Geochemistry of Marl Sediments within Fat'ha Formation at Selected Localities, Northern Iraq

Zeki A. Aljubouri
Department of Geology
College of Science
Mosul University

Hazim A. Al-Kawaz
Dams and Water Resources
Research Center
Mosul University

ABSTRACT

A total number of (32) marl samples of Fat'ha Formation (Middle Miocene) was collected from four selected localities in northern Iraq. Geochemical study included the analysis of (13) major and minor oxides by x-ray fluorescence and wet chemical methods and (7) trace elements by (XRF). The study shows that the oxides (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, FeO, most MgO, Na_2O, K_2O, MnO, P_2O_5 and H_2O^+) are in the detrital fraction which comprises around (58%) of total mineral phases. These are clay minerals (39%), quartz (15%), iron oxides and Ti-minerals (3%) and feldspar (1%). The oxides (CaO, some MgO and CO_2) comprise the chemical fraction, the carbonates (~ 42%). The trace elements (Co, Ni, Ga, Rb, Zr and some Sr) are within the detrital fraction, mainly the clay minerals and iron oxides. The elements (Ba and the remaining Sr) are within the carbonate fraction. The oxides and elements of the detrital fraction, in general, have a negative correlation with oxides and elements of the chemical fraction. The red colour of marl sediments is primary caused by the red pigment of haematite. The green colour is secondary and resulted from the reducing environments, initiated by the presence of organic matter.

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جيوكيميائية رواسب المارل ضمن تكوين فتحة في مناطق مختارة، شمالي العراق

حازم أمين الكواز
مركز بحوث السدود
والموارد المائية
جامعة الموصل

زكي عبد الجبار الجبوري
قسم علوم الأرض
كلية العلوم
جامعة الموصل

الملخص

تم جمع (32) نموذجا من مارل تكوين فتحة (المايوسين الاوسط) من اربعة مناطق مختارة في شمالي العراق. تضمنت الدراسة الجيوكيميائية تحليل (13) اوكسيدا رئيسا بواسطة جهاز الاشعة السينية الوميضية (XRF) والطرق الرطبة وكذلك تحليل (7) عناصر اثرية بواسطة (XRF). وأوضحت الدراسة بأن الاكاسيد (SiO_2 و Al_2O_3 و TiO_2 و Fe_2O_3 و FeO ومعظم MgO و Na_2O و K_2O و MnO و P_2O_5

و H_2O^+) هي ضمن الجزء الفتاتي الذي يشكل حوالي (58%) من الاطوار المعدنية الكلية وهي: المعادن

الطينيـة (39%) والكـوارتز (15%) وأكاسيد الحديد مـع معـادن التيتـانيوم (3%) والفلدسـبار (1%). وتمثل

الاكاسيد (CaO، بعض من MgO و CO_2) الجزء الكيميائي وهو معادن الكاربونات (حوالي 42%) وهي:

الكلسـايت (38%) والـدولومايت (4%). وتوجد العناصـر الاثريـة (Co، Ni، Ga، Rb، Zr وجزء مـن Sr)

ضـمن الجزء الفتـاتي أي ضـمن المعـادن الطينيـة واكاسيد الحديد). وامـا العنصران (Ba والمتبقي مـن Sr)

فيوجدان ضـمن الجزء الكاربوناتي. وترتبط اكاسيد وعناصر الجزء الفتاتي وبصورة عامة ربطا سالبا مع اكاسيد

وعناصـر الجزء الكيميائي. ان اللـون الاحمـر لترسبات المـارل اولـي الاصـل ونـاتج عـن الصـبغة الحمـراء

للهيماتيت. اما اللون الاخضر فهو ثانوي الاصل وناتج عن الظروف الاختزالية في منطقة المشراق، بوجود

المواد العضوية.

INTRODUCTION

The area of study is situated at the northern part of Iraq within Nineva Governorate and includes four localities belonging to the Fat'ha Formation (Middle Miocene) (Fig,1). Three of the localities (Shaikhan, Shaikh Ibrahim and Makhmur) are natural exposures, while the fourth (Mishraq) consists of borehole cores. The lithology consists of alternations, in cyclic fashion, of marls, carbonates and gypsum. A total number of (32) marl sample was collected from the four localities.

The purpose of this work is to study the geochemistry of marl sediments, through the distribution of and inter-element relationships between (13) major oxides and (7) minor and trace elements; to work out the normative mineralogy (mineral contents) from chemical analyses and to study the colour of marl sediments.

ANALYTICAL TECHNIQUES

Seven major oxides (SiO_2, Al_2O_3, Fe_2O_3 total, CaO, MgO, Na_2O and K_2O) and seven trace elements (Co, Ni, Ga, Rb, Sr, Zr and Ba) were analyzed by a Philips P.W. 1450/10 automatic X-ray fluorescence spectrometer. The pellet method (Norrish and Hutton, 1964; Leake *et al*., 1969) was used. The major oxides (TiO_2, MnO and P_2O_5) were analyzed by UV-VIS spectrophotometer, type Zeiss, PM6. Ferrous oxide (FeO) was analyzed by the macrovolumetric method of Wilson (1955). CO_2 was determined by measuring the weight loss of the sample in 10% HCl solution. H_2O^+ was determined by total ignition loss at 1100 ºC after subtracting the weight loss due to CO_2. All analyses were carried out at the Department of Geology, College of Science, University of Mosul, Iraq.

The details of analytical techniques and the analyses of all (32) samples for major oxides and trace elements are given in Al-Kawaz (1980).

NORMATIVE CALCULATIONS

Normative calculations are used in the present study to calculate the percentage of minerals, already found by X-ray diffraction. The method used depends on both X-ray diffraction and chemical analysis.
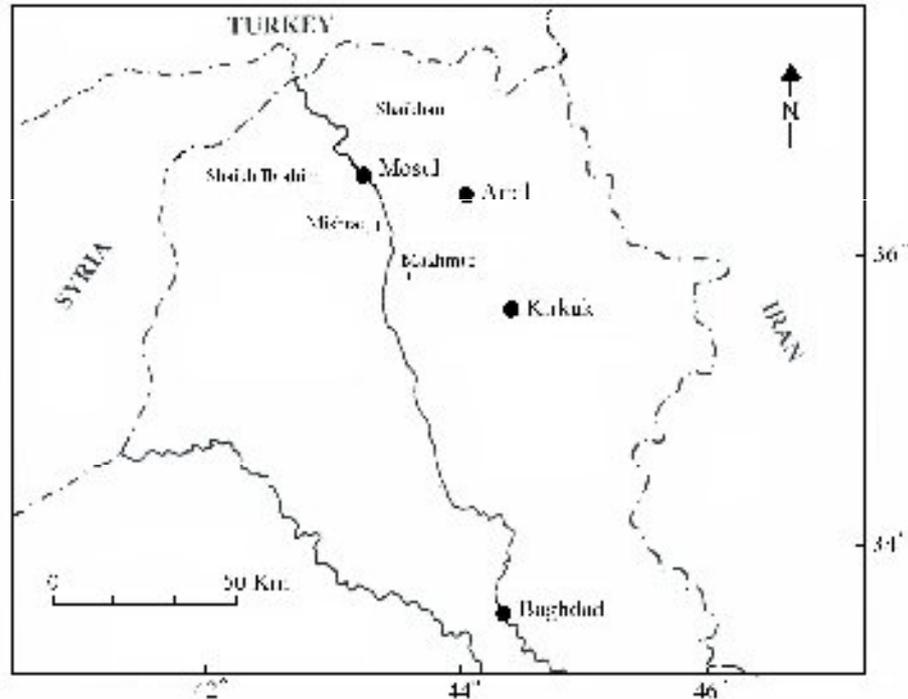

Fig. 1: The studied localities (+).

Using area under curve (Brindley and Brown, 1980) of the X-ray diffractogram of (Fig.2), (Al-Kawaz, 1980; Aljubouri and Al-Kawaz, 2006), the relative proportions of clay minerals and albite are illite (71.64%), chlorite (14.54%), kaolinite (8.81%), montmorillonite (2.20%) and albite (2.64%). These proportions must be converted to real percentages of the marl of present study. This is achieved by using the average chemical analysis of marl in Table 1(A), and the ideal clay minerals and albite analyses in Table (2). Al_2O_3 is only restricted to clay minerals and albite. The total Al_2O_3 in the marl is distributed within clay minerals and albite according to their relative proportions found from (XRD). Using Table (2), the concentration of Al_2O_3 in each mineral is then converted to mineral percentage in the marl (Table 3).

The next step is to calculate the non-clay minerls. Quartz is calculated after subtracting all SiO_2 in the clay minerals and albite from total SiO_2 (Table 1); then the remaining SiO_2 is allocated to quartz. Haematite (Fe_2O_3) and Ti-minerals are calculated after subtracting (Fe_2O_3) and (TiO_2) in the clay minerals. The remainings are allocated to haematite and Ti-minerals (mainly rutile) respectively.

Carbonates (calcite and dolomite) are calculated from the following empirical equation for a mixture of the two minerals from zero to (100%):

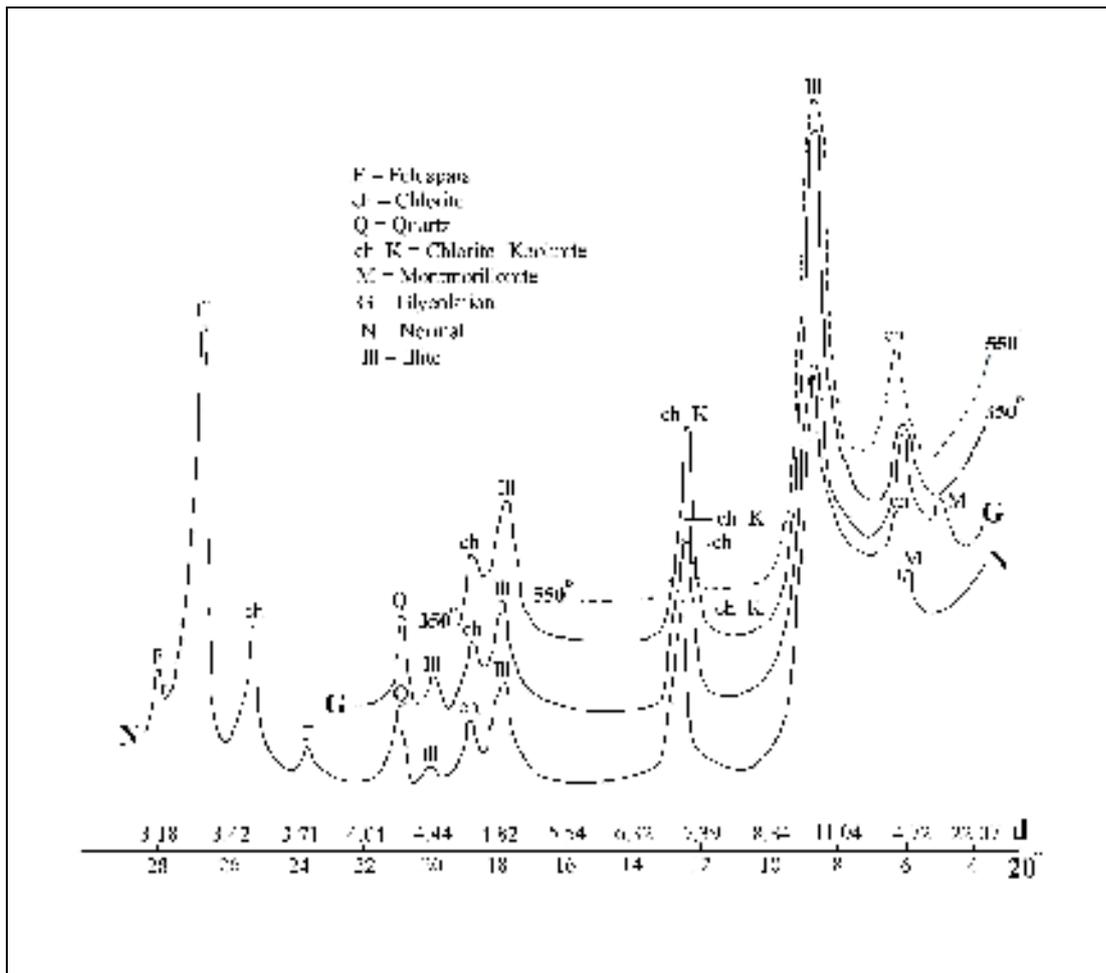*Calcite%= 315.989 + 97.918 x $(CO_2/CaO)^2$ – 354.10 x (CO_2/CaO).*

Fig.2: X-ray diffractograms for the clay minerals in the studied localities.
From: Al-Kawaz, 1980; Aljubouri and Al-Kawaz, 2006).

The equation is deduced from the calculations of the ratio of (CO_2/CaO) for each mix of calcite or dolomite and regressing the values against calcite percent (Fig.3 and Table 4). Figure (3) shows the plot of this ratio versus calcite % or dolomite %, so that either the equation or the figure could be used for calculating dolomite or calcite proportion, which is then converted to real percentage in the marl.

Alternatively, dolomite is calculated first after subtracting (MgO) in the clay minerals from total (MgO), and the remaining is allocated to dolomite. Calcite is then calculated after subtracting CaO in the clay minerals and in dolomite, then the remaining is converted to calcite. The value is chosen (for calcite or dolomite or both) which when added with other mineral phases values gives a total between (99 and 100). The normative mineral composition is given in Table (3).

Table 1: Average analysis of marl of the present study (A) compared with average shale (B), normalized data (C) of (A), red marl (D), green marl (E) and drab marl (F) samples.

Oxide %	(A) Present study n=32	(B) Average shale	(C) Present study *Normalized n=32	(D) Red marl n=12	(E) Green marl n=10	(F) Drab marl n=10
SiO_2	33.77	58.83	58.41	33.98	37.68	29.60
Al_2O_3	8.30	16.63	14.36	8.25	9.45	7.23
TiO_2	0.44	0.77	0.76	0.47	0.49	0.37
$Fe_2O_3 t**_t$	5.59	6.71	9.67	5.79	6.22	4.72
Fe_2O_3	4.22	--	--	5.13	3.49	3.86
FeO	1.23	--	--	0.59	2.46	0.77
MgO	5.37	2.49	2.49	4.05	7.20	5.13
CaO	22.76	2.24	2.24	24.50	17.24	26.20
Na_2O	0.24	0.80	0.42	0.26	0.32	0.14
K_2O	1.33	3.21	2.30	1.22	1.51	1.29
MnO	0.10	0.11	0.17	0.10	0.11	0.08
P_2O_5	0.18	0.16	0.31	0.19	0.18	0.17
H_2O^+	3.61	***5.00	6.24	3.94	3.48	3.38
CO_2	17.78	***2.63	2.63	16.61	15.67	21.29
$^@$Total	99.33	99.58	100.01	99.29	99.28	99.53
Co	13	19	23	14	15	9
Ni	110	50	190	114	113	102
Ga	33	19	57	35	27	35
Rb	62	140	107	57	69	62
Sr	340	170	588	290	513	225
Zr	61	160	106	60	52	72
Ba	778	580	1346	778	779	790

- *Normalized data (C) of present study (A) in relation to average shale (B), that is excess carbonate free data.
- n = number of samples.
- Average shale (B): from Li (2000).
- **Fe_2O_3 t = Fe_2O_3 + FeO x (1.111); Fe_2O_3 t = Total Fe_2O_3
- ***(H_2O^+) and (CO_2) are from Turekian and Wedepohl (1961).
- $^@$ Total : excluding Fe_2O_3 and FeO

Table 2: Average of ideal chemical compositions of clay minerals and albite.

	Illite	Chlorite	Kaolinite	Montmorillonite	Albite
SiO_2	51.26	29.87	45.65	52.38	68.74
Al_2O_3	21.12	14.48	37.37	18.31	19.44
TiO_2	0.29	--	0.80	0.12	--
Fe_2O_3	9.04	7.69	0.72	2.82	--
MgO	3.19	33.06	0.47	3.93	--
CaO	0.48	--	0.48	1.87	--
Na_2O	0.43	--	0.20	--	11.82
K_2O	6.5	--	0.63	--	--
H_2O^+	7.53	14.60	13.26	19.78	--
Total	99.84	99.70	99.58	99.21	100.0

Illite: average of (4) analyses (1,2,5,6,7,8,9,10) Grim (1968, p.580).
Chlorite: Analysis (3) Grim (1968, p.581).
Kaolinite: average of (5) analyses (1-5) Grim (1968, p.576).
Montmorillonite: average of (7) analyses (1-7) Grim (1968, p.578).
Albite: from the ideal formula $NaAlSi_3O_8$.

Table 3: Mineral compositions of marl of the present study (n=32).

Mineral	Percent			
Illite	28	Clay minerals=39%	Detrital fraction=58%	
Chlorite	8			
Kaolinite	2			
Montmorillonite	1			
Quartz	15			
Albite	1			
* Others	3			
Calcite	38			Chemical fraction=42%
Dolomite	4			
Total	100			

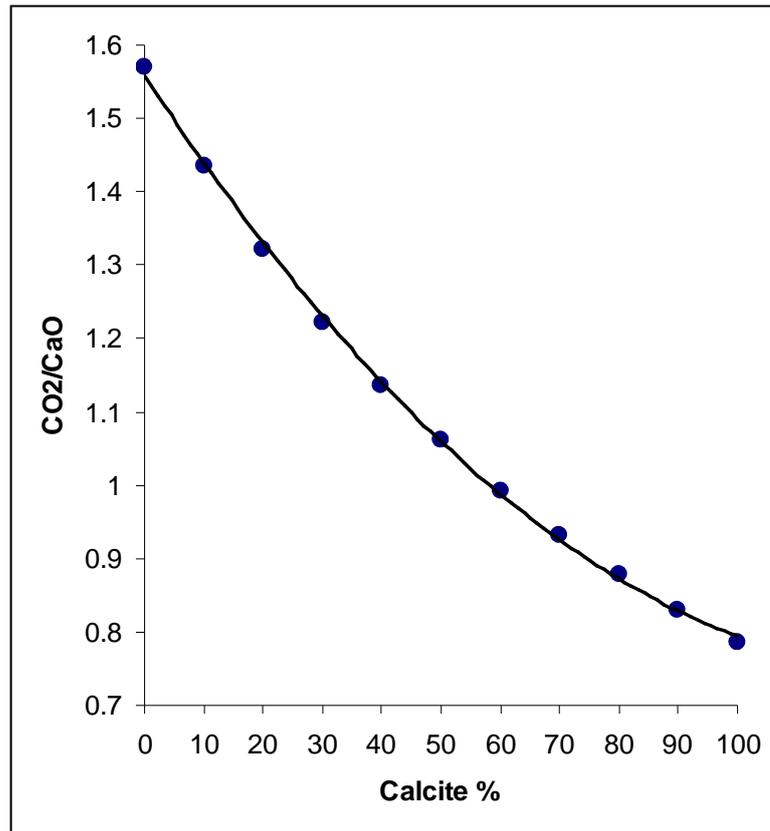* Haematite and Ti-minerals;   n = no. of samples.

Fig. 2: Calcite percent versus (CO_2/CaO) ratio of a hypothetical mixture of calcite and dolomite. Data from Table (4).

Table 4: Mixtures of calcite and dolomite and the ratio of CO_2/CaO.

	Calcite %	Dolomite %	CaO	CO_2	CO_2/CaO
1	0	100	30.41	47.73	1.570
2	10	90	32.972	47.354	1.436
3	20	80	35.534	46.972	1.322
4	30	70	38.096	46.602	1.223
5	40	60	40.658	46.226	1.137
6	50	50	43.22	45.85	1.061
7	60	40	45.782	45.474	0.993
8	70	30	48.344	45.098	0.933
9	80	20	50.906	44.722	0.879
10	90	10	53.468	44.346	0.829
11	100	0	56.03	43.97	0.785

GEOCHEMISTRY

Geochemical study is carried out through the discussion of the distribution of major oxides, minor and trace elements and the comparison with average shale of (Li, 2000) (Table 1). Correlation coefficient matrix (Table 5) is also used for the interpretation of

inter-element relationships. The averages of red and green marl samples (Table 1 DandF) are sometimes referred to, especially when discussing the green colour of marl of present study. The excess carbonate-free average of marl (Table 1C) is also shown to see how much close the marl of present study to the average shale of Li (2000). The table was calculated by fixing the carbonate oxides (CaO, MgO and CO_2) with values as in the average shale, then using the correction factor of (1.7296). This is done to eliminate the dilution factor of the carbonates.

Silica (SiO_2):

Silica in argillaceous rocks, including marl, usually occurs in two main phases; in the clay minerals, in the (SiO_4) tetrahedral sheet and as free silica in the mineral quartz, or as microcrystalline silica in the minerals like chert (SiO_2), jasper (SiO_2) and opal ($SiO_2.n H_2O$).

The average silica content of marl of the present study (33.77%) is much lower than that of average shale (58.83) of Li (2000), Table 1 (A and B). The reason is the relatively high carbonate contents (> 40%) which act as a dilution factor for the silica and other oxides in the marl (Dhannoun *et al.*, 1988). However, when the dilution factor is eliminated by assigning the values for carbonates (MgO, CaO and CO_2) as for the average shale and the average is recalculated on "excess carbonate-free basis", the SiO_2 content of the marl surprisingly becomes very close to (58.41%) to that of average shale, Table 1 (B and C).

Correlation coefficient matrix (Table 5) shows that SiO_2 has positive correlation with the oxides (Al_2O_3, TiO_2, Na_2O and K_2O). These oxides with considerable part of (SiO_2) constitute the clay minerals and together with quartz, and iron oxide, they make up the bulk of detrital fraction, which was formed as mineral phases in the weathering zone and transported to the basin of deposition.

On the other hand, (SiO_2) and the other detrital oxides have strong negative correlations with (CaO and CO_2) which both make up the bulk of carbonate minerals, calcite and dolomite. Normative calculations show that (56.6%) of total (SiO_2) is within the clay minerals and albite and (43.4%) is in the free silica, mainly quartz.

Alumina (Al_2O_3):

This oxide or its cation (Al^{3+}) forms the basic unit of structure of the clay minerals, being in the tetrahedral sheet (in four coordination with oxygen) and in the octahedral sheet (in six coordination with oxygen). This unusual behaviour of (Al^{3+}) is caused by the radius ratio (Al^{3+}/O^{2-}) of (0.36) which makes the aluminium cation on the border between octahedral and tetrahedral coordination (Mason and Moore, 1982).

The average (Al_2O_3) of marl of the present study (8.30%) is much lower than that of average shale (16.63%) of Li (2000), Table 1 (A and B). However, when dilution factor of carbonates is eliminated, the average becomes (14.36) much closer to that of shale, Table 1 (A, B and C). Another reason for the low (Al_2O_3) content is the type of clay minerals. The two most common clay minerals in marl of present study, illite (28.15%) and chlorite (8.33%) (Table 3), both have rather low (Al_2O_3/SiO_2) ratio of (0.41) and (0.48) respectively compared with (0.82) for kaolinite (Table 2).

Table 5: Correlation coefficient matrix for major, minor oxides and trace elements in marl sediments (n=32).

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	H_2O+	CO_2	Co	Ni	Ga	Rb	Sr	Zr	Ba
SiO_2	1																			
Al_2O_3	0.76	1																		
TiO_2	0.82	0.66	1																	
Fe_2O_3	0.42	0.42		1																
FeO	0.36	0.38		-0.47	1															
MgO				-0.43	0.61	1														
CaO	-0.87	-0.83	-0.71		-0.53	-0.56	1													
Na_2O	0.62	0.45	0.56	0.43	0.47	-0.47	-0.47	1												
K_2O	0.51	0.70	0.44	0.47	0.47	-0.70	0.36	0.36	1											
MnO	0.40	0.42	0.34				0.46			1										
P_2O_5	0.43	0.50	0.53			-0.48		0.50			1									
H_2O+		0.33		0.60		-0.39	0.50					1								
CO_2	-0.89	-0.85	-0.80	-0.48			0.74	-0.59	-0.49	-0.49	-0.38	-0.45	1							
Co	0.47	0.64	0.42	0.41				0.42		0.34	0.37	0.32		1						
Ni	0.36	0.36	0.38					0.38	0.39	0.34			-0.63	-0.42	1					
Ga	-0.40	-0.35						0.60	-0.42					-0.42		1				
Rb		0.56			0.38	0.43		-0.45		0.70			0.37	0.32	0.35	-0.27	1			
Sr					0.45	-0.45											-0.17	1		
Zr															0.67	0.12	0.12	-0.62	1	
Ba	-0.46	-0.39				-0.39	0.47				-0.33	0.33				0.14	0.14	-0.62		1

Blank areas, correlation less than (± 0.3); n = Number of samples.

Correlation coefficient matrix (Table 5) shows that (Al_2O_3) has medium to good positive correlation with oxides of detrital fraction (SiO_2, 0.76; TiO_2, 0.66; Fe_2O_3, 0.42 and K_2O, 0.75). These oxides represent the clay minerals, quartz, heavy minerals and iron oxides. On the other hand, it has strong negative correlation with oxides of chemical fraction (CaO, -0.83 and CO_2, -0.85).

Titanium dioxide (TiO_2):
Titanium is one of the most immobile elements and its occurrence in sedimentary rocks is almost wholly restricted to the detrital fractions that is the clay minerals, iron oxides and the heavy minerals. In the clay minerals, (Ti^{4+}) may replace (Al^{3+}) or (Mg^{2+}) in octahedral sites, especially in kaolinite and chlorite (Grim, 1968; Aljubouri, 1972; Phillips and Griffen, 1981). Iron oxides, especially haematite (Fe_2O_3) nearly always contain some amounts of (Ti^{4+}). Most sedimentary rocks contain detrital grains of rutile as a heavy mineral (Sp.Gr. 4.2, Hurlbut and Klein, 1977).

The average (TiO_2) of marl of the present study (0.44%) is less than the average shale (0.77%) of Li (2000) (Table 1A). However, when dilution factor of the carbonates is eliminated, the average becomes (0.76%) and almost identical to that of average shale (Table 1B and C).

In the correlation matrix of table (2), TiO_2 is positively correlated with the oxides of the detrital fraction (SiO_2, 0.82; Al_2O_3, 0.66; Na_2O, 0.56; K_2O, 0.44) indicating its association with the clay minerals.

Normative calculations (Table 3) show that (77%) of (TiO_2) is in the free form possibly in the heavy mineral rutile and only (23%) is in the clay minerals.

Iron Oxides (Fe_2O_3 and FeO):
Iron in the marl of the present study was calculated as Fe_2O_3 and FeO, since both valency states (Fe^{3+} and Fe^{2+}) are present and play an important part in the colour of marl sediments.

A considerable part of Fe^{3+} in the brown marl is present as free iron oxide in the mineral haematite (Fe_2O_3) which is responsible for the brown or red colour of the sediments. In the green marl, haematite is absent and the majority of Fe^{3+} and Fe^{2+} are present within clay minerals.

In all the clay minerals of the present study (illite, chlorite, kaolinite and montmorillonite), Fe^{3+} must appear in the octahedral sheet, either replacing Al^{3+} or replacing Mg^{2+} to balance charge deficiency in tetrahedral sheet, caused by the substitution of Al^{3+} for Si^{4+} as in chlorite. In rare cases, Fe^{3+} is known to replace some Si^{4+} in the tetrahedral sheet of chlorite (Grim, 1968).

The ferrous iron Fe^{2+} seems to be restricted to chlorite where it replaces Mg^{2+} in the octahedral sheet in any proportion. However, haematite may contain minor amounts of Fe^{2+} (Phillips and Griffen, 1981).

The average Fe_2O_3 total of marl sediments of the present study (5.59%) is lower than that of average shale (6.71%) of Li (2000) (Table 1AandB). However, when dilution factor of carbonates is eliminated, the average becomes (9.67%) higher than that of average shale (Table 1C) indicating an enrichment of marl sediments in iron oxides.

Correlation coefficient matrix (Table 5) shows that Fe_2O_3 has rather weak positive correlation with oxides of the detrital fraction (SiO_2, Al_2O_3 and TiO_2). This is possibly

due to the presence of (10) samples of green marl out of (32) samples, where Fe_2O_3 decreases in the reducing environments of the green marl, while the other oxides (SiO_2, Al_2O_3 and TiO_2) increase in these environments (Table 1D and E), thus weakening the rather strong positive correlation between Fe_2O_3 and these oxides.

Normative calculations (Table 3) show that (44%) of Fe_2O_3 $_{total}$ is in the form of free iron oxide (haematite). The remaining (56%) is within the clay minerals lattices, mainly in the octahedral sheet. These results are very close to that of Dhannoun and Al-Dabbagh (1990) (42%) and Aljubouri *et al*. (1994) (42.56%) for the distribution of free iron oxide in the Gercus (Eocene) red clastics.

Magnesium Oxide (MgO), Calcium Oxide (CaO) and Carbon Dioxide (CO_2):
These three oxides constitute the bulk of the chemical fraction calcite and dolomite, which both, in contrast to the minerals of the detrital fraction, precipitated in the basin of deposition. However, a considerable part of MgO is within the detrital fraction, the clay minerals, mainly in the mineral chlorite. This is indicated by the positive correlation (although weak) between MgO and the oxides of the detrital fraction (SiO_2, Al_2O_3 and TiO_2).

The negative correlation between MgO and CaO is partly because most MgO is within the detrital fraction and partly due to the fact that dolomitization (introduction of MgO) reduces the original amount of CaO. From table (3) it could be calculated that for each (1%) dolomitization, (0.3041% CaO) goes into dolomite and (0.2562% CaO) is lost, i.e. goes into solution.

The average (MgO) of marl of the present study (5.37%) is higher than that of average shale (2.49%) by a factor of (2), while the average CaO (22.76%) is higher by a factor of (10). The relatively high (MgO and CaO) causes the dilution of the oxides of the detrital fraction (Aljubouri, 1972; Dhannoun *et al*., 1988; Aljubouri *et al*., 1994).

Correlation coefficient matrix shows that there is a strong negative correlation between (CaO and CO_2) and the oxides of the detrital fraction (> -0.85 with SiO_2 and Al_2O_3 and >- 0.7 with TiO_2), since the precipitation of carbonates is at the expense of the detrital fraction and leads to the observed negative correlation.

Sodium Oxide (Na_2O) and Potassium Oxide (K_2O):
Sodium and potassium in argillaceous rocks usually occur in three forms: within chemical fraction, in the mineral halite (NaCl) and sylvite (KCl); in the detrital potassic and plagioclase feldspars and in the clay minerals. Most of the potassium is fixed in the mineral illite as an inter-layer cation. In the present study, the (K_2O) analysis (1.33%) (Table 1) is insufficient for the illite content (28.15% in Table 3) which requires (1.83% K_2O). This is possibly due to the substitution of (K^+) by molecular water or hydronium ion (H_3O^+) and the excess potassium goes into solution due to its very high mobility (Grim, 1968; Brindley and Brown, 1980; Aswad and Tobia, 2008).

Plagioclase feldspars, especially near albite ($NaAlSi_3O_8$) always contain minor amount of potassium (Hurlbut and Klein, 1977). In the marl of the present study, plagioclase feldspar was identified by (XRD) and by thin section as oligoclase (Al-Kawaz, 1980; Aljubouri and Al-Kawaz, 2006) and hence some potassium could be within this oligoclase.

Smectite (montmorillonite) always contains sodium (and calcium) as an inter-layer cation for charge balance (Phillips and Griffen, 1981, p.258), In the present study, montmorillonite was identified by (XRD) (Al-Kawaz, 1980; Aljubouri and Al-Kawaz, 2006) and the normative calculations gave (1.00%) montmorillonite (Table 3). As well as being within the structure of clay minerals, both Na and K are adsorbed on clay layers with broken bonds (Phillips and Griffen, 1981).

The normalized average Na_2O and K_2O of marl of the present study are (0.42) and (2.30%), respectively and both are lower than the average shale (0.80% and 3.21% respectively, of Li (2000), Table 1 (A and B). The reason is that there is no major mineral containing sodium, while potassium in illite was possibly subjected to substitution by (H_2O) as stated earlier.

Correlation coefficient matrix (Table 5) clearly shows the positive correlation between (Na_2O and K_2O) and the oxides of the detrital fraction (SiO_2, Al_2O_3, TiO_2 and Fe_2O_3) indicating their association with the clay minerals in this fraction. On the other hand, there is a negative correlation between these two oxides and (CaO and CO_2) of the chemical fraction indicating that there are no mineral phases of Na_2O and K_2O in this fraction.

Manganese Oxide (MnO):

The normalized average (MnO) of marl of the present study (0.17%) is higher than that of average shale (0.11%) of Li (2000). The (Fe/Mn) ratio of (50.8) is close to that of average shale (55) and very close to average ratio (50) of igneous rocks and the earth crust (Krauskopf, 1967). This means that nearly all the manganese released in the weathering zone from the weathering of igneous rocks is associated with iron as an oxide or hydroxide and/or both are within the clay minerals.

At the weathering zone, iron starts to precipitate as oxides and hydroxides at a pH from (6) to (8) in an oxidizing conditions, whereas very little (Mn) is precipitated at a pH of (8) due to its higher oxidation potential than iron. However, at a pH of (8.5) and higher iron continues to precipitate and (Mn) starts to precipitate as the oxide (MnO_2) with oxides and hydroxides of iron (Krauskopf, 1967; Maynard, 2003; Stum and Morgan, 1996). However, an important part of iron is fixed within the octahedral sheet of the clay minerals.

Manganese in argillaceous rocks occurs either in the detrital fraction, within the clay minerals, heavy minerals and possibly as an independent phase in the mineral pyrolusite (MnO_2) or in the carbonate phase (Aljubouri, 1972; Tobia, 2005).

In chlorite, (Mn^{2+}) replaces some (Mg^{2+}) in the octahedral sheet, while haematite (Fe_2O_3) contains minor amounts of (Mn^{2+}) (Phillips and Griffen, 1981).

In the correlation coefficient matrix of Table (5) manganese is positively correlated with the oxides of the detrital fraction (SiO_2, Al_2O_3, TiO_2 and Fe_2O_3), whereas it has negative correlation with oxides of chemical fraction (CaO and CO_2). These relationships leave no doubt that (MnO) of the present study is within the detrital fraction, i.e. within the clay minerals, iron oxides (haematite) and the heavy mineral rutile (TiO_2).

Phosphorus Pentoxide (P_2O_5):

The normalized average (P_2O_5) of marl of the present study (0.31%) is almost twice that of average shale (0.16%) of Li (2000) (Table 1A and B); however, it is the same as that for the average shale of Turakian and Wedepohl (1961).

The most common mode of occurrence of phosphorous in sedimentary rocks is in the mineral apatite, either as fluor-apatite [$Ca_5 (PO_4)_3$ F] or carbonate apatite [$Ca_5(PO_4, CO_3, OH)_3(F, OH)$] where it occurs as detrital grains or a primary deposit (Deer *et al.*, 1967).

Phosphates are known to be concentrated in ironstone nodules (Schwertmann and Taylor, 1987). (PO_4^{3-}) anions are known to become adsorbed or exchanged on clay minerals where they replace (OH^-) ions exposed on the planar surfaces or around the edges of clay minerals (Degens, 1965). The ability of kaolinite to fix phosphate ions (PO_4^{3-}) is of great importance in soil science (Deer *et al.*, 1967).

In the present study, the negative correlation between (P_2O_5) and (CaO and CO_2) (Table 5) rules out the probable occurrence of carbonate in the marl. On the other hand, the positive correlation between (P_2O_5) and oxides of the detrital fraction (SiO_2, 0.43; Al_2O_3, 0.42; TiO_2, 0.34; Fe_2O_3, 0.28 and K_2O, 0.50) leads to the conclusion that the bulk of (P_2O_5) is within the clay minerals.

Water of Crystallization (H_2O^+):

Water of crystallization (H_2O^+) is an essential constituent of all clay minerals which are also called "hydrous silicates" of aluminium and of magnesium.

In illite, hydronium ion (H_3O^+) or H_2O^+ replaces some (K^+) in the inter-layers of the structure leading to hydro-muscovite (Deer *et al.*, 1967; Phillips and Griffen, 1981; Aswad and Tobia, 2008). In the present study, the calculated (H_2O^+/K_2O) ratio in illite (Table 3) of (1.59) is higher than that in the ideal formula of (1.16) in illite (Table 2) indicating a possible replacement of (K_2O) by (H_2O) as stated earlier.

The normalized average (H_2O^+) of the marl of the present study of (6.24%) is higher than that of Vinogradov (1962) of (5.0%). There is no average (H_2O^+) in Li (2000) (Table 1B).

Correlation coefficient matrix (Table 5) shows that (H_2O^+) is positively correlated with oxides of the detrital fraction, while it is negatively correlated with oxides of the chemical fraction (MgO, CaO and CO_2) suggesting that the bulk of (H_2O^+) is within the detrital fraction, the clay minerals.

Cobalt (Co) and Nickel (Ni):

These two transition elements are resistant to dissolution processes and remain in the solid products of breakdown processes for long periods and hence they remain in the detrital fraction of the source rocks during weathering. In sedimentary rocks, the two elements occur in two main phases; the clay minerals, where they replace Fe^{2+}, Fe^{3+} and Mg^{2+} in the octahedral layer, since they have similar ionic radii (Co^{2+}, 0.72 Å; Fe^{2+}, 0.74 Å; Fe^{3+}, 0.64Å), and in iron oxides and hydroxides either adsorbed on the surfaces of iron oxide phaes or replacing Fe^{3+} or Fe^{2+} (Goldschmidt, 1958; Frolich, 1960; Aljubouri, 1972; Dhannoun *et al.*, 1988).

The normalized averages of Co and Ni in the marl of the present study are (13 ppm) and (190 ppm) respectively. Cobalt is slightly higher than that of average shale (19 ppm) and nickel is much higher, (3.8 times) as that of the average shale of (50 ppm) (Li, 2000).

In the correlation coefficient matrix of Table (2), the two elements are positively correlated with the oxides of the detrital fraction (SiO_2, Al_2O_3, TiO_2, Fe_2O_3, Co only, Na_2O and K_2O) indicating their similar geochemical behaviour and their possible associations with clay minerals and iron oxides. They are usually adsorbed on iron oxides surfaces which are considered to be as scavengers for these elements (Krauskopf. 1967; Kessler and Muller, 1988; Schwertman *et al*., 1989).

Gallium (Ga) and Rubidium (Rb):
The two elements are often found in the same mineral phases; in igneous and metamorphic rocks; they are usually occur within the K-feldspars ($KAlSi_3O_8$), and micas. Rubidium substitutes for potassium (K^+, 1.33 Å) with similar ionic radius, while gallium substitutes for aluminium (Al^{3+}, 0.51 Å). In sedimentary rocks, the most common mode of occurrence of these two elements is within clay minerals, especially in illite (KAl-silicate).

The normalized average (Ga) content of marl of the present study (57 ppm) is quite higher than that of average of shale (19 ppm) of Li (2000). On the other hand, the normalized average (Rb) content (107 ppm) is lower than the average shale (140 ppm), Table 1 (A and B). While it is possible to explain the low (Rb) content which is due to low K_2O content (2.30%), it is not easy at this stage to explain the high Ga content , since the average Al_2O_3 (8.30) is much lower (about half) than that of average shale (16.62%) (Table 1A and B).

Correlation coefficient matrix (Table 2) shows that rubidium is positively correlated with the oxides of the detrital fraction (Al_2O_3, FeO, MgO and K_2O) having the highest correlation of (0.70) with potassium and leaving no doubt that (Rb) is within the detrital fraction substituting for potassium in illite. On the other hand, gallium has negative correlation with all these oxides and a positive correlation with CaO (+0.60). This is rather unusual for gallium Ga^{3+} which has much smaller ionic radius (0.62 Å) than calcium (0.99 Å) and it has a higher charge too; so it is very unlikely to substitute for calcium.

Marl samples of the present study are divided into two populations or groups, red marl population (12 samples) and green marl population (10 samples). Correlation coefficient matrix for the red marl (Al-Kawaz, 1980) shows that (Ga) has strong negative correlation with oxides of the detrital fraction with the exception of (FeO) where it has strong positive correlation (0.72) and therefore, it may be concluded that the bulk of gallium in the red marl is substitute for ferrous iron (Fe^{2+}) within ferrous minerals. Aljubouri (1972) in his study of marl of Triassic age (Keuper marl) at East Midland area, England, stated that gallium substitutes for Fe^{2+}. In the present study, positive correlation between gallium and CaO (0.70) is perhaps indirect. Possible analytical error for gallium is perhaps responsible for this unusual behavior.

On the other hand, correlation coefficient matrix for the green marl (Al-Kawaz, 1980) shows that gallium has positive correlation with oxides of the detrital fraction (Al_2O_3, TiO_2 and Fe_2O_3) indicating its presence within the clay minerals substituting for (Al^{3+}) and within iron oxides substituting for (Fe^{3+}). In the reducing

environments of the green marl, there was perhaps dissolution and reconstitution of some clay mineral phases leading to redistribution of gallium from the ferrous iron site (within clay minerals) into (Al^{3+}) and Fe^{3+} sites in the octahedral layers.

Strontium (Sr) and Barium (Ba):

The most common modes of occurrence of strontium and barium in sedimentary rocks are: (a) within carbonates and sulphates, substituting for calcium, especially strontium, since it has similar ionic radius (1.12 Å) to calcium (0.99 Å). Barium has relatively larger ionic radius (1.34 Å) and hence smaller amounts of Ba^{2+} compared with strontium could substitute for calcium (Krauskopf, 1967; Deer *et al*., 1967); (b) within clay minerals, either adsorbed on clay mineral surfaces or substituting for inter-layer cations like potassium and calcium. Barium could easily substitutes for potassium (ionic radius 1.33Å) in illite, having very similar ionic radius. Strontium with ionic radius between calcium and potassium can substitute for both (Carrol, 1958; Krauskopf, 1967); (c) as an independent phase in the sulphate (barite, celestite and baritocelestite); in the carbonates strontianites ($SrCO_3$) and witherite ($BaCO_3$).

In addition, smaller amounts of (Sr and Ba) are usually found within feldspars substituting for potassium in the K-feldspars and for calcium in the plagioclase feldspars, which always contain minor amounts of K-feldspars (Phillips and Griffen, 1981). The averages of Sr and Ba contents of marl of the present study (540 ppm and 776 ppm) respectively, higher than the average of (170 ppm for Sr) and (580 ppm for Ba) (Li, 2000), Table 1 (AandB). Correlation coefficient matrix of Table (5) shows that strontium has positive correlation with FeO (0.45) only, and an insignificant correlation with the oxides (Al_2O_3, Na_2O and K_2O) indicating its probable presence in the clay minerals or the detrital fraction.

Barium, on the other hand, has negative correlation with oxides of the detrital fraction (SiO_2, TiO_2 and MgO) and positive correlation with CaO (0.47) and CO_2 (0.33) indicating its association with carbonate phase, in the mineral calcite or perhaps as an independent carbonate phase, witherite ($BaCO_3$). The calculated amount of witherite is (0.11%). Strontium may be present in this phase, replacing (Ba^{2+}) as well as within the clay minerals, replacing potassium.

Both elements or part of them could be within the detrital plagioclase feldspar which was identified as oligoclase (Al-Kawaz, 1980; Aljubouri and Al-Kawaz, 2006, plate 3). In this case, they substitute for potassium in K-feldspr present as minor amounts as well as for calcium in plagioclase.

Zirconium (Zr):

Zirconium in sedimentary rocks is generally accepted to be represented by zircon ($ZrSiO_4$), which is the residual product of physical weathering of igneous rocks (Goldschmidt, 1958; Vlasov, 1964). Zircon is resistant to weathering and chemical alteration. It is usually transported to the area deposition as detrital grains together with the clay minerals. Zircon constitutes part of the heavy minerals having specific gravity of (4.68) and hardness (7.5) (Hurlbut and Klein, 1977).

The normalized average (Zr) content of marl of the present study (106 ppm) is less than that of average shale of (160 ppm) of Li (2000) (Table 1A and B).

Correlation coefficient matrix (Table 5) shows that (Zr) has no significant correlation with any of the major oxides, either in detrital or chemical fractions. This may indicate its presence mainly as an independent detrital grain and hence it is concentrated in very small amounts. It is not much affected by variations, increase or decrease, within the marl sediments.

COLOUR OF MARL SEDIMENTS

In the studied localities, two main colours of marl sediments were observed; these are red and green. Some samples are "drab" in colour (very pale brown to pale yellow) and their colour is considered as a shade of the red colour. The distribution of these colours within the collected samples is shown in Table (6).

The red colour is restricted to Shaikhan (5 samples) and Shaikh Ibrahim (7 samples). All Mishraq (8) samples are green and all Makhmur (4) samples are drab.

There is a vast amount of work on the red and green colours of argillaceous sediments and only few will be cited here. Nearly all workers agree that the cause of red colouration is the dispersion of the very fine grained pigment of haematite between and coating mineral grains of the sediments. The red colour and the presence of haematite are both an indication of oxidizing environment (Carroll, 1958; Aljubouri, 1972; Van Houten, 1973; Al-Rawi, 1983; Aljubouri *et al.*, 1994). Green colour on the other hand, is caused by the presence of green clay minerals (green Fe-chlorite) with relatively high amounts of ferrous (Fe^{2+}) iron in their structure and it is an indication of a reducing environment (Grim, 1951; Dunham, 1955; Velde, 2003).

The ratio ($Fe_2O_{3\ t}$/FeO) is an indicative of the oxidation state of the sediments. The percentage of (Fe_2O_3) or (FeO) alone is not important in influencing the intensity of the colour or the degree of oxidation, but the ratio of ($Fe_2O_{3\ t}$/FeO) is the decisive factor. A ratio lower than (8) indicates reducing conditions, while higher ratios are indications of a more oxidizing environments (Van Houten, 1964, 1968; Friend, 1966; Aljubouri *et al.*, 1994).

However, this is not always true, for example, the ($Fe_2O_{3\ t}$/FeO) ratio in the Gercus (Middle Eocene) red marl (Al-Rawi, 1983) is only (7.36). Ferric oxide (Fe_2O_3) in the red marl is always higher than the green marl, while ferrous oxide (FeO) is the reverse being always higher in the green than in the red marl (Table 1DandE). Total iron ($Fe_2O_{3\ t}$) may be higher or lower in the red than in the green marl. Drab marl represents an intermediate composition in iron oxides. It has been observed that the intensity of red colour increases with the increase of ferric oxide (Fe^{3+}) or with increase of ($Fe_2O_{3\ t}$/FeO) ratio (Aljubouri, 1972; Aljubouri *et al.*, 1994; Mohammed, 2007). There is no published work on the intensity of green colour. From the observations of colours and the concentrations of iron oxides a criteria for the colour of red and green argillaceous sediments in Iraq could be developed and is shown in Table (7).

The decrease in haematite pigment causes the sediments to be drab in colour (Aljubouri *et al.*, 1994). In the present study, the drab marl has an average Fe_2O_3 (Fe^{3+}) of (3.86%) lower than that of red marl of (5.13%) and may indicate leaching of some Fe_2O_3 pigment into the adjacent red marl sediments. Alternatively and since its FeO (0.77%) is higher than the red marl (0.59%; Table 1D and F), it may indicate a mild reducing environments where the reduction of haematite was incomplete.

Table 6: Sample distributions in the studied localities and their colous.

Sample No.	Colur	Sample No.	Colour
1	R	17	R
2	D	18	R
3	G	19	R
4	D	20	R
5	R	21	G
6	D	22	G
7	R	23	G
8	R	24	G
9	R	25	G
10	D	26	G
11	D	27	G
12	R	28	G
13	D	29	D
14	R	30	D
15	R	31	D
16	G	32	D

Samples (1-9), Shaikhan;
Samples (10-20), Shaikh Ibrahim
Samples (21-28), Mishraq
Samples (29-32), Makhmur
R=Red; G=Green; D=Drab

Table 7: Criteria for the colour of red and green argillaceous sediments in Iraq.

Fe-oxides	Colour		
	Red	Drab	Green
Fe_2O_3 $(Fe^{3+})\%$	> 4.5	3.5 - 4.5	2 – 3.5
FeO%	0.5 – 0.77	0.77 – 0.9	0.9 – 2.5
$Fe_2O_{3\,t}\%$	> 5	< 5	> 5
$Fe_2O_{3\,t}$/FeO	7 - 11	6 - 7	< 6

In the present study, the reducing environments at Mishraq was most likely initiated by the presence of sulphate ions from gypsum deposits, organic matter from oil seepages and the sulphate reducing bacteria. The reduction of sulphates produces hydrogen sulphide (H_2S) gas which is oxidized by sulphates and producing native sulphur (Dhannoun and Saleh, 1976). Fe^{3+} in haematite in the red marl is reduced to the ferrous state (Fe^{2+}) which enters the structure of chlorite and forming green chlorites, like berthierene (ferrous, 7Å chlorite) and chamosite (ferrous aluminous 14Å chlorite) (Velde, 2003). The absence of red pigment due to the reduction of haematite and the formation of green chlorites result in the green colour of marl sediments at Mishraq. The presence of chlorite was proved by X-ray diffraction analysis (Aljubouri and Al-Kawaz, 2006) and by normative calculations (Table 3). The other two green samples represent very localized reducing environments due to local enrichment of solution with organic matter.

CONCLUSIONS

Geochemical study of marl sediments concludes at the following points:

1. The marl sediments could be divided into two main fractions: detrital and chemical fractions with the oxides of each, in general, have negative correlation with the other. The mineral phases of the detrital fractions were brought to the basin of deposition from the weathering zone and suffered little alteration. The oxides of this fraction are SiO_2 in the clay minerals and quartz; Al_2O_3 in the clay minerals and feldspars; TiO_2 in Ti-minerals; Fe_2O_3 in the clay minerals and in iron oxides; MgO mostly in the clay minerals and partly in dolomite; Na_2O and K_2O in the clay minerals and feldspars; MnO, P_2O_5 and H_2O^+ are in the clay minerals. The mineral phases of the chemical fraction are the carbonates, calcite and dolomite which were precipitated in the basin of deposition and represented by the oxides (CaO, some MgO and CO_2). The trace elements (Co, Ni, Ga, Rb and some Sr and Zr) are within the detrital fraction, mostly in the clay minerals and iron oxides. Ba and part of Sr are mostly within the carbonate phase.

2. Normative calculations show that detrital fraction constitutes around (58%) of mineral phases and consists of illite (28%), chlorite (8%), kaolinite (2%), montmorillonite (1%), albite (1%), quartz (15%), haematite and Ti-minerals (3%). The chemical fraction comprises about (42%) of mineral phases, with calcite (38%) and dolomite (4%).

3. Colour study of marl sediments shows the presence of three colours: the red, is a primary colour and due to the red pigmentation of haematite from the weathering zone. The drab colour is possibly due to leaching of some haematite pigment from the sediments or due to mild reducing environments. The green colour is secondary in origin and due to the prevailing environments at Mishraq area, caused by the presence of organic matter from oil seepage. The (Fe^{3+}) in haematite was reduced to the ferrous (Fe^{2+}) state which enters the structure of the formed green chlorite minerals giving green colour to the sediments.

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