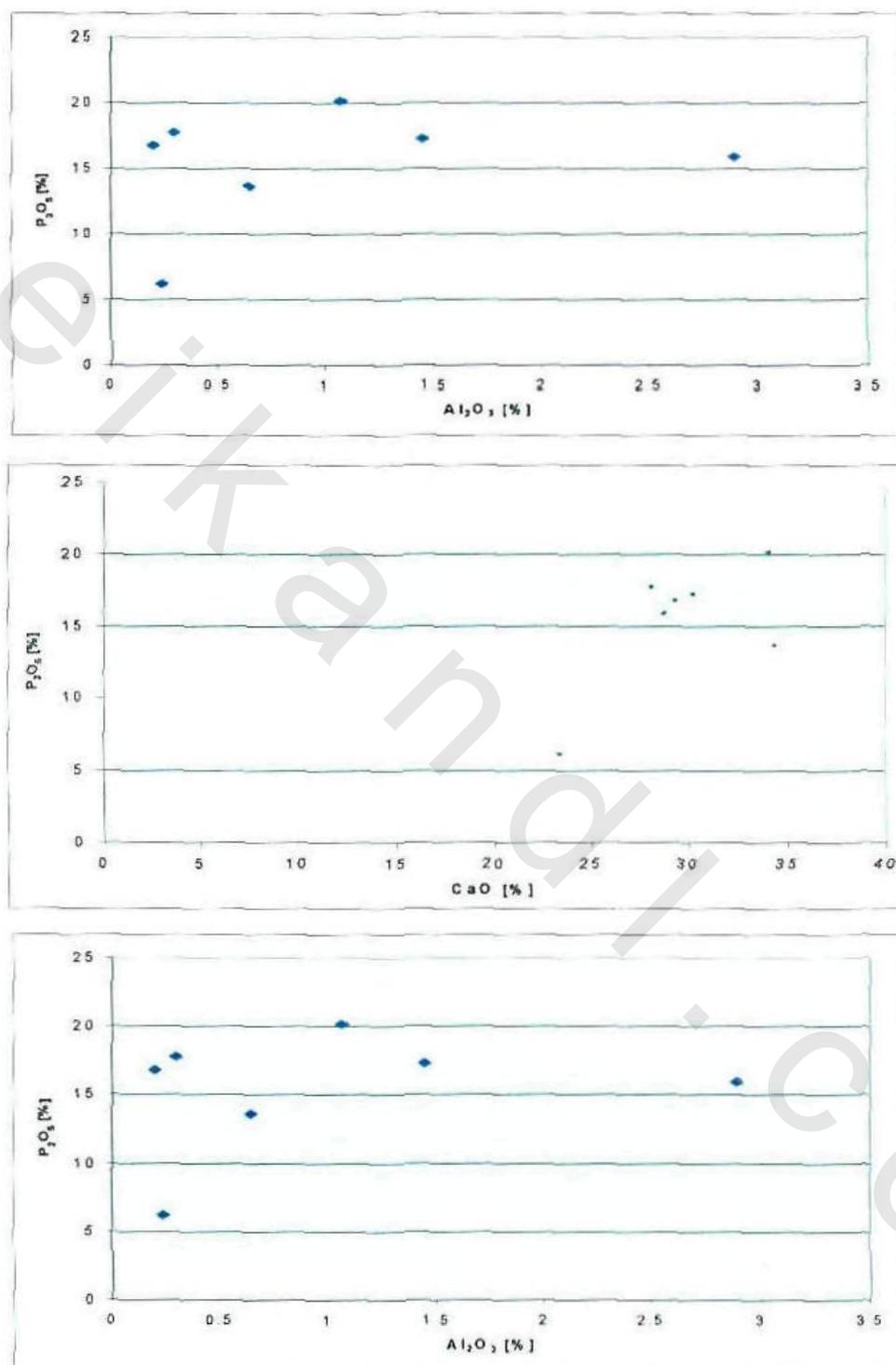

Fig. 18: The relationship between P_2O_5 with TiO_2, CaO & Al_2O_3