Mineralogy and geochemistry of Mishrif Formation from selected oilfield, south east of Iraq

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ABSTRACT

Mishrif Formation (Late Cenomanian) has been studied in four oilfields in southern Iraq, and studied samples were examined by mineralogy and geochemistry analysis using XRF and XRD techniques. The mineralogical study reveals that dolomite and calcite are the main minerals in the rock formation in studied oil fields, whereas quartz and clay minerals (kaolinite, montmorillonite and illite) represent secondary minerals composition. For geochemical classification of Mishrif rock, Ca/Mg ratio was applied and this reveals that Calcitic Limestone is a major type in studied samples.

The paleo - salinity has been examined by using Ca/Mg and Mg/Ca ratios and they referred to moderate salinity during deposition. Mg/Ca and Mn/Ca ratios have been applied to measure paleo-temperature, so infer a moderate paleo-temperature for Mishrif Formation in studied samples. Based on the comparison between low Sr/Ca and the relatively high Ca/Mg ratios, infer that a dolomitization process played the main role among diagenesis processes.

1 - Introduction

Chemical investigation assists in determining the relationships of the mixture of component elements. This investigation useful in determining element content of limestone and paleoenvironment circumstance that prevailing through deposition. Keeping the above usefulness in mind, chemical analyses of a some samples of limestones from Mishrif Formation were carried out for determination of chemical composition, classification of Mishrif rocks, distribution and mutual relationships of the elements and to decipher environmental condition during the time of deposition of carbonate sediments. These types of studies were made by different research workers from time to time [1,2,3].

The geochemical analysis gives a precise idea about the qualitative and quantitative content of different major oxides such as SiO_2, CaO, MgO, Fe_2O_3, Al_2O_3, Mn_2O_3, Na_2O, K_2O, TiO_2, P_2O_5, S (as SO_2) and L.O.I. Moreover, different trace elements such as Sr, Mn, Cr, Cu, Ni, V, etc. Trace element analysis

has been used in the differentiation of shallow and deep water limestone. The aim of this paper is the investigation the inorganic (trace and major oxides elements) part of Mishrif carbonate rock to evaluate the depositional environment for this formation, by use geochemical and mineralogical parameter.

2- Location of the Study Area

The study area includes four oil fields, these are Noor – (well-11), Amarah – (well-14), Buzurgan – (well-24), Halfaya – (well-8) which are bounded between (47° 15′ 36″), (46° 15′ 43″) longitude and (31° 45′ 16″), (31° 15′ 30″) latitude, where is located in Maysan Governorate, southeastern Iraq (Figure-1) the study are is belong to the Mesopotamian zone except Buzurgan oil fields where lies within Hemrin- Makhul subzone from the low folded zone. This entire oilfield located in the south east of Iraq near the Iraqi – Iranian border and east of Tigris River.
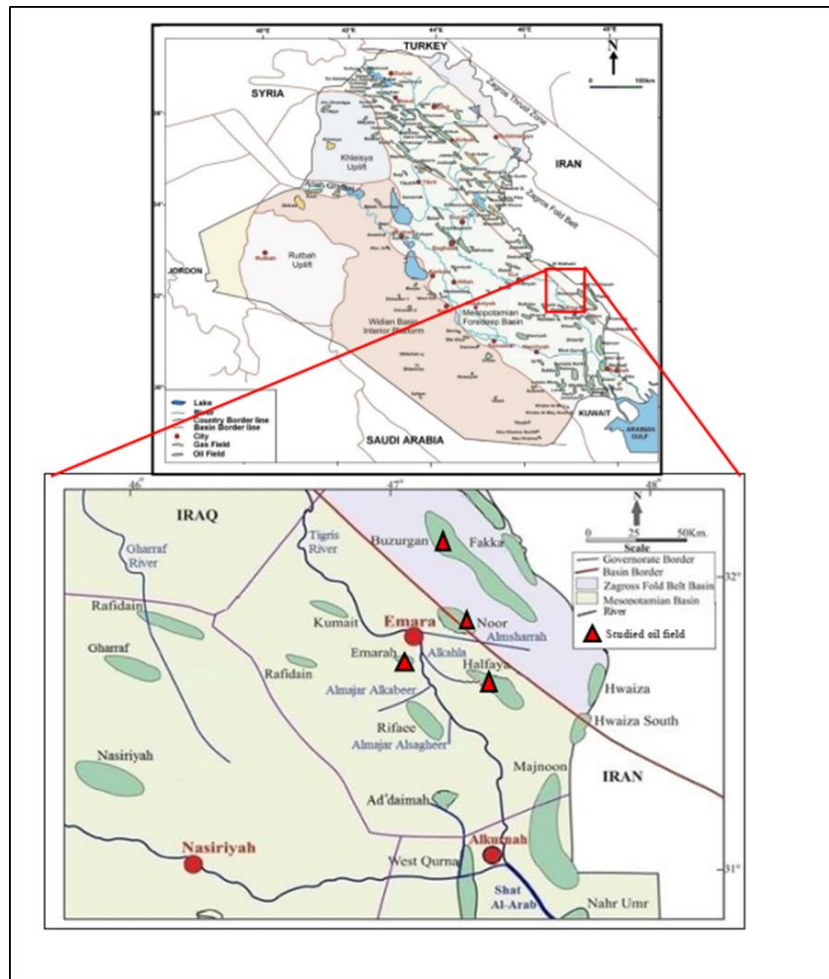
Fig. 1: Location map of the studied wells along with oil fields (after [4]).

3 - Geological Setting of the area

The Cretaceous geologic age in the Middle East is composed of three major shallowing - upwards sedimentological cycles separated by unconformities [5,6], the Thamama Group (Early Tithonian to Late Aptian), the Wasia Group (Early Albian to Early Turonian) and the Aruma Group (Late Turonian to Early Danian). In the study area which represent part from Mesopotamian, Mishrif Formation found in stratigraphic column as a part of subsurface sequence. It is descripted in the zubair area as a very heterogeneous detrital limestone contain some time algal, Rudist and coral reef limestone capped by limonitic fresh water limestone, and this first description was by [6], but in type section area Mishrif Formation compose of grey-white, massive, algal limestone with gastropods and shell fragment in the upper part, and of brown, detrital, porous, partly very shelly and foraminiferal limestones, with banks of Rudists in the lower part [7].

During the Cretaceous period in the Middle East, the majority of stratigraphic stages units contains one or more shallow-marine microporous carbonate reservoirs [5,8]. The Mishrif Formation which belong to Late Cenomanian age [9] is one of the most important oil reservoir in the Mesopotamian Basin (Figure 2), southern Iraq [10,11,5,12], containing about of 30% from Iraq's total oil reserves [13]. It has wide extends throughout the Mesopotamian Basin reaching thicknesses of 100–200 m. The Mishrif Formation facies is dominated by a shallow-water, shelf carbonate sequence composed of bioclastic-detrital limestones, including (in places) algal, coral and rudist bioherms.
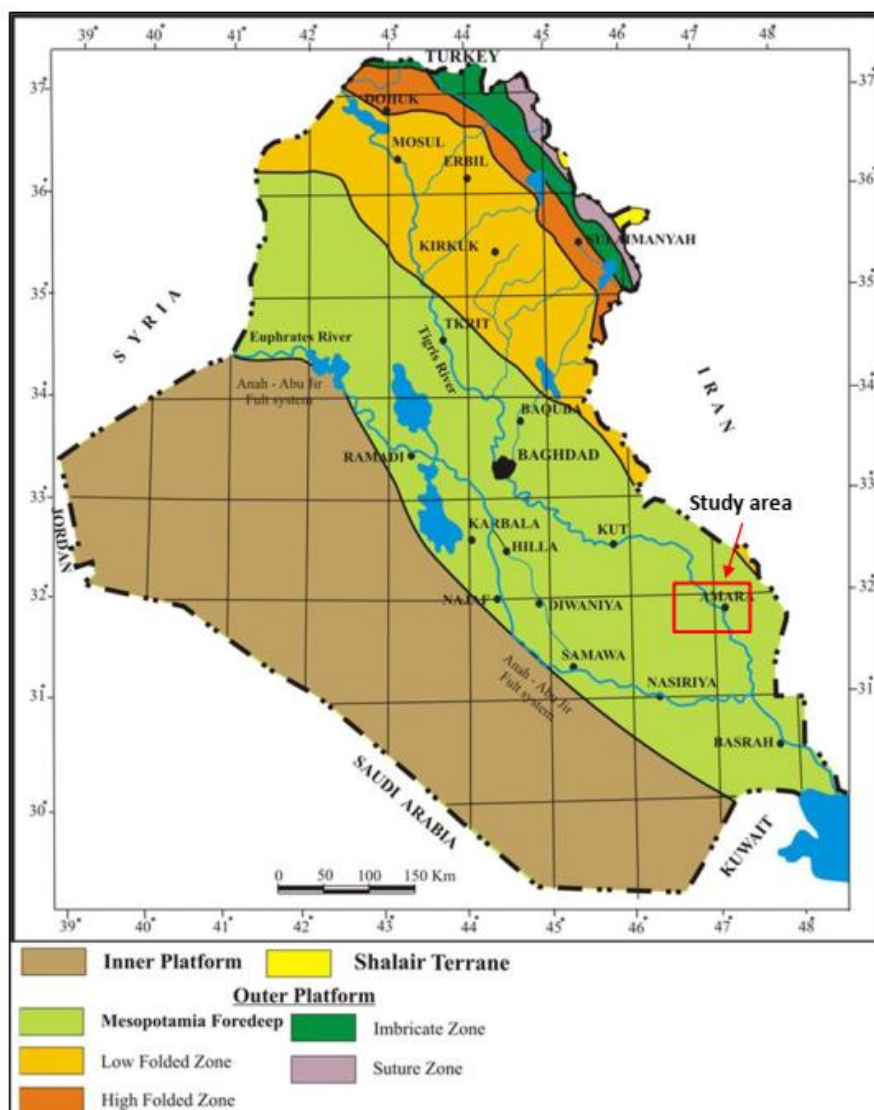
Fig. 2: Tectonic map of Iraq after [14]

4- Methodology

In attempt to determine and construct the depositional environment of the Mishrif Formation, four subsurface sections have been selected from four wells of four oilfields located in south Iraq. They are, (Noor oilfield Well-11), (Amarah oilfield Well-14), (Buzurgan oilfield Well- 24), and (Halfaya oilfield Well-8). For this study, determination the major and trace elements in thirty – three (33) samples was carried out by using XR-Florescence (XRF) technique. For the mineralogical composition, samples are analyzed by XR-Diffraction (XRD), diffraction peaks were measured for angles from 4.5^0 to 70^0. Laboratory work for mineralogy, petrography and geochemical analyses was performed in Iraqi-Germany Lab in college of science, university of Baghdad, Iraq.

5- Results and Discussion

5-1. MINERALOGY

The X-ray diffractometer analysis is an efficient method for recognizing the bulk mineralogy of small sample sizes, but carbonate abundances obtained from this method have significant uncertainty, especially at low carbonate concentration, and results presented here are considered semi-quantitative measures of relative abundances of different carbonate phases [15].

The X-ray diffractograms of the Mishrif samples analysis of the revealed that dolomite and calcite are main minerals with subordinate content of quartz, gypsum and trace amount of clay minerals and evaporite as shown in figures (2, 3).

5-2. Geochemistry

Chemical analysis is very importance in determining the distribution and relationships of the various constituent elements of limestones. Such analysis also helps in classification and determining the environmental conditions that prevailed during the deposition. The geochemical analysis gives a precise idea about the qualitative and quantitative aspects of different major oxides (%) such as SiO_2, CaO, MgO, Fe_2O_3, Al_2O_3, Mn_2O_3, Na_2O, K_2O, TiO_2, and P_2O_5.

Moreover, different trace elements (ppm) such as Sr, Mn.

The major oxides and trace element content of thirty – three (33) bulk limestone samples distributed in four wells represented by four oilfield. The result are show in Tables (1).
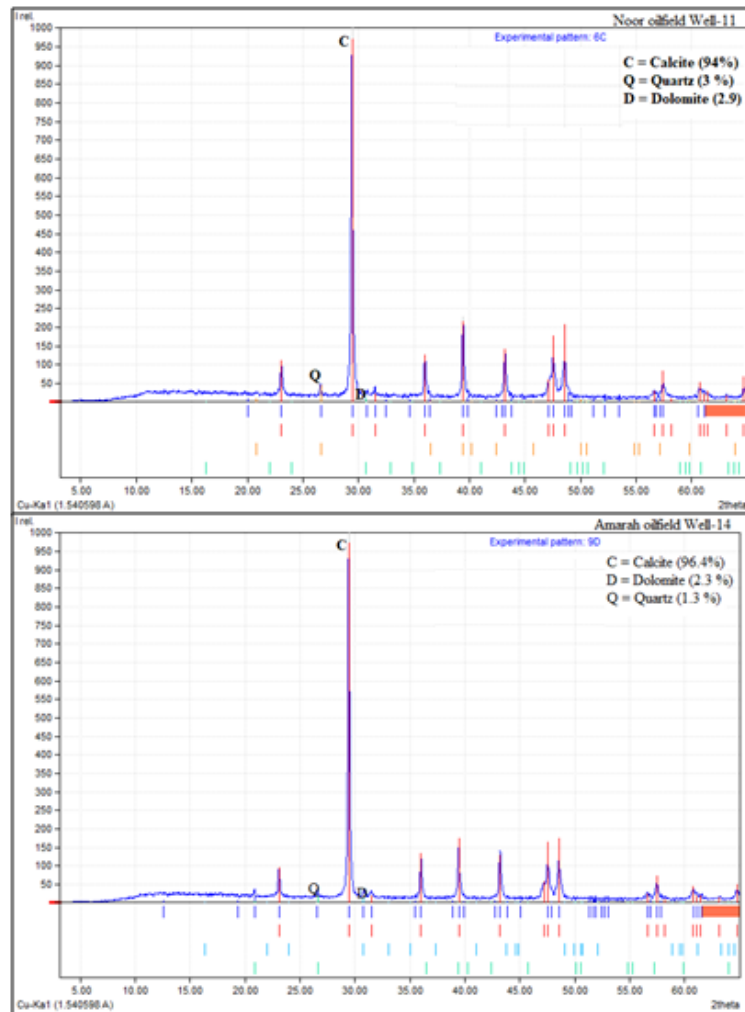

Fig. 2: XR-diffractograms show the reflections of the minerals in Noor and Aamara oilfield.
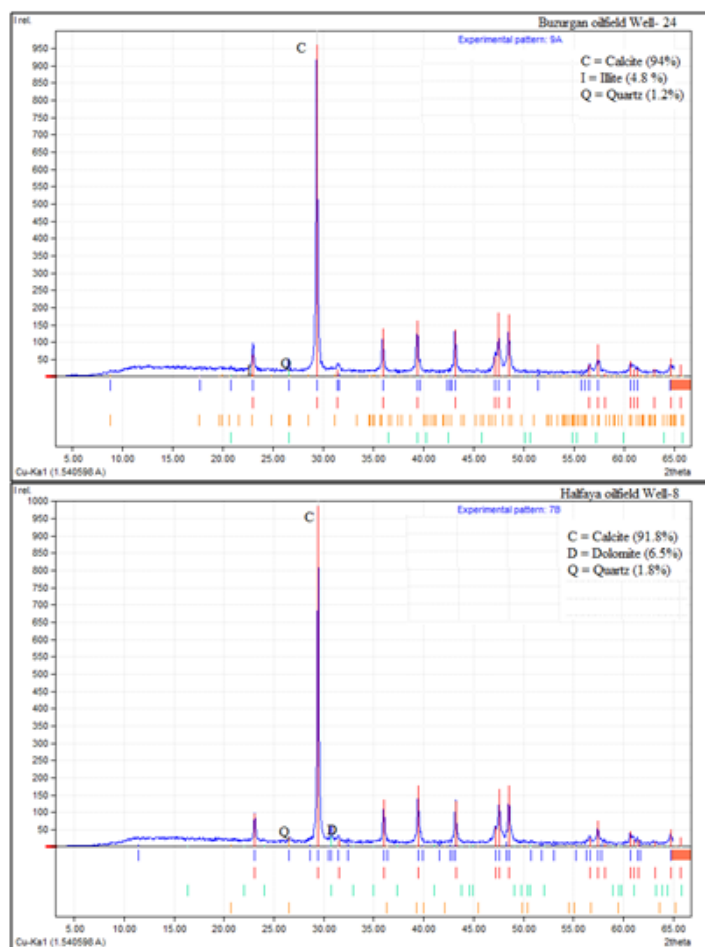
Figure (3) XR-diffractograms show the reflections of the minerals in Buzrgan and Halfaya oilfield.

Table 1: the chemical analysis of studied samples (oxides in % and trace element in ppm).

Depth (m)	SiO₂	CaO	MgO	Fe₂O₃	Al₂O₃	Na₂O	TiO₂	K₂O	P₂O₅	L.O.I	Sr	Mn
Noor oilfield Well-11												

Depth (m)	SiO₂	CaO	MgO	Fe₂O₃	Al₂O₃	Na₂O	TiO₂	K₂O	P₂O₅	L.O.I	Sr	Mn
3320	2.29	54.77	0.19	0.63	0.41	1.07	0.08	0.140	0.189	37.70	369.5	85.4
3418	1.23	58.14	1.01	0.18	0.41	0.69	0.04	0.090	0.002	39.83	457.4	19.3
3484	1.65	58.79	0.66	0.37	0.38	0.80	0.01	0.020	0.011	36.54	593.8	48.3
3520	1.01	60.31	0.58	0.43	0.22	0.79	0.03	0.000	0.008	35.89	565.6	41.6
3578	2.95	57.80	0.68	0.45	0.84	0.79	0.07	0.230	0.035	36.15	535.7	123.6
3608	2.10	59.57	0.79	0.38	0.59	0.79	0.04	0.140	0.019	35.53	491.4	62.6
3644	2.11	58.77	0.53	0.41	0.55	0.77	0.05	0.070	0.013	34.95	410.7	49.8
Min	**1.01**	**54.77**	**0.19**	**0.18**	**0.22**	**0.69**	**0.01**	**0.000**	**0.002**	**34.95**	**369.5**	**19.3**
Max	**2.95**	**60.31**	**1.01**	**0.63**	**0.84**	**1.07**	**0.08**	**0.230**	**0.189**	**39.83**	**593.8**	**123.6**
Mean	**1.91**	**58.31**	**0.63**	**0.41**	**0.48**	**0.81**	**0.05**	**0.100**	**0.040**	**36.78**	**489.2**	**61.5**

Amarah oilfield Well-14

Depth (m)	SiO₂	CaO	MgO	Fe₂O₃	Al₂O₃	Na₂O	TiO₂	K₂O	P₂O₅	L.O.I	Sr	Mn
2932	1.50	60.42	0.44	0.38	0.48	0.79	0.06	0.055	0.008	35.43	348.2	47.6
2974	1.35	58.60	0.55	0.23	0.31	0.71	0.03	0.047	0.017	37.52	384.7	27.5
2998	1.55	60.01	0.66	0.27	0.39	0.75	0.04	0.066	0.010	37.12	446.7	29.4
3022	2.07	56.93	1.15	0.53	0.61	0.75	0.07	0.100	0.022	37.78	529.9	47.2
3064	0.95	56.61	0.29	0.31	0.19	1.20	0.04	0.078	0.184	35.82	589.9	70.6
3136	2.02	61.66	0.75	0.39	0.57	0.78	0.05	0.139	0.040	37.30	744.0	87.3
3166	1.85	57.68	0.97	0.34	0.49	0.75	0.05	0.058	0.016	39.69	462.0	29.9
3202	1.04	58.78	0.76	0.29	0.28	0.75	<0.034	0.022	0.014	37.39	468.3	31.1
3220	1.25	58.90	0.81	0.20	0.31	0.82	0.02	0.052	0.041	32.99	593.9	25.9
Min	**0.95**	**56.61**	**0.29**	**0.20**	**0.18**	**0.71**	**0.02**	**0.020**	**0.008**	**32.99**	**348.2**	**25.9**
Max	**2.07**	**61.66**	**1.15**	**0.53**	**0.61**	**1.20**	**0.07**	**0.140**	**0.184**	**35.43**	**744.0**	**87.3**
Mean	**1.51**	**58.84**	**0.71**	**0.33**	**0.40**	**0.81**	**0.05**	**0.070**	**0.039**	**34.21**	**507.5**	**44.1**

Table 1: continued

Depth (m)	SiO₂	CaO	MgO	Fe₂O₃	Al₂O₃	Na₂O	TiO₂	K₂O	P₂O₅	L.O.I	Sr	Mn
					Buzrgan oilfield Well-24							
2862	2.46	55.16	0.45	0.77	0.70	0.90	0.10	0.34	0.017	37.68	429.6	98.6
3688	3.83	46.53	0.20	1.83	1.04	1.27	0.20	0.61	0.200	38.31	226.8	129.7
3748	1.55	57.26	0.50	0.42	0.55	1.02	0.07	0.19	<0.0069	43.64	331.6	54.3
3784	1.75	55.91	1.02	0.40	0.52	1.59	0.05	0.37	0.001	36.42	407.5	63.0
3820	2.92	56.60	0.45	0.76	0.90	0.90	0.12	0.28	0.007	38.56	533.2	70.2
3946	2.11	55.51	0.54	0.53	0.86	0.96	0.06	0.23	0.006	38.28	416.9	59.9
3970	2.46	55.70	0.74	0.45	0.79	1.07	0.05	0.23	0.004	37.17	439.9	72.2
4000	1.59	56.35	1.42	0.33	0.46	0.89	0.04	0.13	0.003	39.33	346.0	36.1
4036	1.89	54.82	0.58	0.54	0.60	1.18	0.06	0.22	0.005	37.79	346.2	46.7
Min	**1.55**	**46.53**	**0.20**	**0.33**	**0.47**	**0.89**	**0.04**	**0.13**	**0.001**	**36.42**	**226.8**	**36.1**
Max	**3.83**	**57.26**	**1.42**	**1.83**	**1.04**	**1.60**	**0.20**	**0.61**	**0.200**	**43.64**	**533.2**	**129.7**
Mean	**2.29**	**54.87**	**0.65**	**0.67**	**0.72**	**1.10**	**0.08**	**0.29**	**0.031**	**38.49**	**386.4**	**70.1**
					Halfaya oilfield Well-8							
2854	0.83	58.34	0.11	0.41	0.12	1.14	0.03	<0.0012	0.175	37.79	204.5	47.8
2902	1.20	59.09	0.41	0.28	0.31	0.76	0.03	0.05	<0.0069	37.53	335.2	28.8
2938	0.66	59.46	0.57	0.10	0.19	0.85	<0.0034	0.02	<0.0069	39.65	347.6	23.1
2980	1.04	59.27	0.62	0.26	0.34	0.80	0.04	0.08	<0.0069	34.08	375.4	20.8
3004	0.26	57.75	0.19	0.13	0.01	1.18	0.01	<0.0012	0.171	36.54	490.0	11.4
3166	1.08	58.26	0.82	0.30	0.33	0.83	0.03	0.07	0.004	38.54	372.4	45.9
3190	1.33	61.19	1.05	0.22	0.36	0.93	0.03	0.08	0.007	36.88	605.2	24.2
3232	1.32	59.81	0.60	0.17	0.25	0.75	0.02	0.05	0.017	37.27	404.6	23.5
Min	**0.26**	**57.75**	**0.11**	**0.10**	**0.01**	**0.75**	**0.01**	**0.02**	**0.004**	**34.08**	**204.5**	**11.4**
Max	**1.33**	**61.19**	**1.05**	**0.41**	**0.36**	**1.18**	**0.04**	**0.08**	**0.175**	**39.65**	**605.2**	**47.8**
Mean	**0.97**	**59.15**	**0.55**	**0.23**	**0.24**	**0.90**	**0.03**	**0.06**	**0.075**	**37.34**	**391.9**	**28.2**

Geochemical parameters as environmental indicators

The use of elements ratios (Mg, Ca, Sr, Mn) as paleo-environment indicator in some biogenic carbonates is suitable for reconstruction water temperature, because of they are often independent of other environmental variable, especially salinity. Elements ratios can be used for better understanding of the depositional environment of carbonate rocks. Among these geochemical parameters,[16] mentioned that Mn/Sr ratios are less than 3 indicating high degree of preservation of primary geochemical signatures. All samples of the Mishrif Formation have low Mn/Sr ratio, which average (0.130, 0.86, 0.2, 0, 86) in the studied oilfields respectively (table 3). Diagenetic processes are characterized by the precipitation of minerals and dissolution at low temperatures, which are indicated by using some of the geochemical ratios.

–Mg/Ca and Ca/Mg of carbonate rocks: The Mg/Ca ratio used to determine the minerals precipitate from sea waters. Many authors like [17] mentioned 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 Average of Ca/Mg ratios presented in this study are (0.009, 0.010, 0.10, and 0.008) in studied wells respectively (table 3), which suggests precipitation of low Mg calcite. This ratio is important in the classification of carbonate rocks on the basis of geochemical distribution [18]. The carbonate rocks are classified on the basis of Ca/Mg ratio as illustrated in (Table 2). The Average values of Ca/M are (138.38, 115.06, 126.75, and 206.29) in the studied oilfield respectively. Calcitic Limestone is the major type of the rocks in Mishrif Formation (Table 2).

Table 2: Shows the classification of carbonate rocks based on Ca/Mg ratio,[18]

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

-Mg/Ca ratios for paleosalinity: According to [19] who stated from experiment data that Mg/Ca water ratios decrease with decrease salinity. The decrease salinity from 35 to 20 show decrease in Mg/Ca ratios from 2.39 to 1.79 .In the present study, the Mg/Ca ratio have average (0.009, 0.010, 0.10, 0.008), Table (3), which implies the salinity was moderate at the time of deposition.

-Mg/Ca and Mn/Ca for paleotemperature: [20] proposed that The Mg/Ca ratio increases with increasing temperature in coral skeleton. While [21] refer that Mn/Ca ratio increases with increasing temperature. Mg/Ca ratio have average (0.009, 0.010,

0.10, 0.008), and the average of Mn/Ca (0.00015, 0.00010, 0.00018, 0.00007) in the studied borehole respectively (Table3). Which suggests modirate temperature at the time of carbonate deposition.

- 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 [22]. Based on the compare comparison between the low values of Sr/Ca ratio and high values for Ca/Mg ratio in studied samples, that show the main diagenesis process is dolomitization.

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 [22] (Table 3) (Figure 4 - A).

- Dissolution: According to [23] 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) (Figure 4 - B).

Table 3: Molar ratios of Mishrif Formation.

Noor oilfield Well-11					
Depth	Ca/Mg	Mg/Ca	Mn/Sr	Mn/Ca	Sr/Ca
3320	348.34	0.003	0.231	0.00022	0.0009
3418	68.55	0.015	0.042	0.00005	0.0011
3484	105.80	0.009	0.081	0.00011	0.0014
3520	123.06	0.008	0.074	0.00010	0.0013
3578	101.31	0.010	0.231	0.00030	0.0013
3608	89.74	0.011	0.127	0.00015	0.0012
3644	131.86	0.008	0.121	0.00012	0.0010
Avareag	**138.38**	**0.009**	**0.130**	**0.00015**	**0.0012**
Amarah oilfield Well-14					
Depth	Ca/Mg	Mg/Ca	Mn/Sr	Mn/Ca	Sr/Ca
2932	162.37	0.006	0.137	0.00011	0.0008
2974	126.15	0.008	0.071	0.00007	0.0009
2998	107.74	0.009	0.066	0.00007	0.0010
3022	58.61	0.017	0.089	0.00012	0.0013
3064	233.88	0.004	0.120	0.00017	0.0015
3136	98.08	0.010	0.117	0.00020	0.0017
3166	70.63	0.014	0.065	0.00007	0.0011
3202	91.37	0.011	0.066	0.00007	0.0011
3220	86.68	0.012	0.044	0.00006	0.0014
Avareag	**115.06**	**0.010**	**0.086**	**0.00010**	**0.0012**
Buzurgan oilfield Well- 24					
Depth	Ca/Mg	Mg/Ca	Mn/Sr	Mn/Ca	Sr/Ca
2862	146.38	0.007	0.230	0.00025	0.0011
3688	271.86	0.004	0.572	0.00039	0.0007
3748	135.99	0.007	0.164	0.00013	0.0008
3784	64.95	0.015	0.155	0.00016	0.0010
3820	150.64	0.007	0.132	0.00017	0.0013
3946	122.14	0.008	0.144	0.00015	0.0011
3970	89.39	0.011	0.164	0.00018	0.0011
4000	47.19	0.021	0.104	0.00009	0.0009
4036	112.19	0.009	0.135	0.00012	0.0009
Avareag	**126.75**	**0.010**	**0.200**	**0.00018**	**0.0010**

Table 3: continued.

Depth	Ca/Mg	Mg/Ca	Mn/Sr	Mn/Ca	Sr/Ca
		Halfaya oilfield Well-8			
2854	610.66	0.002	0.234	0.00011	0.0005
2902	172.58	0.006	0.086	0.00007	0.0008
2938	124.02	0.008	0.066	0.00005	0.0008
2980	113.22	0.009	0.055	0.00005	0.0009
3004	358.82	0.003	0.023	0.00003	0.0012
3166	84.58	0.012	0.123	0.00011	0.0009
3190	68.85	0.015	0.040	0.00006	0.0014
3232	117.58	0.009	0.058	0.00005	0.0009
Avareag	**206.29**	**0.008**	**0.086**	**0.00007**	**0.0009**
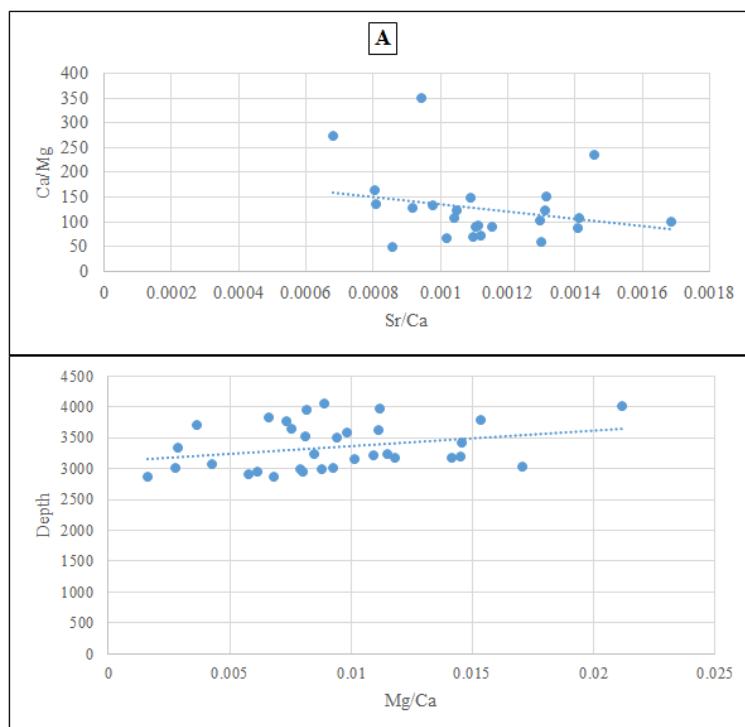
Fig. 4: Shows relation between Sr/Ca with Ca/Mg and Mg/Ca with depth.

Discussion

Oxygen partial pressure influence the oxidation state of some trace elements and control their selective solubility in seawater and consequently their degree of enrichment in marine sediments [24,25,26]. The abundance of trace elements in the sediments and sedimentary rocks allow estimating the oxygenation state of the bottom water and sediments during deposition.

[27] in [28] 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. [19] Claimed from laboratory experiment that the Mg/Ca is positively correlated with 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.[20] proposed that the Mg/Ca ratio increase with increasing temperature in coral skeleton. While [21] 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 Mishrif 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 4 - B)

Conclusion

The main minerals prevalent in the studied samples are calcite and dolomite, with quartz and clay minerals (kaolinite, montmorillonite and illite) as a subordinate components minerals. Depending of using Ca/Mg ratios for geochemical classification of carbonate rocks it is revealed the Calcitic Limestone is the majority type of rock among the studied wells .Application of Mg/Ca and Mn/Ca ratios as environmental geochemical parameters, refer to moderate salinity and temperature during the time of deposition.

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معدنية وجيوكيميائية تكوين المشرف من حقول مختارة في جنوب شرق العراق

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الملخص

تمت دراسة معدنية وجيوكيميائية تكوين المشرف (Late Cenomanian) في أربعة حقول نفطية جنوب شرق العراق باستخدام تقنية XRF و XRD. أظهرت التحليلات المعدنية ان معدني الكالسايت والدولومايت يمثلان المعادن الرئيسية المؤلفة لصخور الحجر الجيري التابعة للتكوين مع معادن ثانوية تمثل الكوارتز والمعادن الطينية (كاؤولين, مونتيمورلونايت و الالايت).

تم تطبيق نسبة (Ca/Mg) لغرض تصنيف صخور الكاربونيت كيميائيا واظهر التصنيف ان نوع الصخور السائد والاكثر شيوعا في تكوين المشرف هو الحجر الجيري الغني بالكالسيوم.

النسب المولية لبعض العناصر من Ca / Mg و Mg / Ca تشير الى نسبة الملوحة المعتدلة خلال وقت ترسيب صخور التكوين. في حين أن Mg/Ca و Mn/Ca تدل على درجة حرارة معتدلة عند ترسب صخور التكوين. بالمقارنه بين نسبة Sr/Ca المنخفضة مع نسبة Ca/Mg العالية نجد ان عملية الدلمتة قد لعبت دور اساسي خلال العمليات التحويرية.