Factors Controlling the Mineralogical and Chemical Distributions in Safra Member (Upper Maastrichtian), Western Desert, Iraq

Khalid J. Aswad Department of Geology College of Science Mosul University Kotayba T. Al-Youzbakey Research Centre for Dams and Water Resources Mosul University

Sameer A. Hirmiz Department of Geology College of Science Mosul University

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ABSTRACT

Safra Member (Upper Maastrichtian) represents the upper part of Digma Formation, which outcrops to the west of Ga'ara depression. It consists of dolostone alternating with claystone, marl and thin beds of phosphorites; limestone occupies the upper part of the rocks.

Factor analysis shows that the mineralogical distribution is represented by four groups; the first is dolomite; the second is montmorillonite and fine grained quartz; the third is palygorskite, sepiolite and apatite and the last is calcite. There are two main factors that control the distribution of elements; the first is the offshore environment factor represented by precipitated calcite and the detrital fraction; montmorillonite and fine-grained quartz. The second factor is represented by the effect of brackish water (schizohaline) nearshore environment, which is enriched with Mg, and caused the complete dolomitization of calcite, and the transformation of the outer part of montmorillonite to palygorskite. Some palygorskite grains adsorbed dissolved silica, which has resulted from the dissolution of fine-grained quartz or from amorphous silica and transformed to sepiolite. Apatite has formed due to decreasing in Mg/Ca ratio. In addition to the less effective third factor which is represented by the presence of X-ray amorphous phosphates (collophane) as teeth and fish bones.

العوامل التي تتحكم بالتوزيع المعدني والكيمياني في عضو الصفرة (المسترختيان الأعلى) في الصحراء الغربية، العراق

الملخص

يمثل عضو الصفرة (الماسترختيان الأعلى) العضو العلوي في تكوين دكمة في الصحراء الغربية العراقية. ويتكون بشكل رئيس من تعاقبات صخور الدولومايت والصخور الطينية والمارل المكونة من معادن المونتموريلونايت والباليكورسكايت وقليل من السيبيولايت فضلاً عن حبيبات ناعمة من الكوارنز مع أفاق قليلة السمك من الفوسفور إيت. وتمثل الصخور الكلسية الجزء العلوي من العضو.

أوضح التحليل العاملي بأن توزيع المعادن لهذا العضو يقسم الى اربعة مجاميع هـــي مجموعـــة الدولومايت ومجموعة المونتموريلونايت والكوارنز ومجموعة الباليكورسكايت والمسيبيو لايت والأبتايـــت و أخيراً مجموعة الكالسايت. ان العوامل الرئيسة المتحكمة في توزيع العناصر ضمن أطوارها المعدنية تتمثل بعاملين رئيسين هما عامل البيئة الساحلية التي أدت السي ترسيب الصخور الكلمسية وأطيان المونتموريلونايت والكواريز والتي تمثل الجزء الفتاتي المترسب في هذه البيئة، بينما العامل الثاني يتمثل بتأثير المياه المختلطة القريبة من الساحل والمشبعة بالمغنيسيوم التي أدت الى حدوث عملية الدلمت وحولت أغلب الكالسايت الى الدولومايت والجزء الخارجي من حبيبات المونتموريلونايت السيكا الذائبة وتحولت الى الميبيو لايت، وقد تكون الأبتايت نتيجة لاتخفاض نسبة المغنيسيوم الى الكالسيوم في المحلول، فضلاً عن وجود عامل ثالث ذو تأثير قليل نسبياً بتمثل بتكون أطوار فوسفائية غير متبلورة من محتوى الرواسب من أسنان وعظام الأسماك.

INTRODUCTION

Safra Member outcrops are located to the west and south west of Ga'ara depression in the western desert of Iraq at a distance of about 100 Km. north of Rutba city (Fig. 1). Safra (Upper Maastrichtian) is the upper member of Digma Formation. It consists of alternations of different rocks; dolostones, claystones, marls, limestones and phosphorites.

This rock assemblage is common in other formations in the western desert, e.g. Akashat and Rutga Formations (Al-Bassam and Al-Saadi, 1985; Shadfan et al., 1985 and Aba-Hussain, 1987).

The late Creataceous Safra Beds of Digma Formation and Early Paleocene Traifawi Member of Akashat Formation represent enormous Palygorskite resources in western desert of Iraq. They are marine black shale facies associated with phosphate and diatomaceous carbonates (Al-Bassam, 1997).

Palygorskite may be found in variety of sedimentary environments as well as in hydrothermal deposits. It has been mainly reported in brackish and lacustrine environments, but marine and fluvial deposits may also contain palygorskite, as well as, weathering products of Mg-rich rocks and soils of arid and semi-arid regions (Singer and Galan, 1984). Palygorskite and sepiolite were formed in shallow-marine environment from saline waters (Hammerly, et al., 2001). The most major deposits were originally formed in shallow seas and lakes as chemical sediments or by the reconstitution of montmorillonite (USGS, 2001).

The studied area is located within the Ga'ara uplift which is the northern part of Rutba uplift. It represents the northern and western limbs of the Ga'ara anticline (Jassim, et al., 1986).

Safra Member overlies the Na'aja Member (the lower member of Digma formation (Upper Campanian-Lower Maastrichtian) and laid by Traifawi Member with conformable surface. The oyster limestone represents the upper bed of Safra member (Hirmiz, 1989).

The aim of this work is to investigate the factors that control the distribution of the major and some trace elements and its mineralogical phases within the Safra Member.

METHODOLOGY

Six outcrops were selected for the study of Safra member located to the west (sections A-D) and southern west (section E) of Ga'ara depression and section F located about 29 Km to the west of Rutba city (Fig. 2). All sections represent a narrow strip of outcrops to the west of Ga'ara depression expanded toward southern desert (Fig. 1).

Fifty-nine samples were analyzed by X-ray diffraction spectrometer (Phillips, PW1130) using Cu_{kx} , 40 Kv and 20 mA, with chart speed of 2θ /minute, using standard charts. The chemical analysis of major and trace elements were carried out by X-ray fluorescence spectrometer (Phillips, PW1450). CO_2 and SO_3 by gravimetric method (Jeffery and Hutchison, 1981). All analyses were done at the department of geology, University of Mosul.

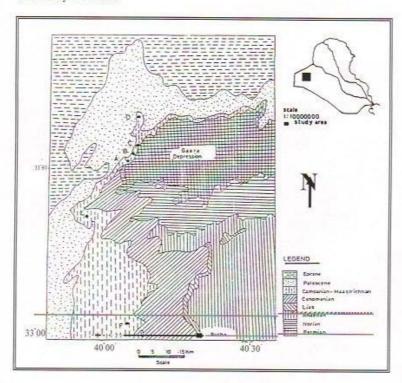


Fig. 1: Location map of the studied sections (Hirmiz, 1989).

LITHOLOGY

Fig. (2) shows the lithology of the studied sections. Claystones found in beds of varied thickness interbedded with other kind of rocks. They are fissile, friable, grey to yellow and red colour due to the iron oxide phases (limonite and hematite). Claystones consist of palygorskite and montmorillonite as the main clay minerals with a little amount of sepiolite, as well as quartz, which is found in fine grains. Phosphates found as phosphatic pellets and bone fragments.

Dolostones are the main rocks in this unit, they are white to grey, fine crystalline with high porosity and have a varied thickness from 1to 2.5m, they are composed of

dolomite and accessory of iron oxides.

Marl sediments represent about 35% of all kind of sediments. They are grey to yellow, fine grains, friable and comprised of montmorillonite, palygorskite and a little of sepiolite as well as quartz, phosphatic materials and iron oxides. The carbonate fraction composed of very fine dolomite.

Phosphorites are thin horizons interbedded with other rocks. They are comprized of pellets, bone fragments and intraclasts with dolomicrite. While limestones represent the upper part of Safra member (in the most sections). They are composed of shelly limestone. The bivalve shells are spary calcite found in groundmass of fine dolomicrite. The shelly limestones are very tough with high porosity (Hirmiz, 1989).

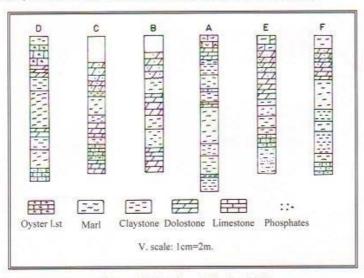


Fig. 2: Litology of the studied sections (Hirmiz, 1989).

RESULTS

Tables (1 and 2) show the ranges of mineralogical and chemical compositions of the studied sections, respectively.

The mineralogical interrelationship is stated in (Table 3). It illustrates that dolomite

displays negative relationship with palygorskite, sepiolite, montmorillonite, calcite, quartz, and apatite. There are positive relationships among palygorskite, sepiolite and apatite, and between montmorillonite and quartz. (Table 4) shows the R-mode correlation coefficients among the major and trace elements.

Table 1: Mineralogical analyses of the studied sections (A-F).

Minerals	A2A14 N=13 Range (%)	B1B11 N=8 Range(%)	C1C12 N=11 Range(%)	D1D10 N=10 Range(%)	E1E11 N=9 Range(%)	F1F9 N=8 Range(%)
Palygorskite	4.20 - 72.00	5.00 - 18.87	1.10 - 22.80	2.30 - 35.20	2.10 - 26.00	22.00-89.50
Montmorillonite	0.50 - 65.00	0.50 - 59.30	0.50 - 67.30	0.00 - 38.10	0.00 - 27.80	46.80-63.0*
Sepiolite	0.20 - 1.90	0.26 - 2.20	0.00 - 1.90	0.00 - 0.50	0.30 - 1.17	1.00 - 7.10
Dolomite	0.00 - 91.00	39.5 - 93.4	10.3 - 92.5	10.4 - 93.20	12.0 - 85.00	0.70 - 16.00
Calcite	****			0.90 - 50.00	12.0 - 96.19	
Quartz	1.00 - 21.30	0.30 - 11.30	0.50 - 14.30	1.8 - 13.60	0.80 - 26.20	0.00 - 5.70
Apatite	0.40 - 7.40	0.30 - 20.00	0.90 - 11.00	0.00 - 6.50	0.00 - 5.70	2.00 - 28.00

^{*} Only in two samples

Table 2: Chemical analyses of the studied sections (A-F)

trace elem. N=13 Range			B1B10 N=8 Range	C1C12 N=11 Range	D1D10 N=10 Range	EIE11 N=9 Range	F1F9 N=8 Range	
		0.86 - 51.88	2.07 - 19.98	1.80 - 52.00		1.73 - 51.92	3.60 - 49.35	
Al ₂ O ₂	-84	0.12 - 11.92	0.28 - 2.75	0.17 - 11.36	0.30 - 9.17	0.30 - 11.96	0.33 - 10.19	
TiO ₂	89	0.00 - 0.61	0.00 - 0.17	0.00 - 0.62	0.00 - 0.67	0.00 - 0.53	0.00 - 0.45	
Fe ₂ O ₂	- 64	0.25 - 5.82	0.28 - 2.28	0.23 - 3.28	0.26 - 3.50	0.09 - 4.14	0.36 - 3.20	
MgO	++	7.00 - 19.47	13.37-21.28	5.55 - 22.60	6.89 - 21.79	1.45 - 17.48	4.33 - 20.15	
CaO	744	2.31 - 33.60	19.84-34.78	4.48 - 36.60	5.50 - 33.65	4.67 - 49.83	7.75 - 37.77	
K2O	**	0.01 - 0.64	0.02 - 0.21	0.01 - 0.69	0.01 - 0.51	0.01 - 0.69	0.10 - 0.43	
Na ₂ O	166	0.02 - 2.47	0.19 - 4.65	0.02 - 2.49	0.04 - 1.18	0.04 - 3.55	0.01 - 0.93	
P2O5	104	0.21 - 3.56	0.33 - 5.75	0.66 - 5.87	0.32 - 5.01	0.39 - 6.51	0.29 - 6.45	
F	**	0.01 - 0.29	0.04 - 0.41	0.03 - 0.50	0.03 - 0.33	0.03 - 0.62	0.02 - 0.65	
CI	-64	0.01 - 0.92	0.01 - 1.72	0.01 - 1.01	0.01 - 0.53	0.02 - 1.16	0.01 - 0.81	
SO ₃	**	0.10 - 0.95	0.20 - 3.49	0.07 - 3.21	0.10 - 2.66	0.09 - 1.44	0.30 - 0.89	
CO ₂	30	1.83 - 44.38	25.39-43.59	10.2 - 43.55	0.68 - 44.85	3.28 - 43.38	16.4 - 41.99	
H ₂ O	240	0.36 - 12.97	0.65 - 6.47	0.24 - 12.70	0.84 - 11.26	0.33 - 11.17	0.67 - 6.22	
MnO (ppm)	39 - 183	38-61	29 - 93	31 - 79	9 – 79	8-81	
V	60	2-273	2-138	3-601	3-601	3-260	4-280	
Cr	+4.	3-267	4-112	4-246	12-210	8 - 226	7-214	
Ni	84	3 - 70	4-18	3-61	3-42	3 - 72	4-68	
Co	14	2-33	2-11	3 - 38	3 - 34	2-53	4-33	
Sr	463	189 - 433	254 - 582	169 - 483	265 - 490	210 - 583	189 - 550	
Rb	10	3 - 33	4-15	3-33	0-20	3-41	4-26	
Y	24	2-25	3-17	2-25	3-8	1-27	2-19	
Zr	MAC .	5-201	4-56	7-192	8-218	6-205	6-18	
U	**	2-12	3-22	3-21	2-16	1-19	3-18	
Ba	44.	4-38	18-41	5 - 43	7 - 40	5 - 52	5-42	
Cu	60	5-23	5-15	6-45	5-17	4-22	4-20	

The factor analysis for mineralogical phases is useful to define the factors that control the mineralogical distribution in Safra beds. There are three main groups; the first is montmorillonite and quartz, the second is dolomite and the third is palygorskite, sepiolite and apatite, as well as the secondary group of calcite (Fig. 3). All these groups are distributed by three main factors with variance of 79% (Table 5). The first factor is

loaded by montmorillonite and quartz perpendicular to the second bipolar clustering factor of palygorskite - sepiolite - apatite loaded on the positive side, while dolomite on the negative side. Calcite has a poor loading on the third factor (Fig 3).

Table 3: R-mode correlation coefficient of minerals.*

	Palygo.	Montm.	Sepiol.	Dolom.	Calcite	Quartz	Apatite
Palygo.	1	- 0.06	0.49	- 0.36	- 0.15	0.06	0.58
Montm.		1	0.15	- 0.52	- 0.15	0.43	- 0.18
Sepiol.			1	- 0.51	- 0.16	0.03	0.59
Dolom.				1	- 0.27	- 0.39	- 0.41
Calcite					1	- 0.08	- 0.11
Quartz						1	- 0.80
Apatite	Bo B					10.10	-1

^{*} Number of samples = 59, confidence level = 95%.

Table 4: R-mode correlation coeficient of oxides and trace elements.*

-array	SiO	Al _k O ₂	TiO ₂	Fe _j O _j	Mgo	CaO	K ₂ O	Na ₂ O	P ₂ O ₂	F	CI	50,	CO:
SiO ₂	1.00	0.98	0.94	0.92	-0.57	-0.93	0.89	0.43	-0.14	-0.22	0.42	-0.15	-0.94
Al _i O ₃	THE REAL PROPERTY.	1.00.	0.94	0.91	-0.57	-0.92	0.91	0.41	-0.13	-0.20	.0.39	-0.15	-0.92
TiO ₂ .		1	1.00	0.87	-0.62	-0.86	0.87	0.47	-0.11	-0.18	0.40	-0.11	-0,88
Fe ₂ O ₂				1.00	-0.46	-0.91	0.84	0.42	40.23	-0.30	0:40	-0.17	-0.91
Mgo:					1.00	0.35	-0.57	-0.26	-0.14	-0.09	-0.21	0.00	0.50
CaO						1.00	-0.79	-0.46	0.15	0.22	-0.43	0:16	0.88
K20						-	1.00	0.45	-0.19	+0.26	0.41	-0.19	-0.84
Na ₀ O						1	1000	1.00	0.01	+0.06	0.90	-0.12	-0.45
P2On								41.20	1:00	0.96	-0.10	0.38	0.07
F									1	1.00	-0.15	0.32	0.13
CI										-	1.00	-0:08	-0.41
SO ₂						1			-			1.00	0.08
CO:													1.00

	H ₂ O	MnO	V	Cr	Ni	Co	Sr	Rb	Y	Zr	U	Ba	Cu
SiO ₂	0.93	0.50	0.66	0.85	0.95	0.96	-0.73	0.92	0.75	0.96	0.30	≥0.85	0.58
Al ₂ O ₂	0.93	0.49	0.68	0.84	0.98	0.97	-0.73	0.95	0.79	0.97	0.32	≥0.84	0.61
TiO ₁	0.91	0.47	0.65	0.80	0.91	0.93	-0.66	0.91	0.71	0.93	0.34	-0.78	0.59
Fe ₂ O ₃	0.88	0.48	0.61	0.78	0.90	0.86	-0.71	0.88	0.70	0.87	0.20	-0.82	0.54
Mge	-0.51	-0.26	-0.36	-0.55	-0.55	-0.60	0.19	-0.56	-0.45	-0.57	-0.27	0.31	-0.3
CaO	-0.88	-0.51	-0.62	-0.88	-0.88	-0.88	0.77	-0.86	+0.74	-0.88	+0.31	0.90	+0.5
K20	0.88	0.49	0.59	0.73	0.89	0.86	-0.60	0.90	0.71	0.87	0.23	-0.74	0.59
Na ₂ O	0.51	0.34	0.28	0.42	0.41	0.37	-0.36	0.46	0.57	0.40	0.20	-0.41	0:34
PzOx .	-0.08	0.19	-8.01	-0.07	-0.13	-0.12	0.35	+0.12	0.05	40.14	0.53	0.17	0.01
F	-D.18	0.12	-0.06	-0.14	-0.20	-0.20	0.40	-0.19	+0:05	-0.21	0.45:	0.25	+0.0
CI.	0.46	0.27	0.30	0.39	0.39	0.37	-0.38	0.42	0.50	0.38	0.12	-0.34	0.34
SO ₂	-0.10	0.01	0.17	-0.08	-0.16	-0.11	0.29	-0.18	-0.07	-0.10	0.22	0.17	-0.13
CO;	-0.92	-0.49	-0.61	-0.85	-0.92	-0.89	0.69	-0.87	-0.70	-0.90	-0.30	0.80	+0.66
H ₂ O	1.00	0.54	0.63	0:76	0.90	0.90	0.68	0.88	0.70	0.89	0.31	+0.78	0.60
MnO.		1.00	0.27	0.35	0.41	0.47	-0.34	0.42	0.39	0.47	0(20)	-0.45	-0.00
V			E00	0.57	0.65	0.67	-0.46	0.63	0.52	0.69	0.27	-0.52	0.42
Cr				1.00	0.83	0.78	-0.62	0.77	0.74	0.84	0.34	-0.72	0.54
Ni					1.00	0.94	-0.72	0.94	0.80	0.93	0.30	-0.80	0,64
Co					1000	1.00	-0.70	0.91	0.71	0.95	0.33	-0.81	0.59
Sr		1			-	-772	1.00	-0.67	-0.53	40.70	-0.09	0.74	-0.3
Rb						-	1500W	1.00	0.79	0.90	0.31	-0.78	0.69
Y								111111111111111111111111111111111111111	1.00	0.73	0:45	-0.64	0.59
Zr						(1.00	0.29	-0.80	0.58
U.											1.00	-0.24	0.38
Ba												1.00	-0.49
Cu												100	1.00

^{*} Number of samples = 59, confidence level = 95%.

Factor analyses for oxides and trace elements show that they are clustered into three main groups: the first is SiO₂, Al₂O₃, Fe₂O₃, TiO₂, K₂O, H₂O, Ni, Co, Rb and Zr which is attributed to clastic fraction of true marine environment corresponding to clay minerals, quartz, iron oxides, anatase and/or rutile and zircon. The second group is P₂O₅, F, SO₃ and U, which is related to phosphate phases. The third group is MgO, CaO, CO₂, Sr and Ba which is attributed to the carbonates (the dolomite dominated system) (Fig. 4).

Table 5: Factors loading for minerals (after rotation).

Minerals	Factor 1	Factor 2	Factor 3	Factors	% of var.	Cum. %
Palygor.	0.490	- 0.218	- 0.826	Factor 1	38.479	38.48
Montmo.	0.185	0.628	- 0.160	Factor 2	24.132	62.61
Sepiolite	0.477	- 0.146	- 0.127	Factor 3	16.555	79.71
Dolomite	- 0.521	- 0.262	- 0.330	1		
Calcite	- 0.057	0.049	0.916			
Quartz	0.177	0.557	- 0.105			
Apatite	0.438	- 0.392	-0.019	17		
Ign. Value	0.999	0.998	1.683			

Table 6: Factor loading for minerals, oxides and trace elements (after rotation).

Min., Oxid. & Trace ele.	Factor 1	Factor 2	Factor 3	Factors	% of var.	Cum. %
Palygor.	0.19753	0.80361	- 0.07228	Factor 1	59.5	59.5
Montmo.	0.46200	- 0.19347	0.01573	Factor 2	10.6	70.1
Sepiolite	0.17351	0.81850	- 0.02656	Factor 3	9.3	79.4
Dolomite	- 0.38542	- 0.53609	0.02145			
Quartz	0.67958	- 0.20416	0.04119			
Apatite	0.05948	0.90961	0.17			
SiO ₂	0.92998	0.22792	- 0.01778			
Al ₂ O ₃	0.93877	0.17165	- 0.00286			
TiO ₂	0.90205	0.05515	0.01984			
Fe ₂ O ₁	0.90205	0.16294	- 0.12561			
MgO	- 0.36526	- 0.20558	-0.17320			
CaO	- 0.93249	- 0.24577	0.01763			
K-0	0.85735	0.02662	-0.08177	200		
P ₂ O ₅	- 0.15877	0.02164	0.94912	3		
F	- 0.24805	- 0.00116	0.91006			
CO ₂	-0.91780	- 0.15426	-0.03641			
H ₂ O*	0.91758	0.07907	0.02340			
Cr	0.80495	0.28252	0.06189			
Ni	0.92138	0.16760	- 0.01002			
Co	0.90432	0.18419	0.00537			
Sr	- 0.77968	- 0.20651	0.26677			
Rb	0.91003	0.04200	0.00254			
Zr	0.91493	0.11340	-0.01851			
U	0.36670	0.04800	0.75312			
Ba	- 0.87177	- 0.24861	0.06338	1		
Ign. value	13.26136	3.01773	2.46988			

GEOCHEMISTRY

Silica and alumina represent the main components of clay minerals (montmorillonite, palygorskite and sepiolite). The excess silica is related to the quartz and amorphous silica. Alumina is distributed among the clay mineral phases in different ratios. (Fig. 5) shows two groups of Al distribution; low Al content group, which reflects palygorskite and sepiolite while the other group, represents high Al content reflected by montmorillonite.

MgO is distributed between clay minerals (palygorskite and sepiolite) and dolomite. Both palygorskite and sepiolite require alkaline environment and high Si and Mg activities for stability (Singer, 1989). Although both minerals are Mg silicates, palygoskite has less Mg and more Al than sepiolite (USGS, 2001, Murray, 2002). K₂O

and some of CaO represent interlayers in montmorillonite; the later is also associated with CO2 in dolomite and calcite.

Ti0₂ correlates with clays in the form of isolated minerals (anatase and/or rutile) which are associated with clay minerals as weathering and leaching products (Millot, 1970; Weaver and Pollard, 1975), or may be substituted for Si and/or Al in crystal structure of montmorillonite (Brindley and Brown, 1980). Fe₂0₃ shows similar behavior in clays by substitution for Al³⁺ and/or as iron oxides and hydroxides; like hematite and limonite-goethite, respectively (Ibanga et al., 1983; Ambrosi and Nahon, 1986).

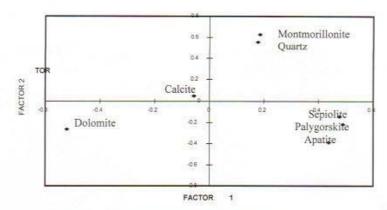


Fig.3: The distribution of minerals by the two main factors (1&2).

P₂0₅, F and some S0₃ represent phosphate minerals, the remaining S0₃ is related to the secondary gypsum. Very few samples reflect the presence of S0₄ in apatite (Fig. 6). S0₄ substitutes for P0₄ in phosphates (Mebta and Simpson, 1975), but most samples show no relation between them. The S0₄ found as a secondary sulphate salts (gypsum). Fluorine, found in apatite; it is necessary for the fixation and deposition of apatite (Aba-Hussain, 1987), and decreasing the dissolving of phosphate rocks (McConnell, 1973). Na₂0 and Cl mostly represented as secondary halite. They have not been used with SO₃ in the factor analysis in this study due to their presence as secondary minerals.

Most trace elements are related to clay minerals and iron oxides in the form of discrete clay fraction minerals, either substituting for Al and Fe, adsorbed on the clay and iron oxide surfaces due to charge deficiency, interlayer element, isomorphic replacement or as exchangeable cations, e.g. Cr, V and Y substituted for Al. Rb for K. Co, Ni and Cr for Fe. Cu and Ni adsorbed on clay mineral surfaces (Millott, 1970).

Apatite is more enriched in U than carbonate (Altschuler, 1980); on the other hand, clay minerals have adsorbed U (Prevot and Lucas, 1980), so that U is distributed between phosphate and clays but more towards phosphate (Fig. 7). It may be released from transformed montmorillonite and then enter the amorphous apatite lattice by isomorphous substitution rather than adsorption. Sr and Ba are present in low concentration (<600 ppm and <55 ppm, respectively) possibly due to dolomitization process. The strong

interrelationship among Sr, Ba, Ca and CO2 reflect the presence of both Sr and Ba in the remaining calcite phase.

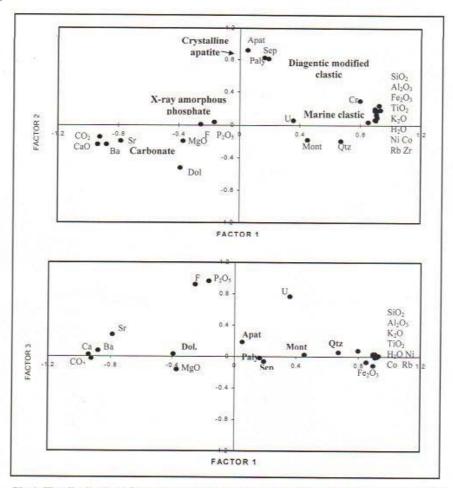


Fig.4: The distribution of minerals, oxides and trace elements by the three factors (1, 2 & 3)

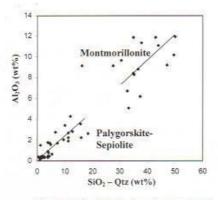
Zr found as discrete fragments within the clay fraction (e.g. zircon), (Weaver and Pollard, 1975).

All these distributions are inherited in palygorskite and sepiolite diagentic process, except Mg which enter the octahedral layer through alteration process.

THE FACTORS

The main factors controlling the distribution of major and trace elements and their mineral phases are:

The offshore true marine affinity factor, which is represented by the clastic fraction montmorillonite, very fine quartz and calcite, as well as minute grains of anatase and/or rutile and zircon. Calcite is extensively replaced by dolomite.



Secondary
Gypsum

Apatite

P₂O₅ (wt%)

Fig.5: Al₂O₃ distribution in two group Clay minerals.

Fig.6: SO₃ distribution in apatite and Secondary minerals.

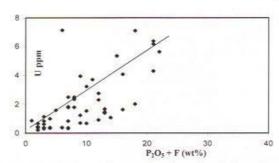


Fig.7: The presence of U in apatite more dominant than in clay minerals.

The second factor, however, is represented by the nearshore diagentic process involving the interaction of fresh and marine waters (schizohaline) and represented by the minerals: dolomite, palygoskite, sepiolite and apatite. Due to the mineralogical and elements interrelationships the factors may mean that the carbonate fraction of true marine sediment was completely replaced by dolomite. The secondary porosity resulted from the diagentic process gave excess for the schizohaline fluid to partially transform montmorillonite to palygorskite. The association of sepiolite with palygorskite may suggest that the diagentic processes have provided excess of Mg to react with amorphous silica or very fine quartz to sepiolite. The tendency of apatite towards palygorskite is

related to the offshore environment.

The third factor exhibited the loading by P_2O_5 and F may be represented by the phosphatic fragments like teeth and fish bones composed of amorphous phosphate phase (Collophane).

DIAGENESIS

Most of the detrital low-potassium smectite (montmorillonite) were probably transformed into palygorskite (Hirmiz, 1989, Al-Bassam et al., 1990 and Qassim, 1993) in the depositional site. The transformation of smectite has been proposed by Weaver and Beck (1977) to be the dominant mechanism by which palygorskite may form in brakish water, (Al-Bassam et al., 1997a).

Near shore schizohaline environment with brackish water supply of Mg- rich solution have led to the transformation of calcite (as sparite and micrite) to dolomite. It is postulated that diagensis of carbonate have increased the porosity and facilitates to higher pH. Such mechanism transforms the outer part of montmorillonite to palygorskite. The solution provides sufficient Mg to transform the soluble silica that comes from very fine grain quartz and may be amorphous silica in such high pH into sepiolite. So there is no evidence of association of montmorillonite with sepiolite only.

In the early transformation stages, the planar character of the parent smectite or illite-smectite is maintained and the palygorskite fibers are stacked within the boundaries of the precursor grains. The palygorskite and sepiolite have similar fibrous or lath-like morphology (USGS, 2001). The following stage shows the growth of short fibers to the outside of the transformed grains (Murray, 2002). The later diagentic outgrowth palygorskite occur as elongated fibers, isolated or in bundles, and sometimes associated with other minerals but usually developed in cavities, (Al-Bassam et al., 1997b).

The growth of palygorskite on the edges of the plate of montmorillonite grains indicates that Al has been provided from montmorillonite, which transformed to palygorskite in situ. As well as, there are no evidences of a detrital origin of palygorskite since all the palygorskite grains are in perfect shape (Aswad et al, 1997). The short fibers of palygorskite grains with, mesh-like texture (Aswad et al., 1997) and linked with montmorillonite indicated that no direct precipitation from solution but formed by such above mechanism.

The decreasing of Mg/Ca in solution due to dolomitization process as well as, transformation of montmorillonite to palygorskite has lead to release of Ca and caused a decrease in pH. All these factors affected the growth of very fine apatite (Bentor, 1980). So that there are more than one phosphatic phase associated with palygorskite and sepiolite. The unassociated P_2O_5 and F with apatite in the factor analysis are due to the presence of teeth and bone fragments in the carbonates which are composed of very fine apatite and/or amorphous phosphate as collophane which undetectable by x-ray diffraction. Figure (8) shows three linear relationships between P_2O_5 and F, which reflect three kind of phosphatic phases. Fluorine has been found as an additional fluorine too, in crystal structure of apatite. The additional F is due to the CO_3 substitution. F substitute for oxygen to reduce the negative (-ve) valance which come from reducing of 3- valance of (PO_4) to 2- valance of (CO_3) and/or (SO_4) which substitute for (PO_4) (Mebta and Simpson, 1975). The percentage of phosphatic phases, very fine apatite and collophane calculated from both P_2O_5 and F show asymmetrical linear relationship. Therefor, it is

clear that there are different phases varied in their content of Fluorine.

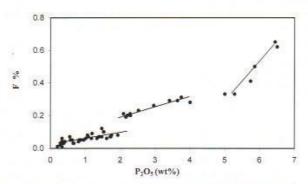


Fig.8: Different F/P2O5 ratio in three kinds of phosphatic phases.

CONCLUSION

The distribution of minerals, major and trace elements in the Safra Member has been controlled by two main factors; the first is the off shore environment factor; the carbonate precipitated as calcite with clastic fraction supplied as clay minerals which are represented by montmorillonite in marine environment together with fine grained quartz and resistant minerals e.g. hematite, anatase and/or rutile and zircon. The second factor is the schizohaline and brackish water near shore environment, which provided sufficient Mg to transform nearly all calcite to dolomite. This mechanism during diagenesis has increased porosity and facilitates infiltration of high pH and supply silica rich solution to transform montmorillonite to palygorskite which has grown around montmorillonite grains. Some of the palygorskite has absorbed colloidal silica, which has been dissolved from amorphous silica and/or from very fine quartz and transformed to sepiolite by diffusion process. Decreasing in Mg/Ca and pH enabled apatite and other phosphate phases to grow. The third factor is represented by the presence of X-ray amorphous phosphates as teeth and fish bones.

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