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Mineralogical and Elemental Compositions of Oil Shale in Duwi Formation Phosphate Mines, Safaga-Quseir Egypt

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Abstract

Upper Cretaceous Duwi Formation oil shale deposits in phosphate mines at Safaga - Quseir area, Red Sea, Egypt are known to have source rock potential. For this reason, the inorganic geochemical characteristics of black oil shale samples were investigated mineralogically using the X-Ray Diffraction (XRD) technique which indicates that, minerals of this shale are consisting predominantly of quartz, calcite, dolomite, gypsum, hematite and pyrite in addition to apatite and fluorapatite. While the clay minerals consisting predominantly of smectite mixed layer in addition to kaolinite with different percentages. The studied shales investigated by Flame atomic absorption instrument for their chemical composition. It shows many trace elements enrichment distribution affected by weathering. The studied shale's exhibit high concentration of Co, Cr, Cu, Ni, V and Zn due to oxidation, weathering and subsequent mobilization of the organic matter.

Key Words: Upper Cretaceous, Duwi Formation, black shale, thermal maturity, source rock potential.

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1-Introduction

Since more than seven decades when discovering of the phosphate deposits in Gabel Duwi Range, the mining have been started in Quseir - Safaga area about 500 Km^2 in the Red Sea western coast. Quseir - Safaga area is located between Lat. 25° 50', 26° 67' N and Long. 33° 45’, 34° 25' E, Fig (1). The Duwi (Phosphate) Formation is extending over several hundreds of kilometers, in the Western Desert up to the Nile River Valley, and in the Eastern Desert up to the Red Sea Coast.

Black shale is restricted with phosphate bed in the Upper Cretaceous and it's recorded at the upper parts of Qusier Formation, Duwi Formation and the lower part of Dakhla Shale. Black shale has been deposited in Quseir- Safaga land stretch and shoreline of the Tethys during Upper Cretaceous. The present study, aims to analysis the black shale deposits of Duwi Formation in some phosphate mines at Safaga – Quseir to evaluate their mineralogy and inorganic trace elements content.

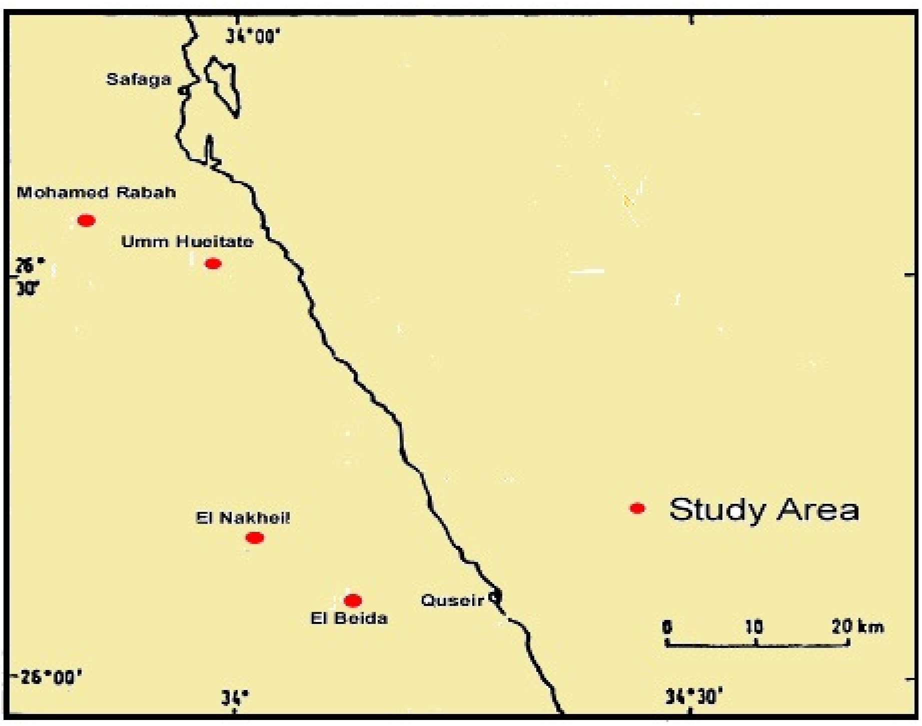

Fig (1). Location map of the study Area

2-Geologic setting

The Red Sea, Gulf of Aden and Gulf of Suez were formed as the Arabian plate separated from the African plate by movement of young and active continental rift system that initiated in the Late Oligocene–Early Miocene in the Late Oligocene–Early Miocene (Coleman 1993, Bosworth et al. 2005, Joffe 1987). During Mid-Miocene–Quaternary time, sinistral strike-slip motion along the Aqaba-Dead Sea transform resulted in a part of the movement (Morgan 1990, Abdel Khalek et al. 1993). The Red Sea Hills on the rift margins were formed as pre- and syn-rift strata and large areas of the Precambrian basement expose together by rotated extensional fault blocks. The stratigraphic units of the Egyptian Red Sea at the area between Safaga and Quseir consist of the following rock units from base to top as Fig (2).

Basement (metavolcanics,meta-sediments and granitoid intrusive (Said 1990).

Pre-rift sediments - Mesozoic-Cenozoic

Syn-rift sediments - Late Oligocene-Miocene to Recent

Sediment sequence reaches about 700 m thick of Late Cretaceous to Middle Eocene pre-rift strata is underlain unconformable by basement contains different strong fabrics. The lower part of the pre-rift sediments represented by130 m massive bedded of Nubian Sandstone (Khalil and McClay 2009). The Quseir, Duwi, Dakhla and Esna Formations 220-370 m thick of inter bedded shales, sandstones and limestones is overlain this Nubian Sandstone (Abd El Razik 1967, Issawi et al. 1969). The Thebes Formation consists of 130-200 m thick of bedded limestones and cherty limestones represent the uppermost pre-rift strata of the Lower to Middle Eocene. Sediment sequences is vary in thickness from less than 100 m onshore to as much as 5 km in offshore basins unconformable overlain the Thebes Formation and represent the syn-rift strata of Late Oligocene to Recent age (Heath et, al.

1998). The lowermost syn-rift strata Nakheil and Ranga Formations are dominantly coarse-grained clastics which overlain by reefal limestone's, clastics and evaporites of Um Mahra, Sayateen and Abu Dabbab formations. Late Miocene; and the Pliocene to Recent syn-rift, carbonates, reefs and clastics overlie the evaporites in the coastal outcrops (Montenant 1998).

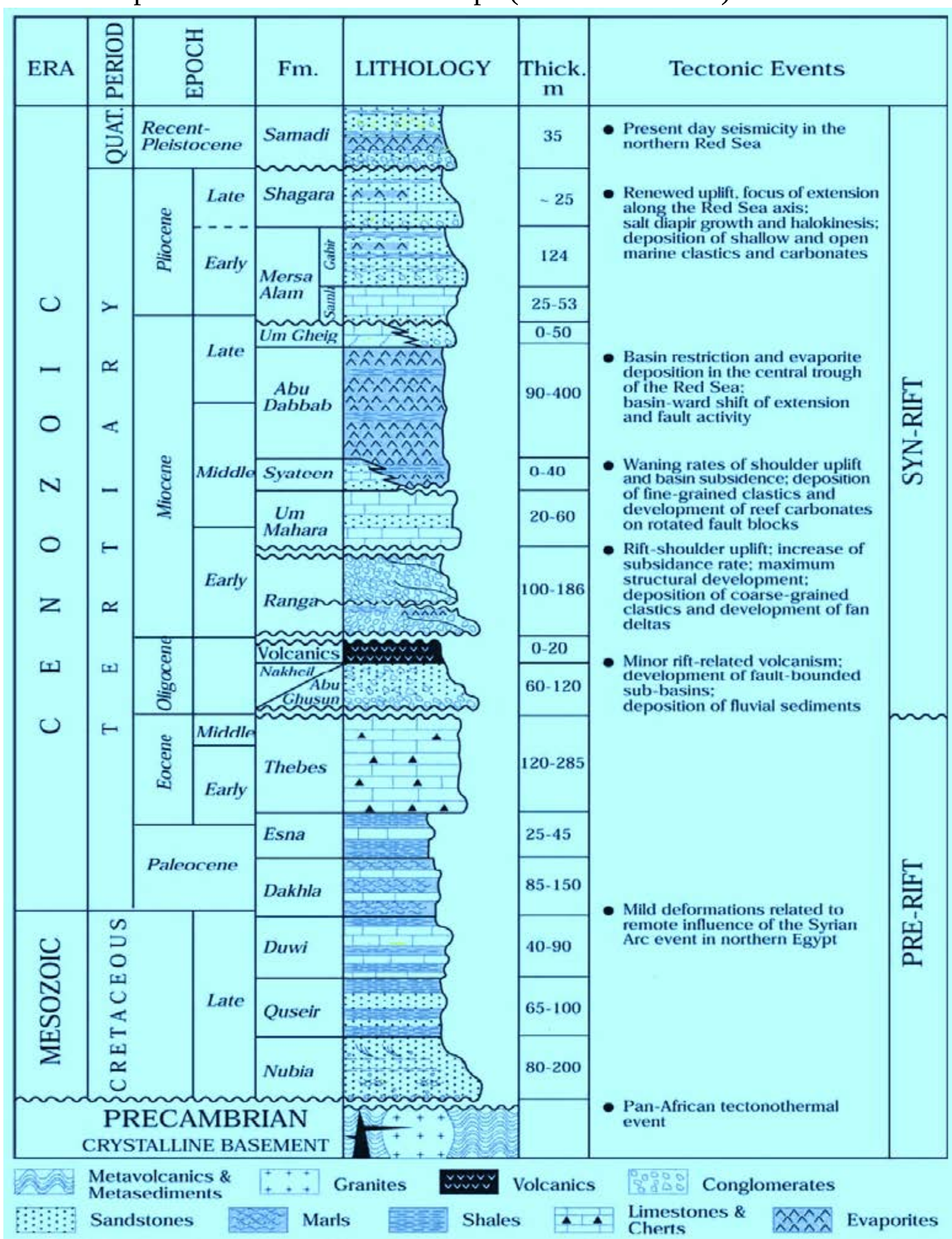

Fig (2). Summary of the stratigraphic sections of the northwestern part of Red Sea coast (Khalil and McClay 2009**).**

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3. Experimental

The samples were examined for the non clay and clay minerals using Philips X-ray diffraction PW 9901 of copper anode tube to obtained copper radiation. The scans run from 4 - 2θ and were stopped at 35○ 2θ for clay fraction and from 4 - 2θ and were stopped at 60 - 2θ for bulk minerals.

Rock samples were prepared to measure trace elements by using Flame atomic absorption instrument (Spectrometer-ZEE nit 700P-analytic jena-Germany). Disintegrate sample to 100-200 mesh then take 0.5 gm of the sample in Teflon then add to it 5 ml H_2O_2 + 10-25 ml HF then put it on hot plate until dry then add 25 ml HCl (1:1) then put on hot plate and steer it until formation a precipitate then take the solution in measuring flask and add distilled water to known volume.

4. Results and Discussion

4.1. Non Clay Minerals

The identified minerals by X-ray diffraction in the studied black shale samples are show in (Table 1 and Fig.3)

The bulk minerals in the samples composed mainly of quartz in all samples with minimum 22.66% and maximum 87.06%. The quartz followed by carbonate and clay minerals (Table 1 and Fig.3).

In some of the studied samples gypsum was identified by its XRD characteristic lines (Table 1 and Fig.3). Gypsum was probably syn-precipitated under reducing conditions primarily as sulphides with shale. After shale compaction, the sulphides oxidixed to sulphates as a result, of biogenic activity, the sulfates react with the calcic cement to form gypsum. Due to the compaction of clays the sulfates will be expelled and concentrated along the bedding planes as gypsiferous bands which can be seen in the field.

Table (1). Semi-quantitative mineralogical composition of the studied bulk samples.

Age	Formation	S.No.	Quartz	Calcite	Dolomite	Gypsum	Pyrite	Hematite	Aptite	Floro-Aptite	Clay
Campanian-Maastrichtian	**Duwi Formation**	1	40.66	9.15	-	5.06	6.50	-	4.55	-	34.09
		2	59.04	10.54	8.16	-	3.85	-	-	-	18.25
		3	75.51	1.48	4.0008	-	2.88	-	-	1.14	14.98
		4	87.06	1.36	-	7.47	0.95	-	-	-	3.17
		5	7.61	85.26	-	-	-	2.47	-	-	4.67
		6	72.59	5.51	-	-	-	10.53	-	-	11.37
		7	87.03	5.31	-	-	-	2.42	-	-	5.25
		8	76.13	5.54	2.23	-	3.36	2.44	4.32	-	5.98
		9	73.91	5.19	-	-	-	9.01	-	-	11.88
		10	7.41	81.06	-	-	-	2.66	0.95	4.86	3.06
		11	78.65	4.81	-	-	-	-	-	-	16.53
		12	43.66	11.69	1.89	11.91	-	2.41	5.54	2.50	22.9
		13	30.47	6.86	16.27	31.03	-	0.96	4.26	3.03	7.12
		14	69.30	0.33	2.84	4.14	-	-	-	-	23.41
		15	62.48	14.99	-	2.04	-	-	9.61	-	10.88
		16	62.76	26.09	-	3.35	-	-	-	2.71	5.1
		17	54.40	26.95	-	2.27	-	-	-	4.02	12.36
		18	30.72	58.95	-	1.44	1.85	-	-	3.43	3.6
		19	22.66	61.42	-	1.41	2.88	-	-	3.99	7.63
		20	31.53	53.62	-	-	-	-	-	5.50	9.35

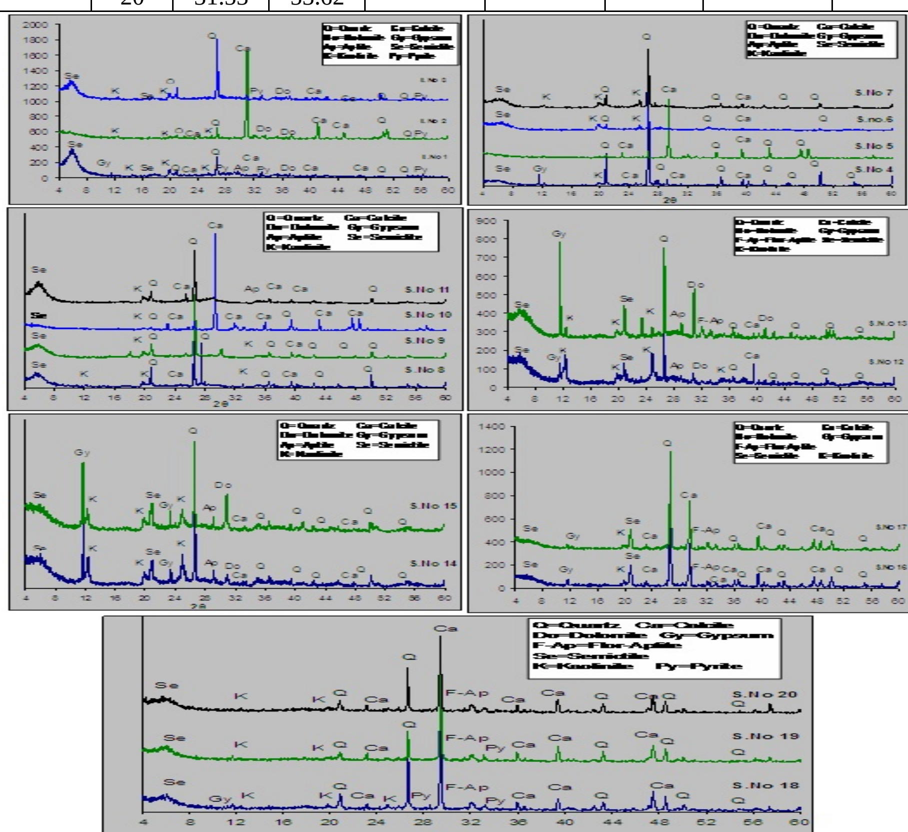

Fig. (3) XRD Mineralogical identification of bulk samples

Concentration of Saline-rich fluids (brines) in sea water may be generated, by evaporation or freezing, or as residual connate fluids in the subsurface while dissolving of previously formed evaporates by meteoric groundwater can form secondary brines (Selley 1988).

In most of the studied oil shale samples of the Duwi Formation pyrite was identified by its XRD characteristic lines (Table 1 and Fig.3). The presence of pyrite indicates reducing depositional environment prevalence. The reduction of sea water sulphate bacterial activity leads to pyrite formation in sediments (Berner 1982). Thus, under euxinic conditions where H_2S exists above or at least at the sediment-water interface, the highly pyritic shale's must have formed. The H_2S will react with Fe^{2+} which was probably delivered into the basin as colloidal material adsorbed on clay minerals to form iron sulphide. A hydrophobic sulphide gel might have been formed by increasing activity of the hydrogen sulphide in presence of iron and organic matter (El-Dahhar 1987).

The apatite and carbonate fluorapatite, phosphate minerals which are traditionally called francolite, are encountered in most of the studied black oil shale samples (Table 1 and Fig.3). The area under peak 2.79 Å is referring to the relative abundance of francolite. The carbonate and phosphate minerals, in the studied oil shale is indicating their deposition in a marine environment Temraz (2005).

4.2. Clay Minerals

Clay minerals in the studied shale samples are predominantly by smectite and kaolinite (Table 2) and Figs. (4 and 5).

Smectite constitute the dominant clay minerals content of the studied oil shale samples of Duwi Formation at Quseir phosphate mines. It ranges from minimum 18% to 96.6% Table (2) and Figs. (4 and 5).

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Table (2) Semi-quantitative mineralogical composition of the studied clay fractions

Age	Formation	Mine Name	Sample Number	Smectite%	Kaolinite%
Campanian-Maastrichtian	**Duwi Formation**	Um Huetate	2	57.51	42.49
			3	96.60	3.40
		Wasif	5	50.52	49.48
			6	82.66	17.34
		Mohamed Rabah	10	81.67	18.13
			11	100	-
		Gharb Younis	12	32.18	67.82
		Younis	15	18.68	81.32
		El Beida	16	77.52	22.48
		El Nakheil	19	61.14	38.86

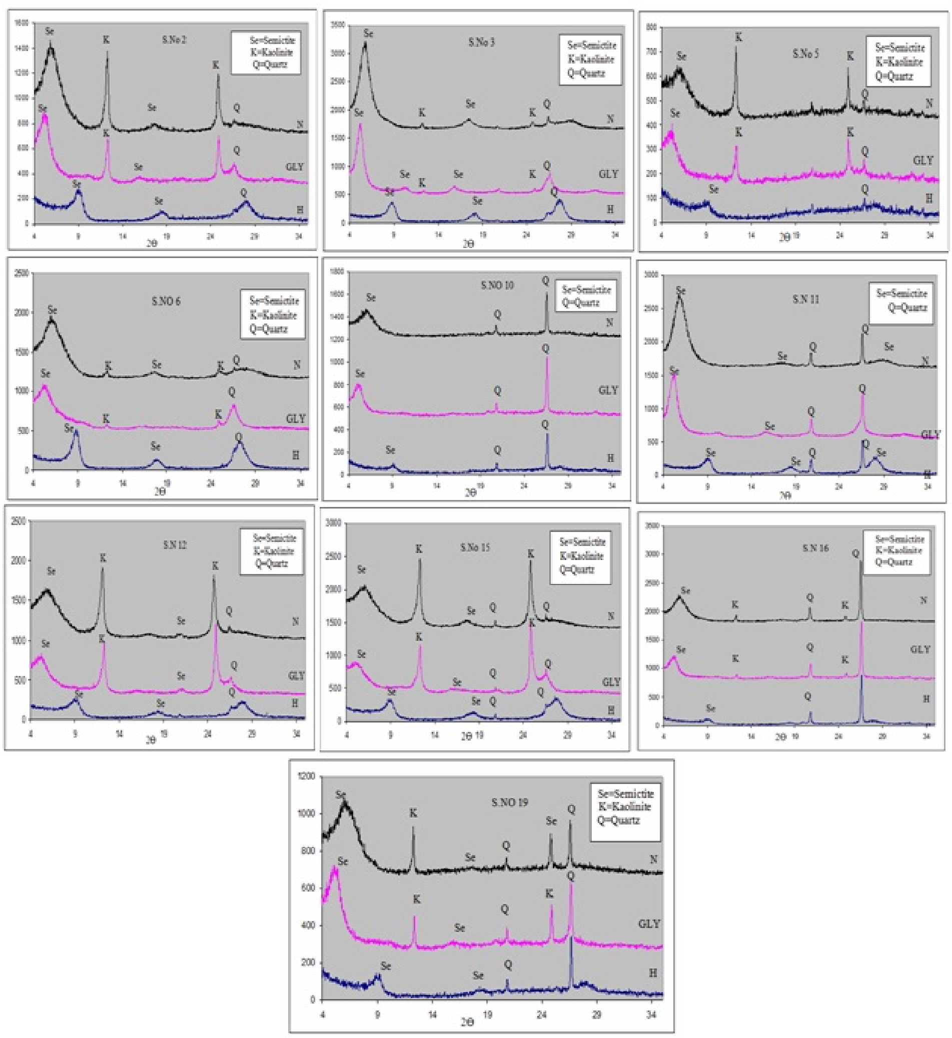

Fig. (4) XRD Mineralogical identification of clay fractions

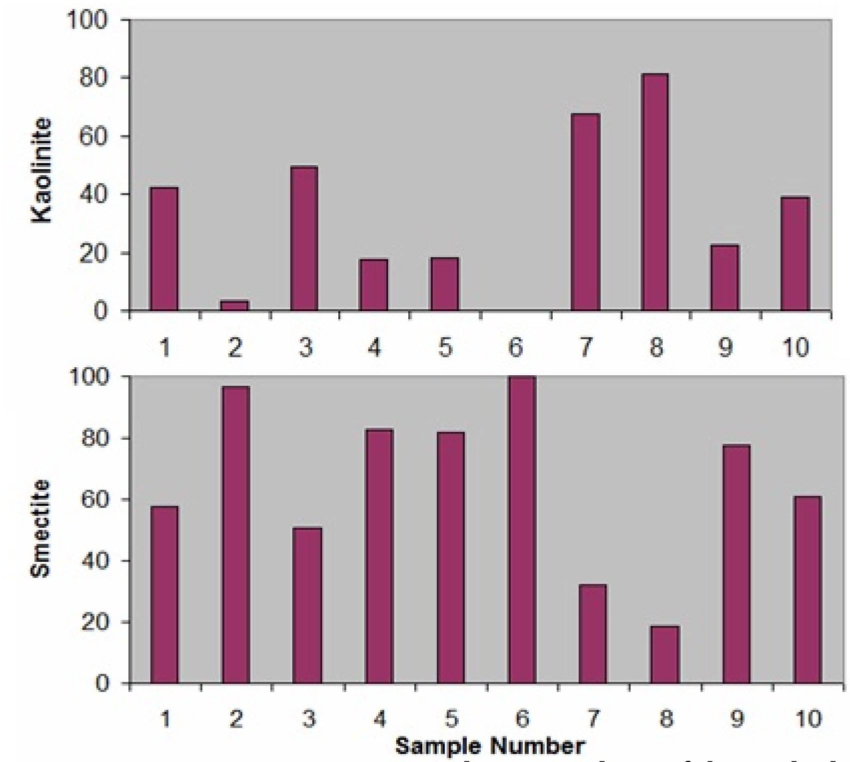

Fig (5) XRD, average Semi-quantitative Clay mineralogy of the studied shales

Marine paleoenvironmental conditions have been detected by using clay minerals in sediments (Jeong and Yoon 2001). By active chemical weathering of rocks under humid temperate to tropical climates, in continental weathering environments, smectite and kaolinite are generally formed (Weaver 1989). Smectite and kaolinite in marine sediments was often ascribed to the chemical weathering in a warm humid environment. According to Moore and Reynolds (1997) the smectite formed by weathering or neoformation as in soils and the alteration of volcanic glass. The absence of any volcanic precursor, such as tuff or glass in the studied shales proves that smectite is mainly of detrital origin.

Kaolinite constitutes the second dominant clay mineral in the studied oil shale of Duwi Formation. It ranges from minimum 3.4% to 81.3% Table (2) and Figs. (4 and 5).

The kaolinite origin in shales has been interpreted as a product of chemical weathering of feldspars under tropical to suptropical humid climatic conditions, being eroded and transported towards the sea by rivers (Chamley 1989, Hallam et al. 1991).

5. Distribution of significant trace elements

The following Table (3) and Fig. (6) show trace elements of the bulk rock samples from studied mines.

Vanadium distribution in the studied shales shows average value of 210.5 ppm and values variation from 61 to 360 ppm. This average is more than those of Turekian and Wedepohl (1961), Vine and Tourtelot (1970). It has been suggested that some V may be complexes within the organic matter.

Nickel distribution in the studied shales shows average value of 136.02 ppm Table (3) and Fig. (6), more than Ni of Turekian and Wedepohl (1961), Vine and Tourtelot (1970). Nickel shows strong positive correlation with Cr, TOC and clays Fig. (6), indicates an association of these elements mainly with the organic matter and clays. Shapiro and Breger (1968) stated that when Ni, present in significant quantities indicate weathering and mobilization by humic acids for ultrabasic and basic rocks. Ni is reaches (up to 300 ppm) in deep marine sediments but much less so in coastal sediments (39 ppm). According Turekian (1978), the United States average contents of Ni are less than 100 ppm in shales, 50 ppm in the black shales, 41 ppm in marine clays, 13 ppm in oil and only a few ppm in limestones.

The chromium distribution in the studied shales shows average value of 155.1 ppm Table (3) and Fig. (6), more than the Cr averages of Turekian and Wedepohl (1961) and Vine and Tourtelot (1970).

The positive correlation among Cr, V Ni and TOC prove that these elements are incorporated in organic matter and clay minerals Fig. (6). The enrichment of Cr and Ni in the studied shales may relate to their basement complex provenance (mafic to ultramafic) for the sedimentary origin (Gill 1981). The enrichment 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).

Studied samples show Co contents 133.6 ppm Table (3) and Fig. (6), more than Co of Vine and Tourtelot (1970).

Studied samples zinc average content shows 315.3 ppm Table (3) and Fig. (6), more than Zn of Turekian and Wedepohl (1961), Vine and Tourtelot (1970). Like chromium, zinc shows a positive correlation with the Ni element which may be explained as related to organic matter.

The copper distribution in the studied shales shows average value of 133.6 ppm Table (3) and Fig. (6), more than copper of Turekian and Wedepohl (1961) and Vine and Tourtelot (1970).

Table (3) Trace elements distribution in the studied black shale samples

<table>
<tr><th>Mine name</th><th>Sample number</th><th>Co</th><th>Cr</th><th>Cu</th><th>Ni</th><th>V</th><th>Zn</th></tr>
<tr><td rowspan="3">Um Huetat</td><td>1</td><td>129</td><td>139</td><td>20</td><td>116</td><td>240</td><td>330</td></tr>
<tr><td>2</td><td>150</td><td>210</td><td>53</td><td>117</td><td>125</td><td>235</td></tr>
<tr><td>3</td><td>161</td><td>119</td><td>28</td><td>112</td><td>182</td><td>460</td></tr>
<tr><td>Wasif</td><td>6</td><td>148</td><td>68</td><td>8.5</td><td>71</td><td>Nil</td><td>36</td></tr>
<tr><td>Mohamed Rabah</td><td>10</td><td>137</td><td>190</td><td>33</td><td>148.5</td><td>330</td><td>424</td></tr>
<tr><td>Younis Gharb</td><td>12</td><td>177</td><td>206</td><td>37</td><td>142</td><td>127.5</td><td>85.6</td></tr>
<tr><td>Younis</td><td>15</td><td>165</td><td>70</td><td>7.6</td><td>90</td><td>Nil</td><td>50</td></tr>
<tr><td rowspan="2">El Beida</td><td>16</td><td>124</td><td>235</td><td>41</td><td>180</td><td>61</td><td>850</td></tr>
<tr><td>17</td><td>118</td><td>188</td><td>58</td><td>136.7</td><td>258.4</td><td>487</td></tr>
<tr><td>El Nakheil</td><td>18</td><td>133</td><td>226</td><td>97</td><td>247</td><td>360</td><td>195</td></tr>
<tr><td colspan="2">Average</td><td>144.2</td><td>165.1</td><td>38.31</td><td>136.02</td><td>168.39</td><td>315.26</td></tr>
</table>

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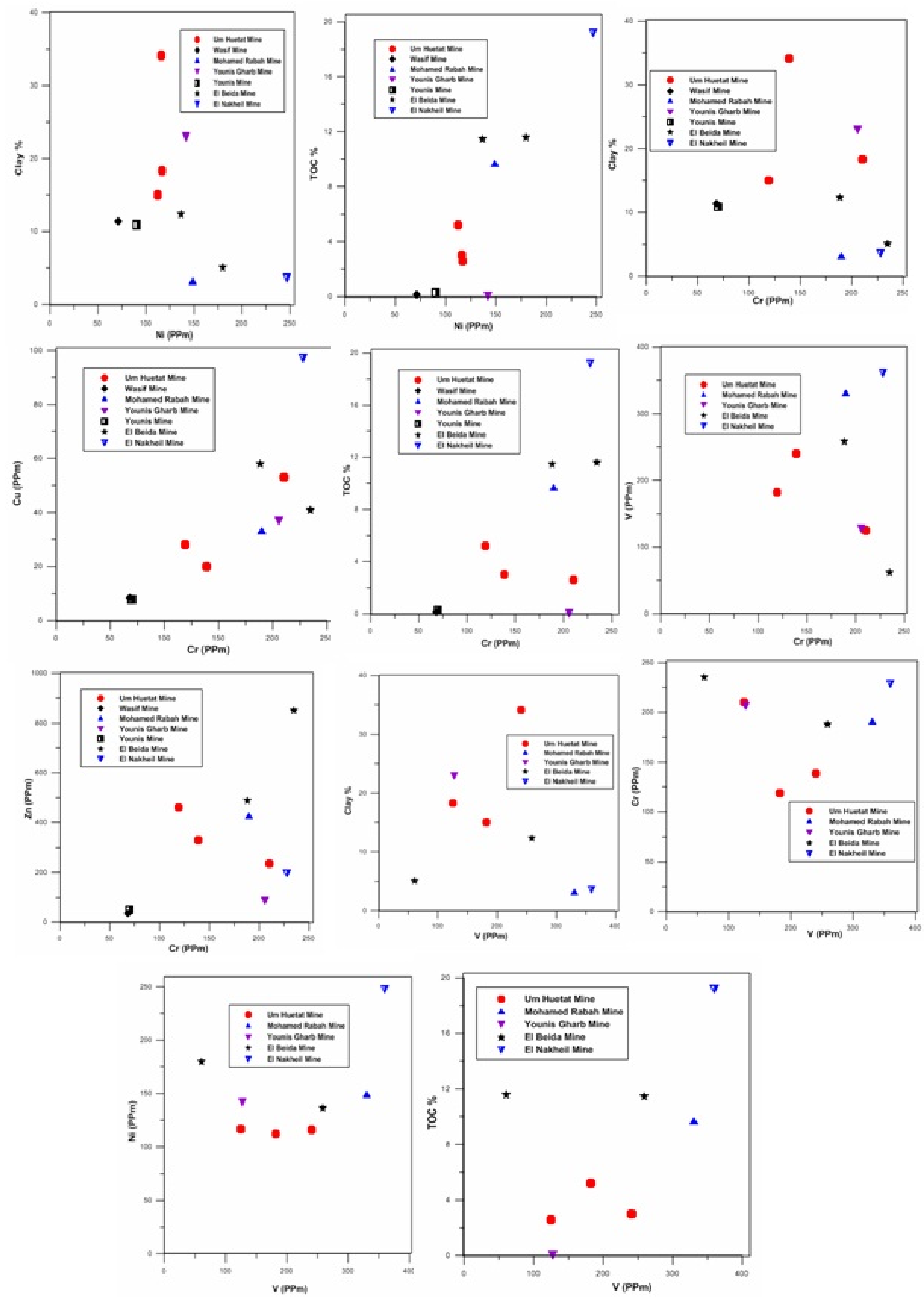

Fig (6) Trace elements destribution in the studied shales.

6. Provenance analysis for sedimentary rocks

The Cr distribution enrichment in the studied shales shows average value (155.1 ppm) and its strong positive correlation with Ni indicate that mafic to ultramafic components were the main components among the basement complex source rock provenance. The enrichment of Cr and Ni in shale's is 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).

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

6- Conclusion

Black shales of Upper Cretaceous Duwi Formations in the phosphate mines at Safaga – Quseir were studied to infer their mineralogical and geochemical characteristics. Quartz, carbonate minerals (calcite and dolomite), in addition to phosphate minerals are the main bulk minerals. Smectite with kaolinite association is indicating detrital origin and deposition in open marine environments. The smectite dominance and clay minerals associations in the studied shales at Quseir-Safaga, suggest a terrestrial provenance that had not attained intensive weathering, a warm and semi-arid climate and the resulted materials were carried by fluvial action, which finally interfered and admixed with marine environments. The Cr and Ni enrichment indicate that mafic to ultramafic components were the main components among the basement complex source rocks. The V enrichment (average 222.34 ppm) indicates deposition under reducing environment.

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