Mineralogy and Geochemistry of Yamama Formation (Late Beirriasian-Early Valanginian), Southern Iraq

Abdul-Mutalib H. Al-Marsoumi **Rafed A. H. Al-Mohamed**

Department of Geology
College of Science
Basrah University

Haitham G.F. Hmood

Department of Geology
College of Science
Basrah University

(Received 19/1/2003 , Accepted 7/10/2003)

ABSTRACT

A total of 138 core samples were collected from six subsurface sections of Yamama Formation. These sections were randomly distributed in West Qurna and Nasiriya oil fields. The collected samples were analyzed for; Ca, Mg, Fe, Na, Mn, Sr, Pb and insoluble residue using wet chemical analyses, in addition of representative samples were examined by X-ray.

X-ray diffractograms revealed that the bulk samples consist of calcite, dolomite, and subordinate detrital quartz. Whereas, the clay fractions of insoluble residue consist of kaolinite, illite, illite- montmorillonite mixed-layer.The kaolinite percentage shows a marked increase in Nasiriya field (i.e. towards the paleoshoreline).

The concentration of Mg and Na progressively increases as water salinity increases. The Fe and Mn concentrations are function of the clay content of the sediments, while the concentration of Sr is largely controlled by the fossil debries. Regarding Pb no systematic trend in its distribution was noted,i.e. it has an eratic distribution.

Ca/Mg molar ratio showed a less effective dolomitization process while Sr/Ca and Fe/Mn atomic ratios proved that Yamama Formation were deposited in a shallow marine-lagoonal-brackish environment.

جيوكيميائية و معدنية تكوين اليمامة (البرياسيان المتأخر-الفالنجين المبكر) جنوبي العراق

المستخلص

تم جمع 138 نموذج لبابي من ستة مقاطع تحت سطحية من تكوين اليمامة. هذه المقاطع موزعة عشوائيا على حقلي الناصرية وغرب القرنة. حللت النماذج المجموعة إلى عناصر الكالسيوم و المغنيسيوم والحديد والصوديوم والمنغنيز والسترونشيوم والرصاص والفضالة غير الذائبة ، كما أن 10% من مجموع النماذج تم تحليلها بالأشعة السينية الحائدة .

مخططات الأشعة السينية الحائدة لكل نموذج أظهرت وجود المعادن الآتية: الكالسايت والدولومايت والكوارتز، أما المعادن الطينية الموجودة ضمن الفضالة غير الذائبة فتشمل على معادن الكاولينايت و الالايت و الالايت-السمكتايت المختلط الطبقات، وقد لوحظ زيادة في الكاولينايت في حقل الناصرية مما يشير إلى القرب من خط الساحل القديم.

تراكيز المغنيسيوم والسترونتيوم تزداد تدريجيا مع زيادة الملوحة بأن الحديد و المنغنيز فيهما دالة لمحتوى المعادن الطينية في الرسوبيات، أما السترونتيوم فيعتقد أن مصدره الراجعي هياكل المتحجرات اما الرصاص فلوحظ انه لا يمتلك اتجاه محدد ، وبينت نسبة الكالسيوم/المغنيسيوم المولارية قلة فاعلية عملية الدلمتة. اما بخصوص نسبة السترونتيوم/المغنيسيوم ونسبة الحديد/المغنيسيوم اثبتت أن تكوين اليمامة ترسب في عدد من البيئات تمتد من البيئة البحرية الضحلة-اللاغونية والى البيئة المختلطة.

INTRODUCTION

The stratigraphic column of southern Iraq is characterized by thick Cretaceous successions with important hydrocarbon accumulations within many formations. Yamama represents one of the most widely distributed formations in Iraq and neighboring areas (Fig. 1).It also forms one of the most important oil production reservoirs, in southern Iraq that extends from Late Berriasian to Early Valangian within the main retrogressive depositional cycle (Berriasian-Aptian) south of Iraq. Yamama Formation was first described by (Steinicke and Bramkamp, 1952), cited in (Van Bellen et al., 1959), from its type locality at Yamama area, Saudia Arabia as a member of Yamama Group, beside, Sulaiy and Buwaib Formations. Yamama Formation in this area is composed of fragmental limestone.There is no any surface exposure for Yamama Formation is expected in Iraq and the reference section for this formation has been selected by (Rabanit, 1952), cited in (Van Bellen et al., 1959), in Ratawi well no.1, at depth interval (3665-3814 m). It consists of detrital limestone with oolitic development. The Formation is conformably overlain and underlain by the Ratawi and/or Sulaiy Formations respectively (Buday, 1980).

Yamama Formation was laid down in a depositional basin of a wide geographic extent. It covers a large area southern Iraq and extent toward its central and northern parts, where it is replaced by Zangura and Garagu Formations. Zangura Formation consists of thickly bedded limestone and clayey limestone whereas, Garagu Formation consists of algal coral and oolitic limestone (Buday, 1980). In Kuwait Yamama is replaced by equivalent Minagish Formation (Roberston, 1979), cited in (Mutlak, 1999).

Yamama Formation has been studied by many workers owing to its economic importance. These studies have dealt with stratigraphic, sedimentologic and microfacies aspects. The purpose of this work is to through more light on these mineralogical and geochemical characteristics of this formation in order to elucidate its depositional and diagenetic conditions.

METHODOLOGY

A total of 158 samples were collected from six subsurface sections of West Qurna (WQ) and Nasiriya (Ns) oil field, southern Iraq (Fig. 2). The distribution of samples are as follow; 29, 30 and 31 from Ns-2, Ns-3 and Ns-5 Samples 17, 15 and 16 from WQ 12, WQ-14 and WQ-15 respectively. The uneven distribution of the samples throughout the boreholes is attributed to the lack of some cores in some boreholes. The petrographical

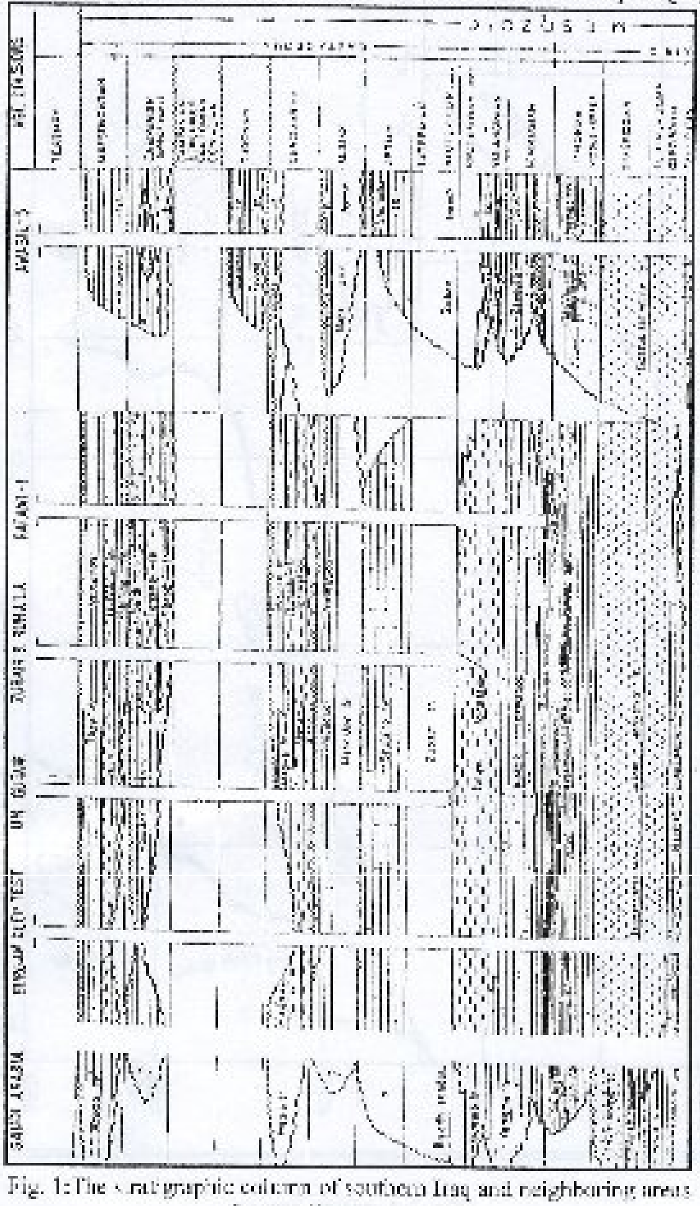

Fig. 1: The stratigraphic column of southern Iraq and neighboring areas (Van Bellen et al., 1959).

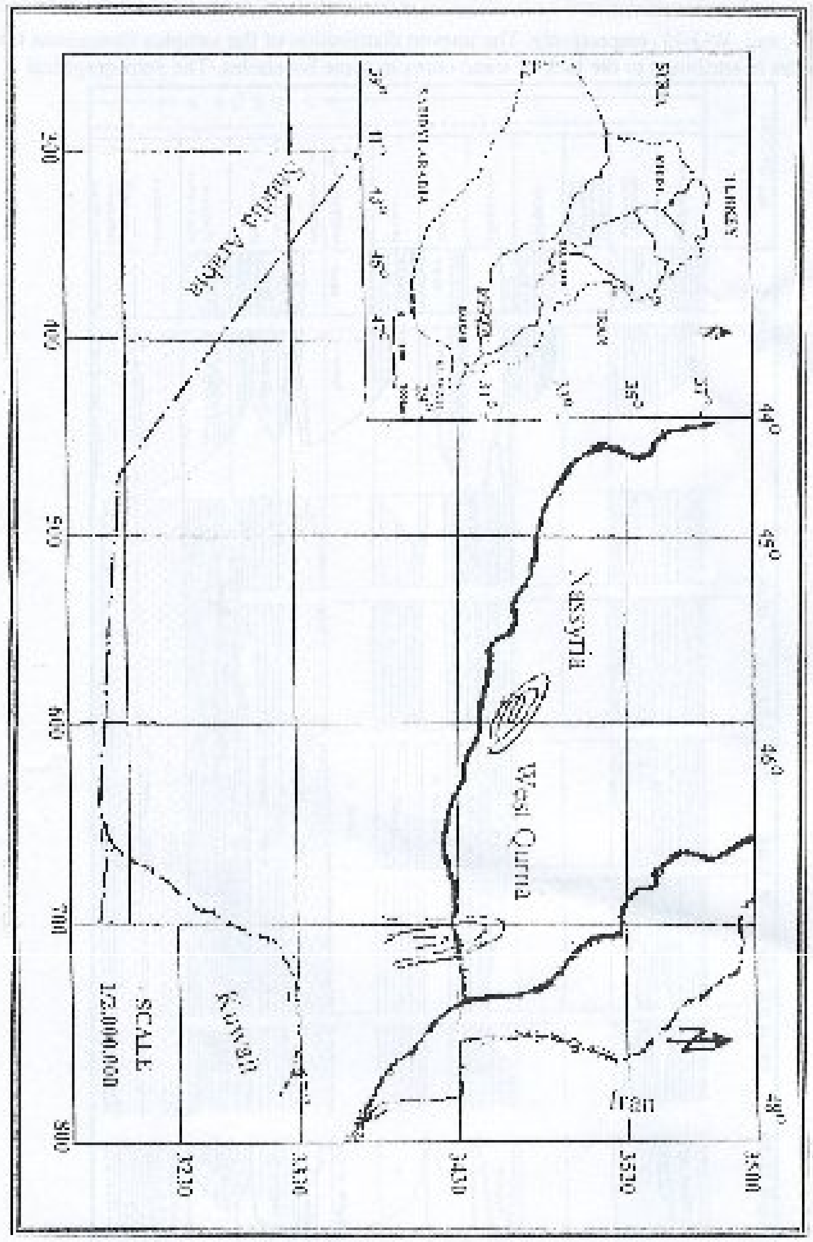

Fig. 2: Location map.

characteristics of Yamama Formation have been discussed previously by (Al-Mohamed, 2002). Therefore, only the geochemical and mineralogical studies is given here. The collected samples were firstly cleaned by toluene using soxhaliate, crushed and totally digested following the method suggested by (Al-Kufaishi, 1975). The concentrations of Na, Fe, Mn, Pb and Sr were determined by using a Perkin Elmer, 306 atomic absorption spectrophotometer (AAS), while Ca and Mg were determined by wet chemical analysis, through the titration against EDTA following the method suggested by (Bisque, 1961). The insoluble residue (I.R) was determined using dilute hydrochloric acid (10%), following the method of (Ireland, 1971), the clay fractions was separated according to the pipette method (Folk, 1974). The oriented slides from each sample were prepared following the method of (Gipson, 1966). The X-ray diffraction analyses were carried out first on the oriented samples, then on glycolated and lastly on heated samples to 550C°.

The identification of clay minerals in the obtained diffractogram were based mainly on the first basal reflection and according to the method of (Grim, 1968) and (Carrol, 1970). Furthermore, the bulk samples were also examined by (XRD). The XRD analyses were carried out using Philips PW 1050 100-spectrometer with Cu-Kα radiation source and Ni filter.

To insure the reproducibility of the analytical results, the precision of the chemical analyses was determined following the methods of (Stanton, 1966), (Maxwell, 1968) and (Rose et al., 1979). And were within the acceptable value at both 68 and 95% confidence level, the applied methods were of high analytical accuracy (1-2%).

The resultant raw data were statistically treated. The range, mean and standard deviation (Std.) for the components together with their correlation coefficients was calculated (Table 1). Furthermore, frequency histograms were constructed using long-normal intervals according to the method suggested by (Lepeltier, 1969).

MINERALOGY

The mineral contents of the Yamama Formation samples could be categorized into two groups:

1-Carbonate minerals: The XRD analyses diffractograms (Fig. 3) depict the occurrences of the following minerals according to their abundance: low Mg calcite, dolomite with trace amounts of pyrite (Fig. 4).

2-Clay minerals: Kaolinite, illite and illite-montmorillonite interstratification. All these minerals were previously recorded in the Iraqi carbonate oil reservoirs (Al-Marsoumi and Al-Hamadani, 2001).

Kaolinite in carbonate rocks is usually of detrital origin whereas illite may be of detrital or diagenetic origin (Pettijohn, 1975); smectite (montmorillonite) on the other hand could be the result of illite transformation into smectite in soils and subsequent transportation to marine basins (Flugel, 1982). Mixed-layered clay minerals could be either detrital (Carrol, 1970) or diagenetic (Hsinger and Peaver, 1988).

Kaolinite forms the major part of clay minerals that encountered within the I.R of Yamama Formation. The dominance of kaolinite with well-crystallized form reflect the near shore environment (Flugel, 1982), and the detrital origin, wet climate and low topographic relief of the neighboring area (Millot, 1970). Moreover, the amount of kaolinite shows a marked increase in Ns-field i.e. towards the paleoshoreline.

Table 1: Minimum, maximum, mean and standard deviation of the studied components in West Qurna (WQ) and Nassyria fields and their correlation coefficient.

West Qurna Field	Component	CaO %	MgO %	Sr ppm	Na ppm	K ppm	Fe ppm	Pb ppm
	No. of samples	50	50	50	50	50	50	50
	Range Min.	14.175	0.13	60	701	7	35	13
	Range Max.	54.711	1.25	1192	2442	317	4234	150
	Mean	31.75	0.58	347	920	72	1041	34
	St.D.	4.04	0.33	59	480	47	880	7

Nassyria Field	Component	CaO %	MgO %	Sr ppm	Na ppm	K ppm	Fe ppm	Pb ppm
	No. of samples	40	90	40	90	90	90	90
	Range Min.	25.77	0.195	115	250.0	11.2	24.5	9.50
	Range Max.	35.8	2.18	608	1980.0	82.0	1561.0	48.5
	Mean	34.70	0.559	257.6	795.9	38.7	160.00	14.72
	St.D.	2.75	0.46	93.03	427.45	16.45	380.7	5.77

West Qurna Field	Ca	Mg	Na	Fe	Mn	Pb	Sr	Ni
Ca	1.00	-0.22	-0.203	-0.13	-0.095	-0.005	.069	.095
Mg		1.00	.102	-.045	-.038	-.045	-.014	-.103
Na			1.00	.193	.22	.081	-.081	-.111
Fe				1.00	.153	-.005	0.13	0.246
Mn					1.00	-.065	-.091	.467
Pb						1.00	.039	.006
Sr							1.00	0.043
Ni								1.00

r = West Qurna Field
Less than 0.19 poor
0.20-0.40 fair
0.41-0.50 possibly good
0.51-0.70 good
0.71-1.00 v. good

Parry, (1983)

Nassyria Field	Ca	Mg	Na	Fe	K	Pb	Sr	Ni
Ca	1.00	-0.21	0.073	-0.38	0.227	0.084	0.096	0.006
Mg		1.00	0.1	0.124	-0.125	.91	-0.005	0.024
Na			1.00	0.145	-0.161	-0.365	0.000	0.121
Fe				1.00	0.082	0.042	-0.215	0.200
K					1.00	0.23	0.415	0.140
Pb						1.00	0.203	[illegible]
Sr							1.00	[illegible]
Ni								1.00

r = Nassyria Field
Less than 0.19 poor
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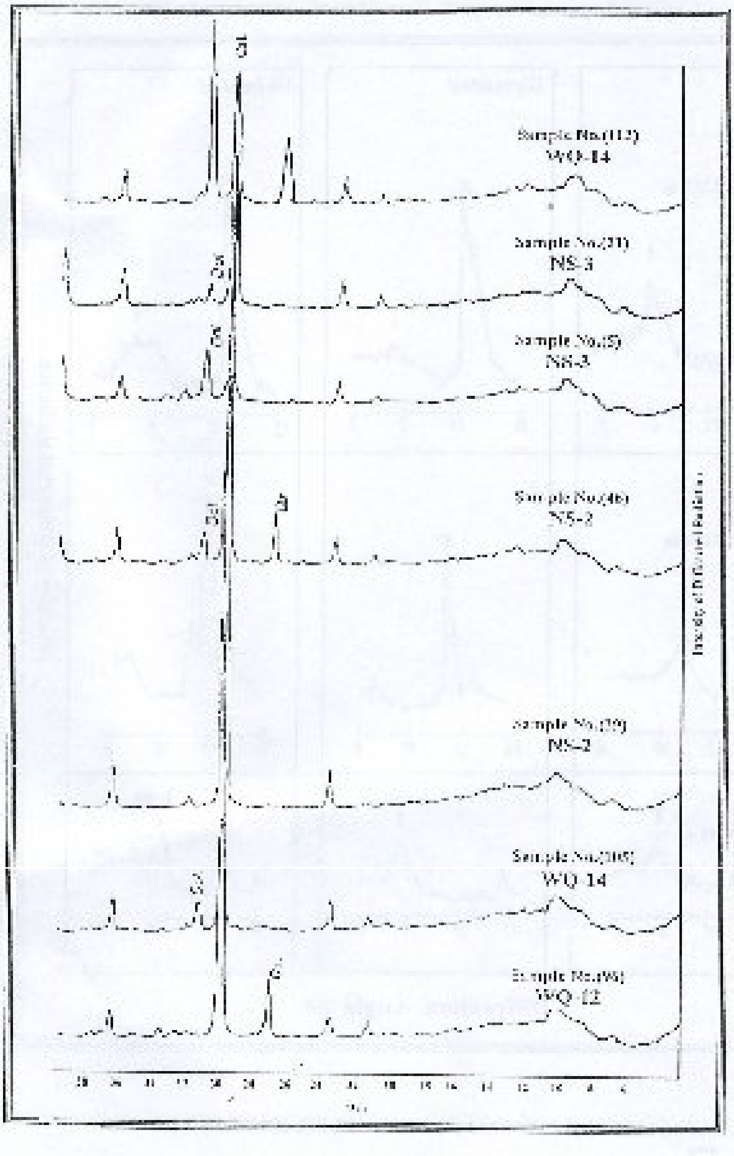

Fig. 3: X-ray diffractogram of the Yamama carbonate bulk sample.

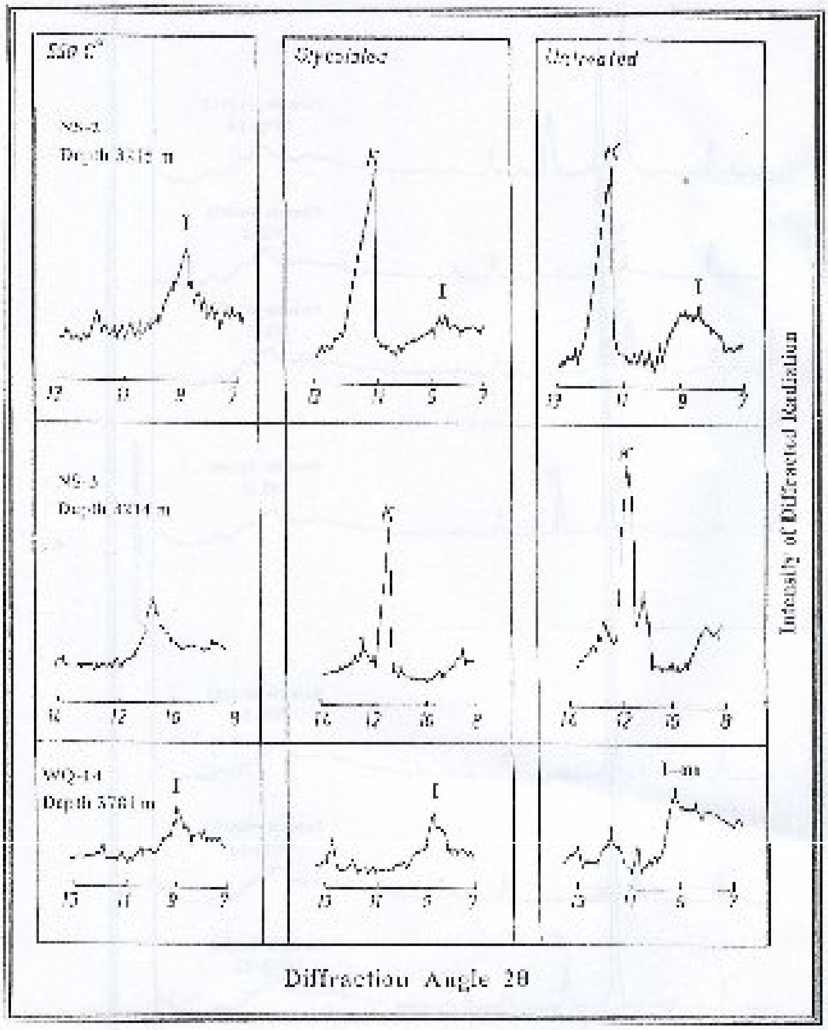

Fig. 4: X-ray diffractograms of clay minerals within I.R.

Illite montmorillonite mixed layers constitute the minor part of the detected clay minerals. Illite seems to be of diagenetic origin formed by the addition of silica layer to the ordinary sheets of kaolinite, as shown by the elongation in 10 A° peaks together with the weakness or disappearance of the secondary reflections. Based on (Tucker, 1985), the present illite-montmorillonite mixed layer represents a transition stage in the smectite to illite transformation (with increasing depth in oil borehole) which involve the incorporation of K ions into the smectite structures and loss of interlayer water, this process is largely depth and temperature dependant.

GEOCHEMISTRY

The geochemical characteristic of Yamama Formation has been discussed according to the distribution of major and trace components as well as the inter-elemental relationships.

The average of CaO and MgO concentrations in Yamama Formation in WQ and Ns-fields were 31.73%, 0.38%, 34.76% and 0.57 % respectively (Table 1), which are less than those reported by (Pettijohn, 1975) and (Flugel, 1982) (Table 2).The low Mg content reflects low degree of dolomitization which could be attributed to:

1-The relative low salinity of dolomitizing solution.

2-The depletion of the available Mg throughout the aragonite-low Mg calcite inversion.

Table 2: The average concentration of the selected components of Yamama Formation in comparison with other carbonate rocks.

Component / Author		Major Oxides %				Trace element ppm		
		CaO	MgO	FeO	Na_2O	Mn	Sr	Pb
Pettijohn, 1975		42.61	7.9	0.54	0.05	500	-	-
[illegible], 1998		30.32	4.7	0.33	0.04	1100	610	9
Al-Marsoumi and Al-Hamadani, 2001		34.25	0.67	0.51	0.53	154	326	-
Present study	WQ	31.73	0.38	0.105	0.09	79	342	7
	Ns	34.76	0.57	0.016	0.09	25	253	35

The Fe content varies from 33 to 4234 ppm with an average value of 1071 ppm in WQ, whereas it varies from 25 to 3381 ppm with an average of 160 ppm in Ns-field. A comparison between Iraqi and international carbonate composition is shown in (Table 2). The interesting point is that the Fe content of Yamama carbonates in WQ-field is seven times that of Ns-field. The present high Fe value is related to two main factors:

1-The abundance of clay minerals in the lime mudstone facies which has a wide distribution in WQ-field (Al-Mohamed, 2002).

2-The presence of pyrite within the I.R.

Iron has a unimodal distribution in both fields under study but platy kurtic in WQ and Leptokurtic in Ns-field as shown in (Fig. 5). This more likely attributed to a uniform supply of Fe to WQ depositional basin. Moreover, a negative correlation between Fe-Mg, and Fe-Ca is recorded in Ns and WQ-field respectively. These relationships indicate that Fe^{2+} substitute Mg^{2+} and Ca during diagenesis as mentioned by (Veizer, 1977, i.e. Fe is mainly associated in dolomite in Ns and Mg-calcite in WQ-field). Finally, Fe concomitant sympathetically with Mn and such relationship illustrates the similarity in geochemical behavior between Fe and Mn as they substitute each other in the carbonate minerals (Faure, 1998).

Regarding Sodium, this element is known to be used as a useful indicator of salinity of depositional and diagenetic solutions (Land and Hoops, 1973). The average Na contents in WQ and Ns-field is greater than that reported in common carbonate rocks (Table 2), which implies that the depositional basin of Yamama Formation tectonically unstable leading to the diversity of lithological microfacies (Al-Mohamed, 2002).

Sodium possesses a similar unimodal distribution in both fields under study (Fig. 5), but WQ-field shows a wide distribution with platykurtic whereas Ns-field shows leptokurtic peak, which means that Na in the former field was shared among many minerals in comparison with the later. The absence of any significant correlation between Na and other measured components reflects the independent behaviour of this element which resulted from high Na dissolution rate as well as through diagenetic processes (Aragonite-Calcite inversion and recrystallization), and the rate of deposition (Rao et al., 1998).

The Mn content in the present carbonate sediments is lower than that documented in the common carbonate rocks (1420 ppm) reported by (Mason and Moore, 1982), (Ronov and Ermishkina) cited in (Megharaoi, 1968). They found that Mn content in carbonate formed under humid climate (average=810 ppm) is greater than that formed in an arid climate (average=320 ppm). On the other hand, (Beneiri and Turi, 1974) and (Shcimugen and Pedicon, 1983) suggested that Mn content in sediment increases with depth. Therefore, the present Mn content could indicate that Yamama Formation was deposited in a shallow basin developed under arid climate. Moreover, the Mn in the studied carbonate rocks seems to be associated with clay minerals as evident by the direct relationship between Mn and I.R in both fields under study. It is worth mentioning that the statistical treatment of Mn data shows that it has a unimodal distribution in WQ and Ns-fields (Fig. 5). Nevertheless, Mn in WQ-field exhibits wide and homogeneous distribution in comparison with Ns-field. This may elucidate the systematic detrital supply of terrigenous materials for WQ depositional basin.

The strontium content in recent carbonate sediments and ancient carbonate rocks varies in a wide range. Generally its contents in recent carbonate is about ten times than that in ancient carbonate rocks (Siegle, 1961). This variation is attributed to salinity, paleogeography and paleoclimate of depositional basin as well as the diagenesis processes. The average Sr content of Yamama carbonate sediments in WQ-field (347 ppm) is greater than its average contents of (285 ppm) in Ns field. This result is attributed to the following factors:

1-The WQ-field is situated in deeper part of the depositional basin relative to Ns-field.

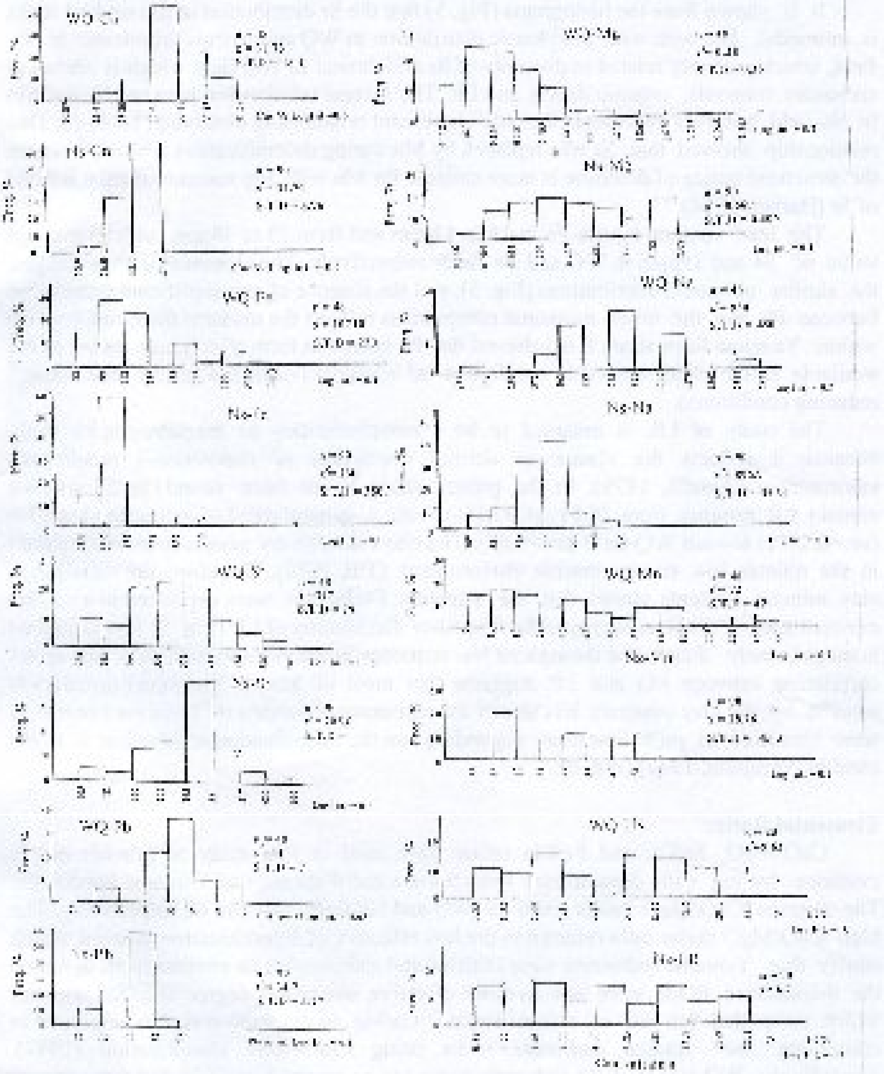

Fig. 5: Histograms showing the distribution of the studied components in West Qurna (WQ) and Nassyria (Ns).

2-The loss of Sr during dolomitization process is more intensive in Ns than in WQ-Field. This conclusion is supported by the work of Shearman and (Shirmohammadi, 1969) cited in (Dhannoun and Al-Dabagh, 1976) who found that during the dolomitization of limestone approximately half of Sr content was lost.

It is shown from the histograms (Fig, 5) that the Sr distribution in the studied rocks is unimodal. But with wide platykurtic distribution in WQ and narrow leptokurtic in Ns-field, which probably related to diversity of Sr enrichment in WQ field which is related to carbonate minerals, organic debris, and I.R. The inverse relationship between Sr and Mn in Ns-field, however, represents the only significant relationship observed (Table 1). This relationship showed that Sr was replaced by Mn during dolomitization process, because the structural lattice of dolomite is more suitable for Mn with Mg accommodation instead of Sr (Barber, 1974).

The lead content ranges from 18 to 43ppm and from 23 to 48ppm with an average value of 34 and 35ppm in WQ and Ns-fields respectively. The closeness in Pb averages, the similar unimodal distributions (Fig. 5), and the absence of any significant correlation between Pb and the other measured components reflects the uniform distribution of Pb within Yamama Formation. It is believed that Pb occurs in form of sulphide owing to the available sulfur under reservoir conditions of Yamama Formation (acidic medium and reducing conditions).

The study of I.R. is assumed to be a complementary to the petrographic study because it reflects the clastic or detrital conditions of depositional conditional environment (Assafli, 1979). In the present study it has been found that all samples contain I.R ranging from (0.85 to 33.1%) with a general trend of increasing from Ns (av.=6.71%) toward WQ-field (av.=9.63). The clay minerals are generally more abundant in the quieter low energy marine environment (Till, 1979). Therefore, the variation in clay mineral contents shows that the Yamama Formation were deposited in a marine environment of various energy. The frequency distribution of I.R (Fig. 5) Shows that its homogeneously distributed throughout Ns- sequence in comparison with WQ. The direct correlation between Mn and I.R suggests that most of Mn in Yamama Formation is adsorbs by the clay minerals. Eventually the carbonate sediments of Yamama Formation were classified as pure limestone depending on the classification of (Barth et al., 1939) cited in (Pettijohn, 1975) (Fig. 6).

Elemental Ratio:

CaO/MgO, Sr/Ca, and Fe/Mn ratios were used in this study to provide ample evidence dealing with depositional environment and diagenesis of Yamama Formation. The average CaO/MgO molar ratio in WQ and Ns-field is 44 and 60 respectively. The high CaO/MgO molar ratio referred to the less effective of dolomitization process, which clarify that Yamama sediments were lithified and stabilized in an environment, in which the dolomitized fluids were not so much effective, due to low degree of initial porosity which controlled the rate of dolomitization. Ca/Mg molar ratio was also employed in classifying the studied carbonate rocks using Chilingars classification (1957). Accordingly WQ and Ns-field carbonate rocks can be grouped into five and three groups respectively (Fig. 7).

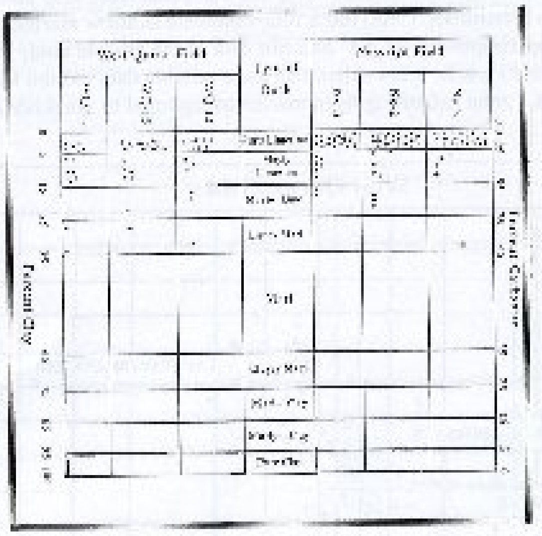

Fig. 6: Classification of Yamama carbonate rocks owing to (Barth et al.,1939) in (Pettijohn, 1975).

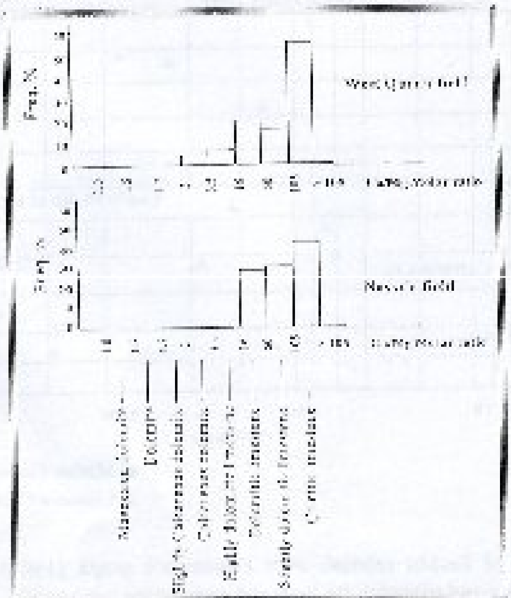

Fig. 7: Classification of Yamama carbonate rocks according to (Chilingar, 1957).

The mean value of Sr/Ca atom ratio in WQ and Ns-fields were 1.53 and 1.147×10^{2} respectively. Owing to (Friedman, 1968) these ratios indicate shallow marine tendency.

According to superimposing of Fe and Mn data of the present study (Fig. 8) with standard (Friedman, 1968) graph, it is evident that the available data exhibit that Yamarna Formation is located in a zone extending from marine to lagoonal to brackish sector.

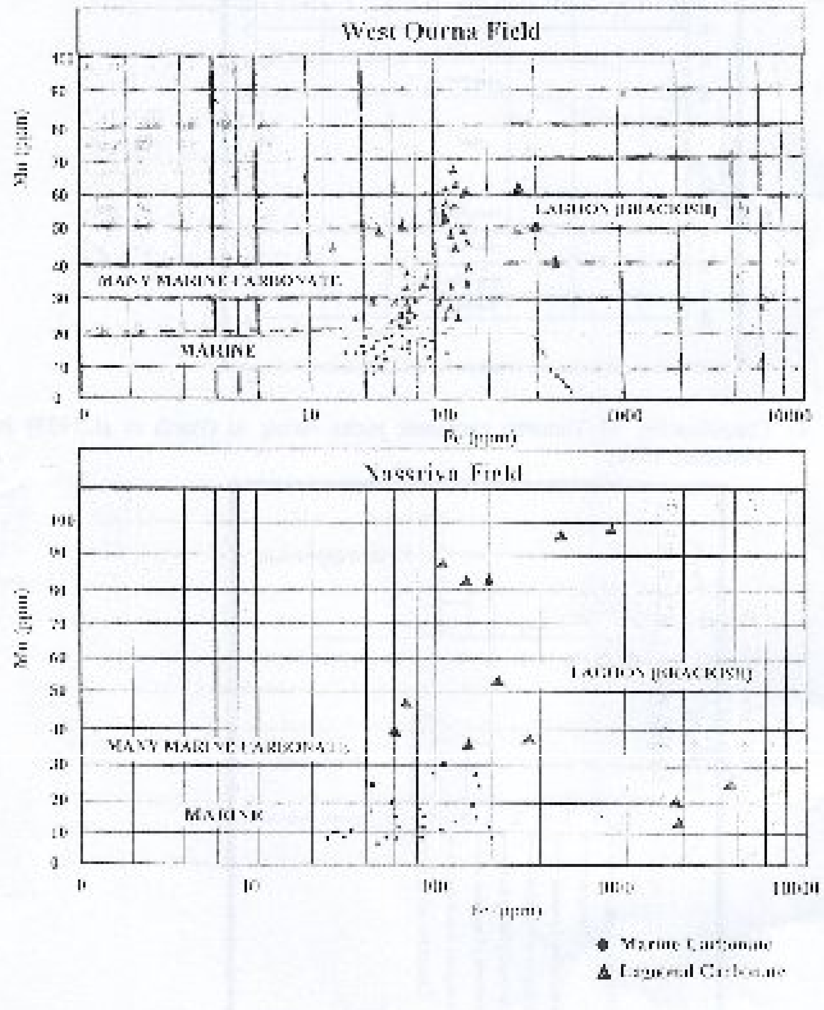

Fig. 8. Superimposing of Fe-Mn relation over Friedman's graph (1968). Circles for marine carbonates and triangles for lagoonal carbonates.

Vertical Distribution

The present chemical components reveal different patterns of vertical distribution throughout studied sequence (Figs. 9 and 10). Ca and Mg behave in opposite manner, this is due to the substitution of Ca for Mg during dolomitization. Fe and Mn have a similar pattern of distribution as a result of their similar geochemical behavior. Furthermore, Na and Sr vary in reverse way although both of them depending upon the salinity of sea water but they behave in reverse way, which means that the source of the present Sr is the organic fossil remains, while the fluctuation in Na content could be attributed to the variation in paleosalinity of sea water. Finally, no serious changes in Pb contents observed throughout the sequence confirming the independent behavior of this element.

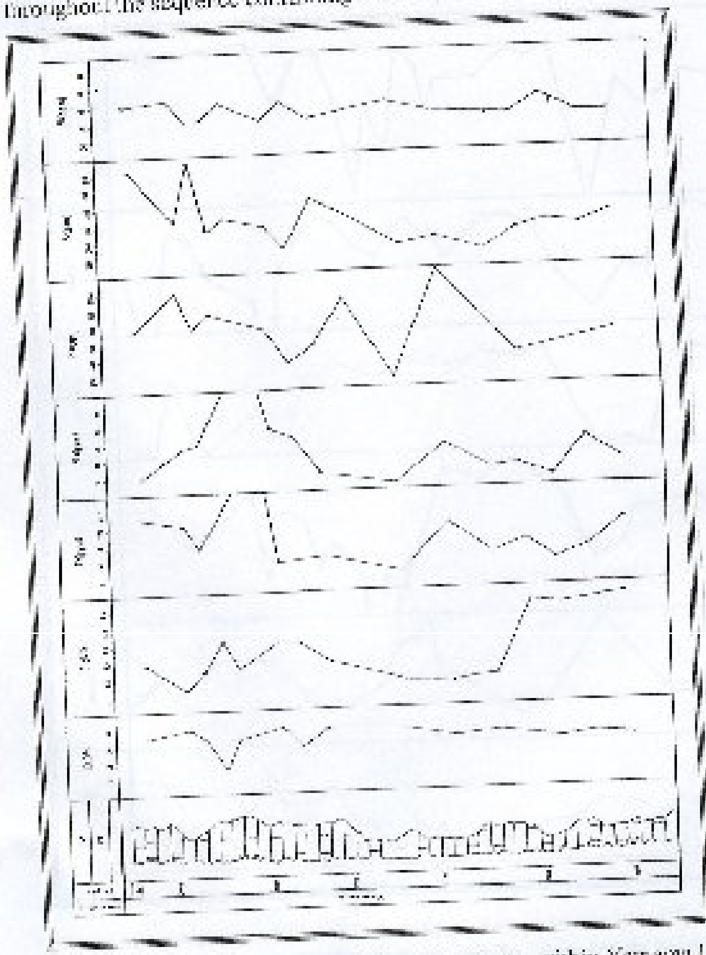

Fig. 9: Vertical distribution of the studied components within Yamama Formation in WQ-12.

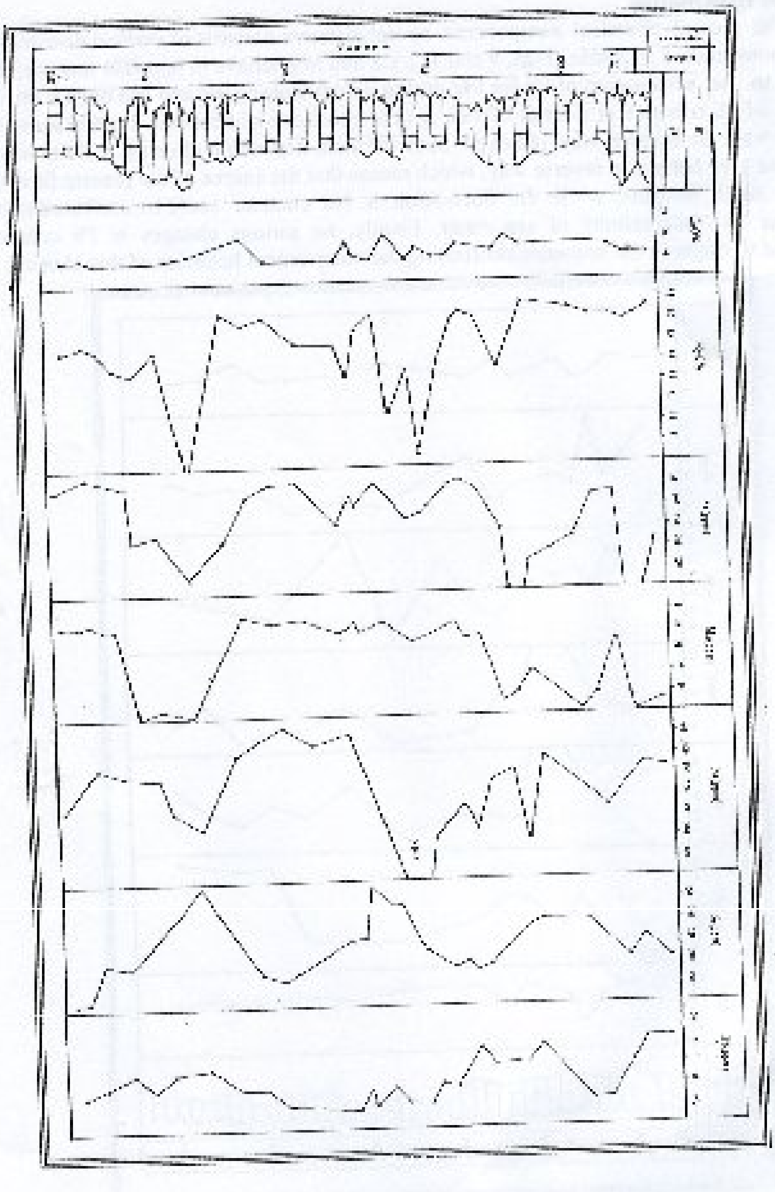

Fig. 10: Vertical distribution of the studied components within Yamama Formation in Ns-5.

CONCLUSIONS

Based on the geochemistry and mineralogy of Yamama Formation the following conclusions have been drawn:

1- Low-Mg calcite, dolomite, illite, illite-smectite mixed layer and pyrite are of diagenetic origin, whereas, kaolinite and quartz are of detrital origin.

2- A detrital influx was inferred to be associated with the Yamama carbonate deposits. This study suggests that such an influx is mainly composed of kaolinite and quartz.

3- The abundance of kaolinite and low-Mg calcite showed that the studied lithostratigraphic unit deposited in a shallow marine environment and suffering from low effective dolomitization.

4- The presence of illite and interstratified illite-smectite may indicate an authigenic origin. This is because of the possibility of the formation of the two minerals by fixation of K between the layers of kaolinite or montmorillonite during the deposition and/or the diagenesis.

5- The distribution of major and trace elements showed no distinct trend of variations toward upper and lower contacts, which reflects the instability in depositional conditions.

6- The low Mn contents detected within Yamama Formation suggest the shallow depositional environment, and low clay minerals supply because of arid paleoclimate.

7- Owing to the insoluble residue and Ca/Mg molar ratio, it has been found that about 70% and 60% of Yamama carbonate were classified as pure limestone and clastic limestone respectively.

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