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MINERALOGY AND GEOCHEMISTRY OF JERIBE FORMATION FROM SELECTED AREAS, EAST OF IRAQ

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ABSTRACT

The mineralogy and geochemistry of the Jeribe Formation are examined by XRF and XRD techniques. The formation belongs to the Miocene sequences, which are exposed in the eastern part of Iraq within the low folded Zone. Dolomite and calcite are the main minerals making the carbonate rocks of the formation with subordinate minerals of quartz and clay minerals (kaolinite, montmorillonite and illite).

Application of Ca/Mg ratio for classification of carbonate rocks reveals that the majority of the rock dolomitic in the formation. The molar ratios of certain trace elements of Mo/U, V/Cr and Ni/Co reveal Oxic-Redoxs conditions and Ca/Mg, Mg/Ca, and Ba/Ca ratios imply moderate salinity at the time of sedimentation. While Mg/Ca and Mn/Ca ratios infer low temperature at the carbonate deposition. Comparing the low Sr/Ca with the moderately high Ca/Mg ratios indicate that the dolomitization process played the main role in the diagenesis processes.

معدنية وجيوكيميائية تكوين الجريبي في مناطق مختارة شرق العراق

سعد زكي المشايخي و مصطفى اسعد علي

المستخلص

تمت دراسة معدنية وجيوكيمائية تكوين الجريبي والذي يعود الى عصر المايوسين الأوسط ويمثل تقدم بحري.

يتكون تكوين الجريبي بصورة رئيسية من المعادن الكاربونيتية مع وجود الكوارتز والمعادن الطينية وبصورة ثانوية. تم استخدم النسب الكيميائية لاستخراج الظروف الترسيبية من حرارة وملوحة ومعرفة نطاق الترسيب وتصنيف الصخور. تم استخدام النسبة الكيميائية Ca/Mg لغرض تصنيف الصخور حسب جالنجر (1957) واستخدمت النسب الكيمائية V/Cr، Mo/U و Ni/Co حيث حددت نطاق الاكسدة اثناء الترسيب واظهرت النسب الكيمائية Ca/Mg، Mg/Ca، Sr/Ca و Ba/Ca ملوحة معتدلة متوافق مع ما اظهرت النسب الكيميائية Mg/Ca، Mn/Ca من حرارة قليلة اثناء الترسيب. إن لاستخدام المقارنة بين نسبة Mg/Ca و Sr/Ca دور في معرفة العمليات التحويرية المسيطرة خلال الترسيب واظهرت الدلمتة العامل الرئيسي في العمليات التحويرية.

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INTRODUCTION

The Jeribe Formation belongs to the Middle Miocene Subcycle, which represents a new transgression on the foredeep shelf area. The subcycle is represented by evaporatic lagoon sediments of the Fatha Formation with the transgressive and pure carbonate Jeribe Formation at the base (Jassim and Goff, 2006). The Jeribe Formation comprises the basal transgressive, limestone dominated part of the Middle Miocene Subcycle. It is reverting to the Latest Eocene-Recent Megasquance AP11, which is associated with the closing of the Neo-Tethys and collision along N and E sides of Arabian plates (Buday, 1980). The Jeribe Formation was deposited in two main centers, which are trending NW – SE comprising four separated depocenters (Jassim and Goff, 2006). (Fig.1). Many Previous works deal with petrographic characteristics of the Jeribe Formation to interpret the depositional environment. On the other hand, only one of the two studies utilize the traditional geochemical parameters of the formation in the type locality in Mosul basin and Western Desert regions.

This paper is the first study of the geochemical characteristics to investigate the depositional environment, mineralogy and diagenesis of the Jeribe Formation in the Kirkuk – Dezfol basin.

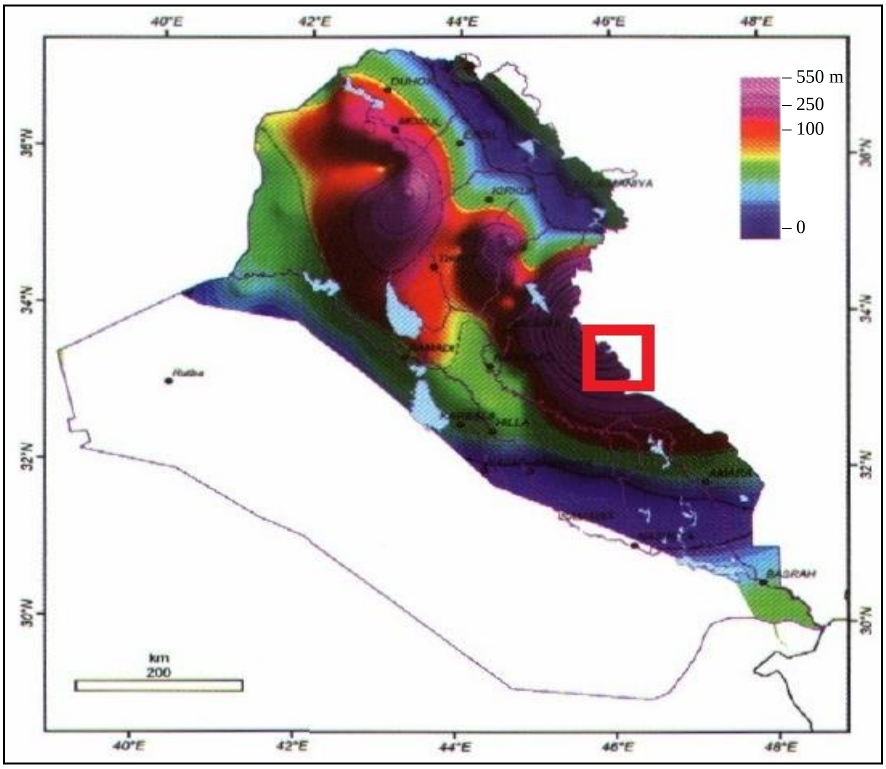

Fig.1: Shows the two main basins of the Jeribe Formation (after Jassim and Goff, 2006). The rectangle refers to the study area

GEOLOGY AND STRATIGRAPHY

In general, the Zagros Province lies on the north-eastern edge of the Arabian plate and form the Taurus thrust suture zone of south-eastern Turkey and the Zagros thrust suture zone of southern and western Gulf of Aden.

The tectonic classification of Fouad (2010) suggests two main basins of Jeribe Formation which exist in the unstable shelf of the Arabian plate in the outer foredeep platform within

Mesopotamia in the Low Folded Zone. The Alpine horizontal movement had a much larger and deeper effect on the NW culmination, effectiveness with the structures of the Zagros Foothills. This setting has a direct effect on structural geometry, fracture intensity and depositional setting of the Formation. Structurally, The Hemrin – Makhul Subzone is the deepest part of the Foothill Zone. The subzone was the depocentre of the Neogene molasse but has been a subsiding unit throughout the Mesozoic and Neogene. Jassim and Goff (2006) stated " The paleo geographic evolution of the shelf during the Early and Middle Miocene is marked by the development of a broad but relatively shallow basin and the axis of the basin passed through the Foothill Zone, the Jezira Subzone (submerged Khlesia High) and the Mesopotamian Zone". Numan (1997), pointed that the depositional sequences of the Jeribe Formation have coincides with continental collision between Arabian and Eurasian Plates extending from the Eocene up to the Recent. He claimed this phase to be characteristic by shallow epicontinental sea. The Jeribe Formation comprises 70 m of recrystallized, dolomitized, massive limestones. The lower contact with Dhiban Formation is conformable and is overlain by gypsum and marl beds of the Fatha Formation.

THE STUDY AREA

The study area is located east of Wasit and Dyiala Governorates near Zurbatiyah town in the eastern part of Iraq. It includes two exposed sections selected in the depocenter of Kirkuk – Dezful basin. The two sections are located within Himreen Structure. All structures attain NW – SE trend and change to N – S northwards near the Iraqi – Turkish border (Figures 1 and 2).

The Ja section is selected in the core of Koolic1 anticline of 33 Km long within the Hemrin structure at coordinate E605200 N3679973. It is exposed in the core of the anticline and the axis is truncated by Cea Koran reveres fault and three strike slip faults, (Mouhmuod *et al.*, 2014). The Ja section located on the SW flank consists of thick dolomite beds and with dark colour in the middle part. The upper contact is conformable with the overlying Fatha Formation and characterized by exposure of thick gypsum bed, while the lower contact is distinguished by the appearance of massive gypsum of Dhiban Formation. The total thickness of Ja section is 69 m.

The second Jb section is selected in the core of Koolic (3) anticline of 33 Km long and belongs to the Hemrin structure at coordinate E594885 N3696629. It is trending NW – SE and changes to N – S toward the north. The Jeribe formation exposed in the core of the anticline in Show-Shareen valley represents the strike slip fault of general trend of ENE – WSW. The Jeribe Formation consists of thick dolomite beds with dark colour in the middle part. The upper contact is conformable with the overlying Fatha Formation by appearance of thick gypsum bed, while the lower contact is distinguished by the massive gypsum of Dhiban Formation (Figure 3).

METHODOLOGY AND MATERIALS

Field work includes description and sampling of the two sections for geochemical study. Laboratory work includes preparing twenty-one (21) samples for XRF and XRD analysis. Each sample is pulverized at the engineering college/ University of Technology. The rock powder is sieved with 75-mesh BSS sieve. XRF analysis is carried out using instrument type (D2 phaser Bruker X-ray) German, in the Germany Lab in X-ray lab in the department of geology, college of Sciences in the University of Baghdad, with conditions: Target Cu tube, power: 40 kV, current 20 mA, speed 1 cm/min, Ni Filter. The samples were analyzed to determine the percentages of SiO_2, MgO, Fe_2O_3, Al_2O_3, CaO, Na_2O, and K_2O. XR-Diffractometer is used to determine the mineralogical constituents of the studied samples e.g. calcite and dolomite with other minerals. The scanning angle is 2θ to 60 for the bulk samples as the most basal reflections.

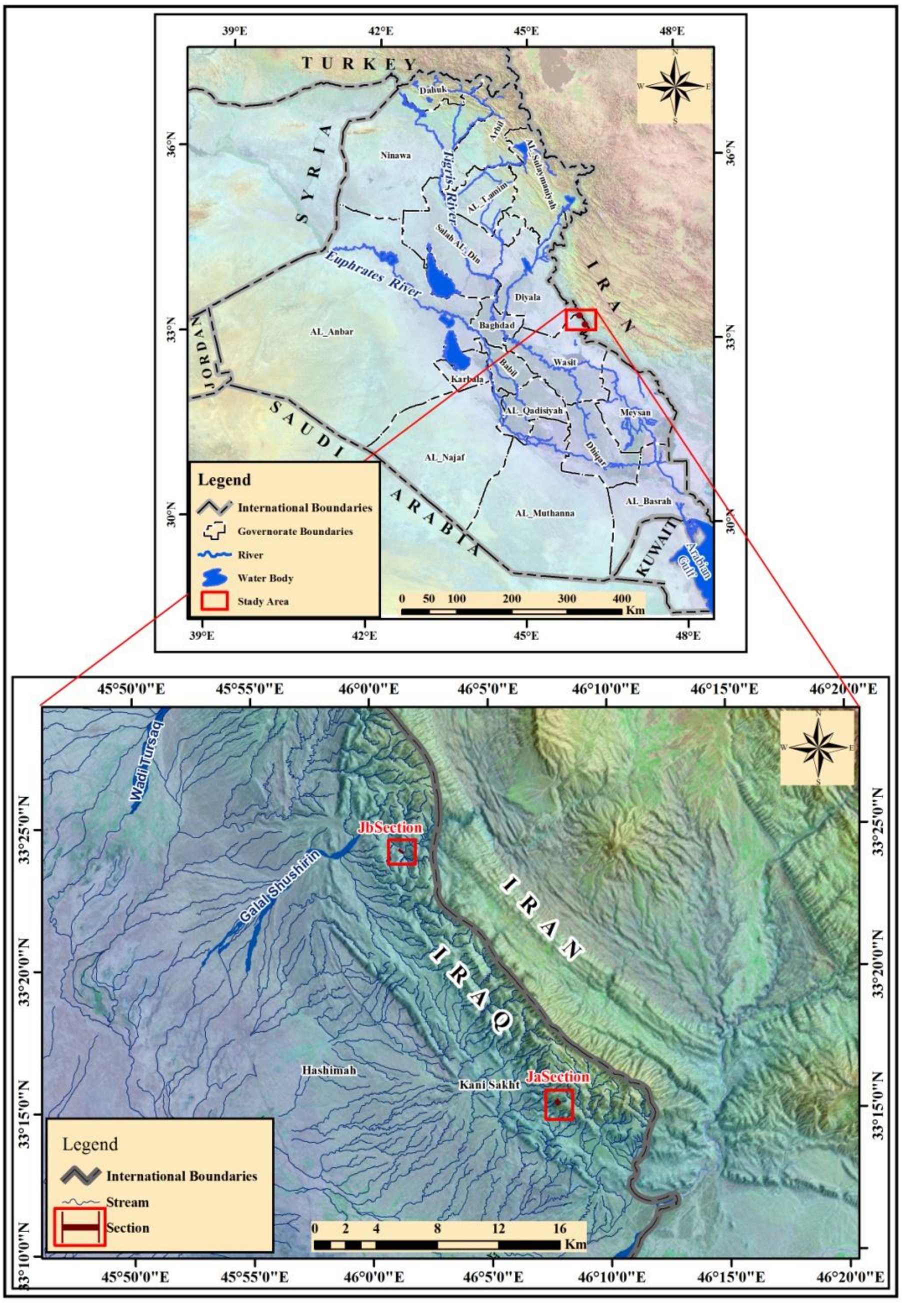

Fig.2: Location map of the two studied sections of study area

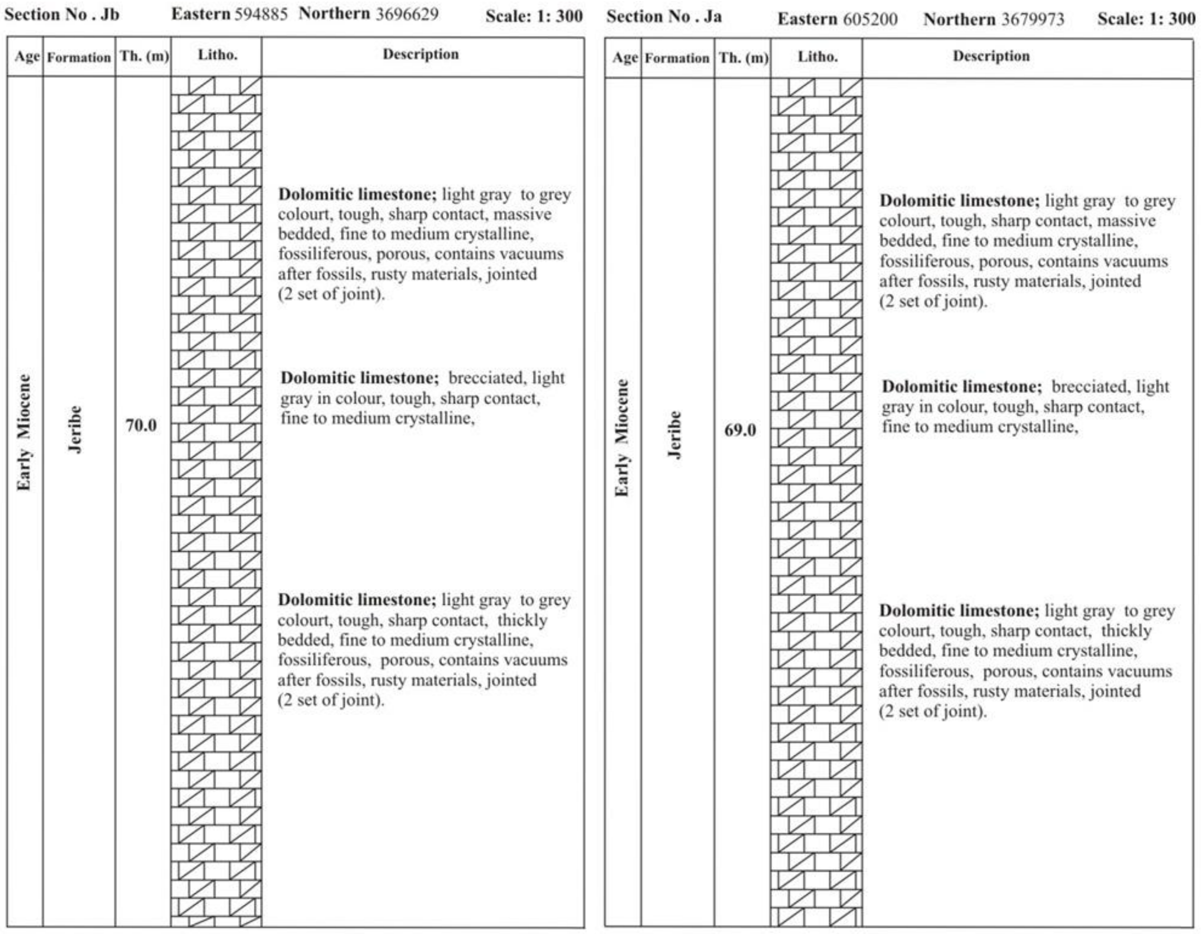

Fig.3: Column section of the two succession were sampling

MINERALOGY

The XRD analysis of the Jeribe samples reveals dolomite, calcite, quartz, gypsum and trace amount of clay minerals. The geochemical relationships and molar ratios are used to give information on the mineral composition. The identified minerals are;

- **Dolomite**

Dolomite is the main carbonate minerals detected in XRD analysis, with percentage range of 51 to 98.7%. Some of dolomite mineral is *Ferro dolomite* (Figure 4).

- **Calcite**

Calcite is the second main carbonate minerals detected by XRD analysis with percentage ranges from 2.5% – 48.8% (Figure 4).

- **Quartz**

Quartz is a subordinate constituent in the studied carbonate rocks and mostly of detrital origin. The detected percentages range from 0.4% to 1.7% (Figure 4).

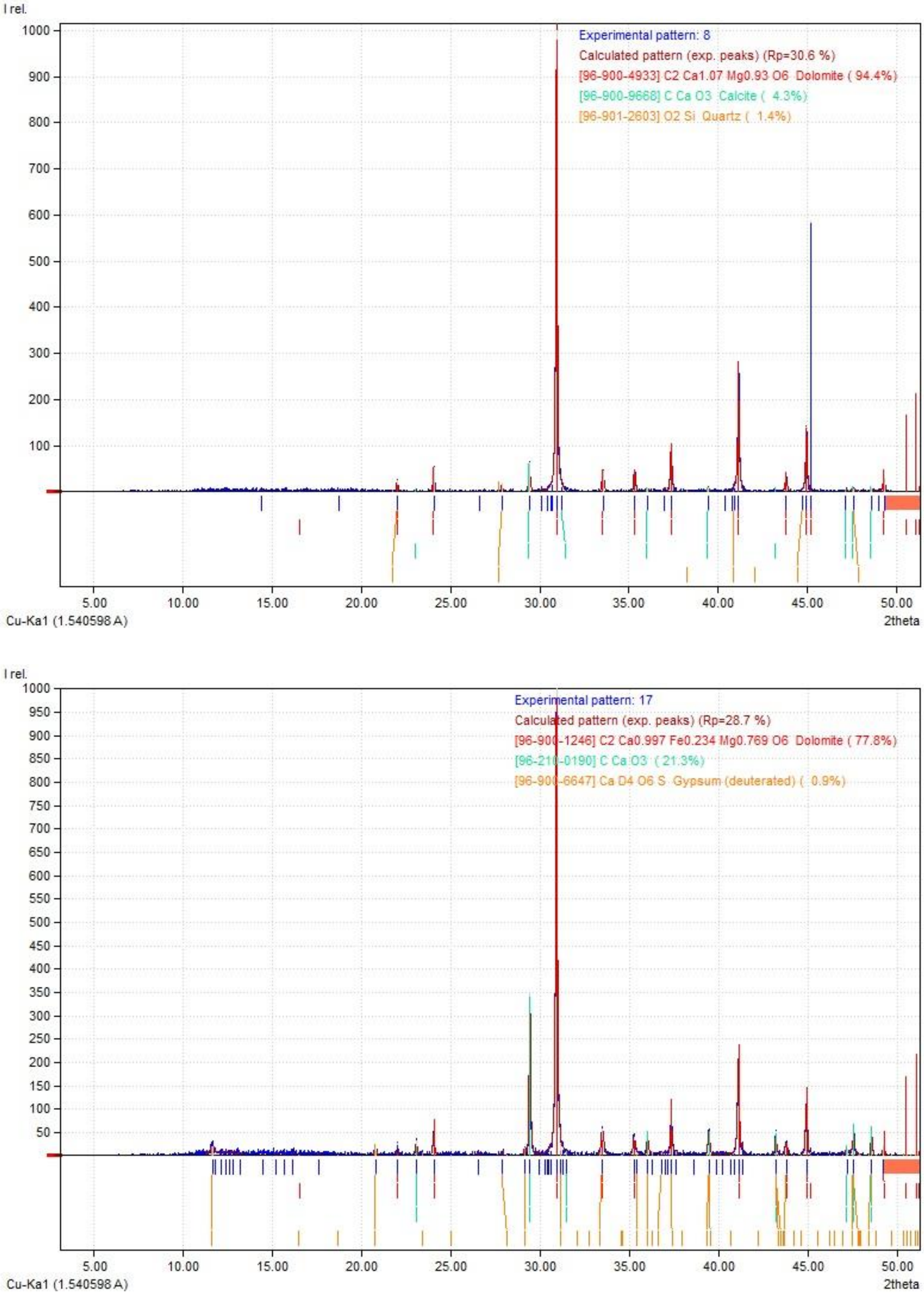

Fig.4: XR-diffractograms show the reflections of the gypsum minerals

- **Clay minerals**

The clay minerals are used as indicator to the geochemical relationships, which shows strongly positive relation between SiO_2, Fe_2O_3, Al_2O_3 and K_2O (Table 1). Although GEOSURV found kaolinite mineral in the XRD analysis in other sections but the studied sections do not show clay minerals in the XRD chart. In the studied samples of the Jeribe formation, the K_2O/Al_2O_3 display noticeable variation, which ranges from 0.0 to 0.44%. These percentages are probably suggest illite, montmorillonite and kaolinite minerals. In general, the value of K_2O/Al_2O_3 in clay minerals ranges from 0.0 to 0.3% in illite and mostly approximately (0.3), while in other clay minerals (montmorillonite and kaolinite) is around 0.0 because K_2O replaces Al_2O_3 in illite and does not the same in montmorillonite and kaolinite (Cox *et al*., 1995; Abou El-Anwar *et al*., 2013).

- **Sulfates (Gypsum)**

Gypsum is recognized in one sample of Jeribe carbonate formation with percentage of 0.8%.

Table 1: Shows correlation among major oxides contents of Jeribe Formation

	SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	Na_2O	K_2O	TiO_2
SiO_2	1							
CaO	-0.098	1						
MgO	-0.134	-0.8	1					
Fe_2O_3	0.8	-0.23	-0.05	1				
Al_2O_3	0.9	-0.1	-0.18	0.89	1			
Na_2O	0.006	-0.17	0.01	0.13	0.02	1		
K_2O	0.96	-0.23	-0.01	0.87	0.92	0.04	1	
TiO_2	-0.194	-0.119	0.18	-0.06	-0.21	-0.22	-0.19	1

– **Geochemical parameters as environmental indicators:** Elemental ratios could be used for better understanding the depositional environment of carbonate sediments. Among these geochemical parameters, Veizer and Hoefs, (1976) claimed that Mn/Sr ratios are less than 3 indicating high degree of preservation of primary geochemical signatures. All samples of the Jeribe Formation have low Mn/Sr ratio, which range from 0.09 to 0.64 with average 0.30.

– **Mg/Ca and Ca/Mg ratio of carbonate rocks:** The Mg/Ca ratio is a function used to determine the minerals precipitate from sea waters. Many authors like Lowenstein *et al.* (2001) claimed the reduction in the Mg/Ca ratio is in favors of precipitation of calcite over aragonite. While the molar Mg/Ca ratios < 2 refers to precipitation of low-Mg calcite, and Mg/Ca ratios > 2 refers to precipitation of aragonite + high-Mg calcite.

The range of Mg/Ca ratios presented in this study range from 0.15% to 0.37% with average of 0.35%, which suggests precipitation of low Mg calcite.

This ratio is important in the classification of carbonate rocks on the basis of geochemical distribution (Chilinger, 1956). The carbonate rocks are classified on the basis of Ca/Mg ratio as illustrated in Table (2). The highest value of Ca/Mg is 6.6, which represents highly dolomitic limestone and lowest value in the histogram is 2.1 represents calcareous dolomite. Calcareous dolomite is the major type of the rocks in Jeribe Formation (Table 3 and 4) (Figure 5).

Table 2: Shows the classification of limestone and dolomites based on Ca/Mg ratio, Chillinger, (1956)

Ca/Mg ratio	Terminology
1.5	Magnesium dolomite
1.5 – 1.7	Dolomite
1.7 – 2.0	Slightly Calcareous dolomite
2.0 – 3.5	Calcareous dolomite
3.5 – 16.0	Highly dolomite Limestone
16.0 – 66.0	Dolomite Limestone
66.0 – 105.0	Limestone
> 105	Calcitic Limestone

Table 3: Shows the major oxides and Trace elements of the Jeribe Formation

Sample No.	%									ppm						
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	L.O.I.	Na_2O_3	K_2O	Mn	Sr	V	U	Ni	Ba	Mo
Jb42	1.4	0.12	0.32	47.37	8.467	0.16	45.6	0.64	0.03	96.58	149.58	28.57	1.6	8.565	23.4	9.5
Jb39	0.96	0.09	0.22	39.32	12.57	0.14	45.85	0.64	0.01	71.02	123.28	24.64	1.3	7.150	0	8.7
Jb37	3.0	0.4	0.63	36.19	13.15	0.23	44.52	0.63	0.22	61.65	110.85	30.25	2.6	13.51	35.5	7.3
Jb31	1.32	0.14	0.32	35.85	12.57	0.25	48.62	0.69	0.05	45.30	113.56	32.49	2.4	16.26	14	5.7
Jb27	1.49	0.26	0.33	36.81	14.46	0.21	46.61	0.92	0.08	60.02	136.39	35.85	1.5	13.90	93	7.4
Jb21	1.0	0.09	0.19	35.47	14.79	0.68	46.59	0.90	0.05	31.9	136.22	32.49	2.3	8.72	15.6	6.6
Jb17	1.4	0.18	0.32	36.84	14.27	0.19	45.93	0.63	0.11	30.20	123.54	35.85	1.9	8.56	10.3	15.4
Jb15	2.2	0.30	0.51	35.22	14.9	0.107	45.82	0.59	0.15	49.87	95.97	34.17	6.2	14.14	11.3	7
Jb11	1.4	0.10	0.31	41.28	12.89	0.18	45.55	0.69	0.07	34.078	131.99	49.29	4	15.008	33.8	5.8
Jb9	1.0	0.11	0.29	35.54	15.85	0.13	45.99	0.58	0.04	25.32	100.96	56.02	12.9	5.42	0	6.8
Jb7	2.6	0.19	0.45	35.39	16.07	0.24	46.44	0.72	0.16	27.64	81.26	26.88	2.3	9.03	10.5	6.9
Ja3	0.8	0.08	0.19	39.25	14.7	0.1	45.98	0.55	0.008	36.55	139.18	48.73	6	6.28	0	12.5
Ja9	2.0	0.14	0.45	39.08	12.94	0.14	44.31	0.56	0.12	38.26	194.99	68.90	7.2	10.13	21.6	7.9
Ja13	0.71	0.07	0.11	40.27	14.08	0.12	46.19	0.58	0.006	26.875	213.51	39.21	5	6.05	37.9	10.6
Ja17	2.4	0.27	0.51	38.52	13.6	0.15	45.46	0.59	0.14	39.80	193.21	20.72	3.1	8.64	35	11.6
Ja21	0.7	0.12	0.16	36.82	15.17	0.15	46.13	0.54	0.01	27.10	118.29	33.61	3.4	7.70	0	12.3
Ja23	0.6	0.04	0.16	41.16	12.85	0.14	46.01	0.622	0	40.19	288.34	45.93	3.2	6.28	24.2	7.9
Ja25	0.5	0.03	0.11	35.98	15.63	0.16	46.8	0.565	0	26.95	104.26	49.85	4.9	8.17	12	4.4
Ja31	0.7	0.04	0.14	36.76	15.31	0.16	46.14	0.55	0.02	29.66	129.88	36.41	3.4	8.09	16.8	9.1
Ja35	2.8	0.2	0.46	40.07	12.79	0.15	44.33	0.534	0.20	40.97	449.35	24.08	1.8	11.55	158.8	8.7

Table 4: Molar ratios of Jeribe Formation

Sample No.	Ca/Mg	Mg/Ca	K2O/Al2O3	Mn/Sr	Sr/Ca	Ba/Ca	Mo/U	Mn/Ca
Jb42	6.63	0.15	0.10	0.64	0.0004	6.91	5.93	0.0002
Jb39	3.70	0.26	0.05	0.57	0.0004	0	6.692	0.0002
Jb27	3.017	0.33	0.24	0.44	0.0005	0.0003	4.93	0.0002
Jb21	2.84	0.35	0.26	0.23	0.0005	6.15	2.86	0.0001
Jb7	2.61	0.38	0.36	0.34	0.0003	4.15	3	0.0001
Ja13	3.38	0.29	0.05	0.12	0.0007	0.0001	2.12	9.33
Ja21	2.87	0.34	0.07	0.22	0.0004	0	3.61	0.0001
Ja23	3.79	0.26	0	0.13	0.0009	8.22	2.46	0.0001
Ave.	**3.6**	**0.29**		**0.33**	**0.0005**	**3.17**	**3.95**	**1.16**

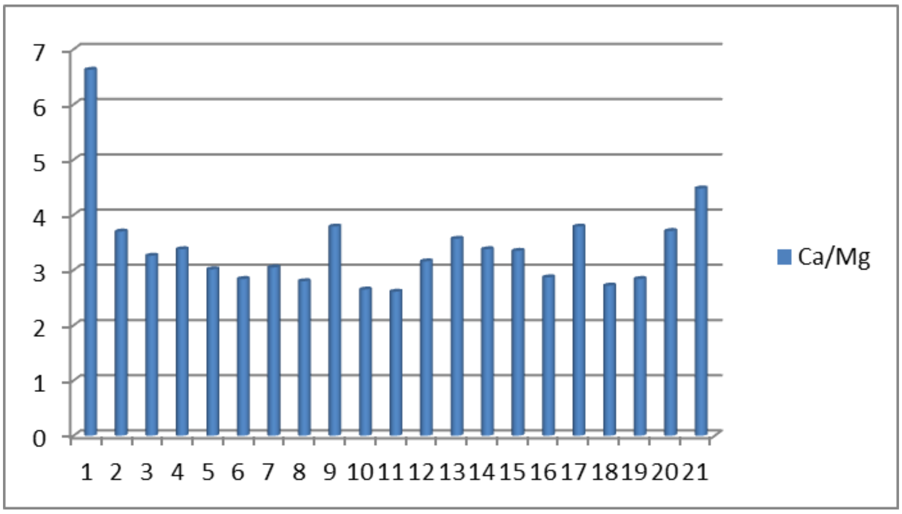

Fig.5: The histogram of Ca/Mg ratio of Jeribe carbonate samples

– **Mo/U, V/Cr and Ni/Co ratios for Oxic-Redoxs condition:** Redox-sensitive trace concentrations recorded in chemical sediments have been used to obtain information on marine environments (Frimmel, 2009). Many elements, such as U, V, Mo, Cr, Co, and Ce, can display somewhat different abundance and valences under various redox conditions. Generally, molybdenum is enriched in more reducing sediments, especially in the presence of free H_2S (Crusius *et al*., 1996; Algeo and Maynard, 2004). Other redox-sensitive elements like Co and Cr behave in a similar way, in which they tend to be more soluble under oxidizing conditions and less soluble under reducing conditions (Algeo and Maynard, 2004). Recent research suggests that the geochemical ratios of Mo/U (mole ratio), V/Cr and Ni/Co are important indicators of redox conditions in the bottom water (McManus *et al*., 2004).

Hua (2013) pointed out that the redox sensitive condition have Mo/U, V/Cr and Ni/Co ratios larger than 8, 4.25, and 7, respectively.

In the current study Mo/U mole ratios range from 2.1 to 6.6 with average of 3.95, while depletion of redox sensitive trace elements e.g. Co and Cr, cannot be applied to the evaluation of V/Cr and Ni/Co ratio suggesting oxic condition at the carbonate deposition (Table 3, 4 and 5).

– **Ba/Ca and Mg/Ca ratios for paleosalinity:** According to Celine (2015) who stated from experiment data that Mg/Ca water ratios decrease with decrease salinity while Ba/Ca increases with decreased salinity. The decrease salinity from 35 to 20 show decrease in Mg/Ca ratios from 2.39 to 1.79 while Ba/Ca show 0.45 to 0.04. In the present study, the Mg/Ca ratio ranges from 0.35 to 0.15 with average of 0.33. Moreover, Ba/Ca ratios range from 6.9 to 0.0 with average of 3.17 respectively (Table 3, 4 and 5), which implies moderate salinity at the time of carbonate deposition.

– **Mg/Ca and Mn/Ca ratios for paleotemperature:** Prieto and Stoll (2010) proposed that the Mg/Ca ratio increases with increasing temperature in coral skeleton. While Freitas *et al*. (2006) claimed that Mn/Ca ratio increases with increasing temperature.

Mg/Ca ratio ranges from 0.15 to 0.35 with average of 0.33 and Mn/Ca ratio ranges from 0.0001 to 9.33 with average of 1.16, which suggests low temperature at the time of carbonate deposition (Table 3, 4 and 5).

Table 5: Shows major oxides and trace elements, minimum, maximum and statistical parameter in weight percentage of Jeribe Formation

Sample No.	Element	Unit	Range		Mean	Median	Std Dev	Threshold (mean+2St.dv)
			Min	Max				
1	**CaO**	%	35.22	47.37	38.307	36.84	2.9667	44.2404
2	**MgO**		8.467	16.07	13.713	14.08	1.7918	17.2966
3	**SiO_2**		0.580	3.051	1.4515	13.09	0.79081	3.03312
4	**Fe_2O_3**		0.037	0.405	0.15339	0.1258	0.0969	0.34719
5	**Al_2O3**		0.109	06347	0.30275	0.3115	0.15501	0.61277
6	**TiO_2**		0.006	1.679	0.10762	0.0266	0.36078	0.82918
7	**SO_3**		0.107	1.027	0.23235	0.1609	0.21865	0.66965
8	**LOI**		41.33	48.62	44.948	45.03	1.6759	48.2998
9	**Na_2O**		0.534	0.926	0.6504	0.622	0.11715	0.88478
10	**K_2O**		0	0.227	0.0738	0.051	0.07111	0.216086
11	**Cl_2**		0.015	0.296	0.0685	0.0389	0.08085	0.230254
12	**Sr**	ppm	81.2	449.3	162.68	132	86.387	33.45
13	**Mn**		25.3	96.58	42.406	38.26	17.809	78.024
14	**V**		20.7	68.90	37.347	34.172	11.891	61.129
15	**Mo**		3.3	15.4	8.3524	7.9	2.8871	14.1266
16	**Ni**		5.422	16.26	9.5568	8.5652	3.2166	15.99
17	**U**		0	12.9	3.6667	3.1	2.782	9.2307
18	**Ba**		21	0	158.8	26.462	15.6	36.7891

- **Diagenesis**

Diagenetic processes are characterized by the precipitation of minerals and dissolution at low temperatures, which are indicated by using some of the geochemical ratios.

– **Dolomitization:** Several factors seem to affect the Sr/Ca and Ca/Mg ratios by dolomitization process. The Sr/Ca ratio have higher in the non-dolomitic and non-recrystallize rocks, while low Sr/Ca ratio might be due to diagenetic processes (Al-Bassam, 1977). Comparison of the low Sr/Ca with moderate high Ca/Mg ratios have indicated that the dolomitization process is playing the main role in the diagenesis. Furthermore, the low content of Sr and the negative correlation with Mg is due to dolomitization and recrystallization processes, which considered the important factor in the expulsion of significant amount of Sr from its parent limestone (Al-Bassam, 1977) (Table 3, 4 and 5) (Figure 6).

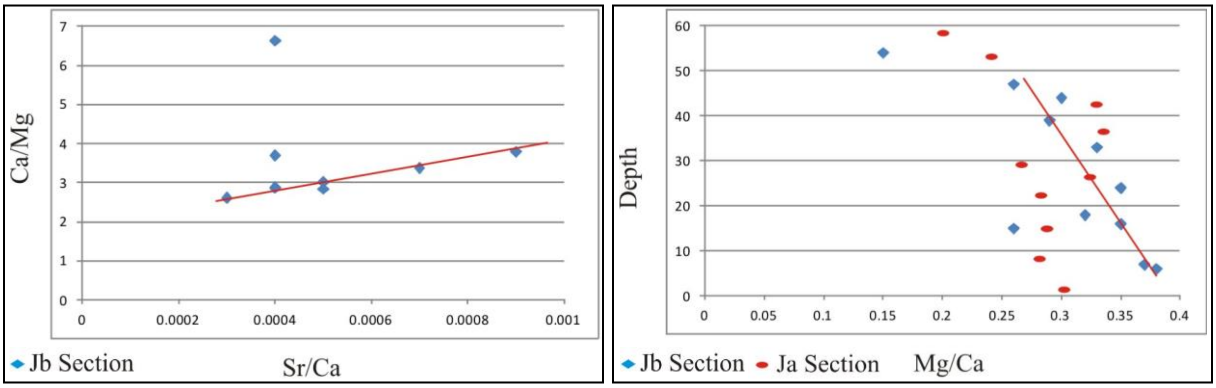

Fig.6: Shows relation between Sr/Ca with Ca/Mg and Mg/Ca with depth

– **Dissolution:** According to Saelen (2009), well-preserved low-Mg calcite tests of modern benthic foraminifera show decreasing Mg/Ca ratios with increasing water depth. In this study, the decrease in Mg/Ca ratio suggests dissolution process acting in post-depositional dissolution (Table 3, 4 and 5) (Figure 6).

DISCUSSIONS

Oxygen levels in the sea water column influence the oxidation state of some trace elements and control their selective solubility in seawater and consequently their degree of enrichment in marine sediments (Arnaboldi and Meyers, 2007; Azmy *et al*., 2009, in Hua *et al*., 2013). The abundance of trace elements in the sediments and sedimentary rocks allow estimating the oxygenation state of the bottom water and sediments during deposition. The U, V, Mo, Co, Cr elements and ratios of V/Cr, Ni/Co and Mo/U (mole ratio) are sensitive elements for enrichment or depletion.

Cox *et al*. (2016) claimed that Mo, V and U element contents are used together to highlight crucial redox, which controlle abundance variations specifically Mo Algeo and Tribovillard (2009) suggest that Mo/U mole ratios larger than 7.9 indicate anoxic/ sulphide environment from modern marine environments because Mo is soluble in water of oxidizing conditions and less soluble under reducing conditions.

The Jeribe samples show depletion of Cr and Co elements, which are mobile in oxic condition, therefore, the V/Cr and Ni/Co ratios do not indicate redox conditions, while Mo/U ratios range from 6.6 to 0.8 with average 3.168. Furthermore, depletion of Co, Cr and Ce elements e.g. redox sensitive elements, and including some amount of Mo and Ni reflect together the presence of oxidation state in the sea water column or sediment during the deposition.

Marshner (1968, in Bora *et al*., 2013) pointed that Ca/Mg ratio indicate stability condition during the formation of carbonate rocks and any decrease in Ca/Mg ratio is related to corresponding increase in salinity. Celine *et al*., (2015) claimed from laboratory experiment that the Mg/Ca is positively correlated with salinity, while the Ba/Ca is of negative correlation with the salinity. The relatively high Ca/Mg ratio (3.14) indicates comparatively low evaporation of sea water during the carbonate deposition. The Mg/Ca ratio are low with average 0.33, while the Ba/Ca ratio is high (average 3.17) indicates moderate salinity at the time of carbonate deposition. Prieto and Stoll (2010) proposed that the Mg/Ca ratio increase with increasing temperature in coral skeleton. While Freitas *et al*. (2006) claimed that Mn/Ca ratio is increased with increasing temperature.

In the studied samples, the ratios imply relatively low temperature at the time of deposition of the Jeribe Formation. The Sr/Ca ratio has positive relationship with Ca/Mg, which implies dolomitization process. The Mg/Ca shows negative correlation with depth, which infers shallowing upward sequence (Figure 6).

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