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Petrography and geochemistry of Pila Spi Formation (Middle- Late Eocene) in Selected Sections / Northern Iraq

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Abstract

The Pila Spi Formation (middle – late Eocene) was studied in terms of field character, Petrography and geochemistry from two outcrops (Bakhar and Bani bawy) sections, Northern Iraq. The field studies showing massive, lithified limestone to marly limestone high effected by dolomitization. The petrography studies shows that most of the skeletal grains was destroyed due to digenetic processes specifically the dolomitization, and the vast majority of carbonate rocks are mudstone and few beds of wackestone. The geochemical study reveals low CaO% and high MgO% content due to the intense effect of dolomitization, and the carbonate rocks was classified as impure limestone generally of slightly calcareous dolomite. Ca/Mg and Sr/Ca ratios have been used to evaluate the depositional environment and indicate near shore and shallow depth environment and the basin become shallower upward in both sections.

Keywords: Bani bawy, Bakhar, Pila Spi, geochemistry, dolomitization, limestone.

بتروغرافية وجيوكيميائية تكوين البيلاسبي (الايوسين – المتوسط الأعلى) لمكاشف مختارة / شمال العراق

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الخلاصة:

تم دراسة تكوين البيلاسبي (الأيوسين– المتوسط الأعلى) حقلياً، بيتروغرافيا و جيوكيميائيا لمقطعين مختارين (باخير و بنباوي) شمال العراق. بينت الدراسة الحقلية بأن التكوين يتألف من صخور كاربونية كتلية الى متطبقة تتكون من الحجر الجيري والحجر الجيري المارلي المتأثر بشده بعملية الدلمتة. الدراسة البتروغرافية اوضحت بأن معظم الحبيبات الهيكلية تحطمت نتيجة العمليات التحويرية وخصوصا الدلمتة، ومعظم الصخور الجيرية هي صخور جيرية طينية (Mudstone) وطبقات قليلة من (Wackestone). بينت الدراسة الجيوكيميائية للأكاسيد الرئيسية والثانوية وبعض العناصر الاثرية قلة محتوى CaO% وزيادة MgO% وذلك للتاثير الشديد للدلمتة، وصنفت هذه الصخور الجيرية بأنها غير نقية وعموما من مصنف الدواومايت قليل الجير. استخدمت نسبة Ca/Mg و Sr/Ca لاستنتاج البيئة الرسوبية و بينت نتائجها بأن صخور التكوين ترسبت في بيئة ضحلة قريبة من الساحل وتصبح أكثر ضحالة في الجزء العلوي من كلا المقطعين.

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Introduction:

The outcrops of Pila Spi Formation represent by ridge of carbonate rocks series extended from the NW to the SE North Iraq. It deposited during the Middle-Late Eocene. These rocks are deposited to the SW of an emergent uplift during the final phase of subduction and closures of the remnant Neo-Tethys Ocean, while the Red beds were deposited in the basin to the NE of the uplift area. The resistant Pila Spi Formation formed a conspicuous ridge between the recessive weathering Gercus and Fatha formations throughout the high folded zone north Iraq [1]. The Pila Spi Formation was described by [2]. The original type section was submerged under the water the Derbendikhan reservoir Dam. A supplementary type section was described at Kashti, on the Barand Dagh Mountain [1].

The upper part of the formation comprises well bedded bituminous chalky and crystalline limestones with bands of white chalky marl and chert nodules toward the top. The lower part composed of well bedded hard porous or vitreous bituminous white poorly fossiliferous limestone [1]. The formation was deposited in shallow lagoonal setting [1] while [3] believed that the formation was deposited in a shelf and shallow lagoonal environment. [4] subdivided the Pila Spi Formation in Taq Taq oil field and Haibat Sultan Mountain in to four lithologic units from bottom to top are: lower brecciated and silicified unit, dolomitized tidal flat limestone, lagoonal limestone, dolostone and upper brecciated dolomitic limestone. Also [5] interpreted new facies in Pila Spi Formation at Sulaimanyia, NE, Iraq, such as massive and high fossil contents of algae, corals, bryozoans and bioclasts, also floatstone, bindstone, framstones, bafflestones and rudstone microfacies have been identified, these facies revealed new environmental and paleogeographic setting for the Middle-Late Eocene in NE Iraq. [6] was studied selected sections in Pila Spi Formation, northern Iraq and recognized three units of rocks based on different lithological bedding characters.

The present study aims to give an idea about the field and petrographic characters, integrated with geochemical interpretations to evaluate the depositional environment, digenetic process and assess the suitability of Pila Spi Formation rocks for the manufacturing of cement near Dohuk and Erbil cities. Two outcrop sections have been selected, the first one at about 3 km north Dohuk city at Bakhar anticline and the second is of about 25 km NE Erbil city at Bani bawy anticline near Gomaspan valley. Figure-1 shows the locations of these sections in the study area.

Lithology and stratigraphy:

During the field work of the studied section at Bakhar anticline, Duhok area, it was found that the Pila Spi Formation represented by succession of limestone and marly limestone with thickness about 240m Figure -2. The lower contact of the formation with Avanah Formation was recognized by the change of limestone lithology from lithified massive limestone with chert nodules to grey color well lithified bedding altered with thin beds of marl and considered as conformable contact (plate-1A). The upper contact of the formation with Fatha Formation is recognized by the presence of basal conglomerate, which indicates erosion surface or unconformity (Plate-1B). [6] indicated the presence of basal conglomerate between the upper part of the Pila Spi and the lower part of Fatha Formation in many sites northern Iraq, also [7] cited to the basal conglomerate layer between the two formations in the area extend between the high folded zone and the low folded zone.

The succession of Pila Spi Formation at Duhok area are composed of successive lithified and massive limestone from the base to the top as follows Figure-2, plates (1-A, B, C, D).

1. Grey color well lithified bedding to thin beds of marly limestone (10m).
2. Lithified well bedded white chalky limestone to dolomitic marly limestone (85m).
3. Mudstone with thin beds of marl (30m).
4. Massive cherty limestone (Plate-1C) (20m).
5. Massive limestone (Plate-1D) with highly weathered layers interbedded with marl and marly limestone (50m).
6. Lithified grey limestone and marly limestone (50m).

Erbil section located NE city of Erbil about 25km at Bani bawy anticline formed of about 100m of limestone (Figure-3 and plates-2A, B, C, D), The lower contact of the PiIa SPi Formation with Gercus characterized by change in lithology and color from carbonate to clastic red beds (Plate-2A), while the upper contact between Pila Spi and the overlying Fatha Formation is unconformable as indicated by the presence of basal conglomerate (Plate-2B), described in the field as follows from the base to the top:

1. Layer of 10 m thickness limestone of Pila Spi Formation change to clastic red beds of Gercus Formation, interbedded with 1.5m layer of calc conglomerate (Plate -2A).
2. Massive vug limestone changed to brown marly limestone (35m), underlying by red marl and clay of 5m thickness.
3. Massive dolomitic limestone with cherty nodules (5m) (Plate-2C), followed by (5m) of well bedded dolomitic limestone.
4. Well bedded white dolomitic chalky limestone (10m).
5. Marly limestone (15m).
6. Lithified grey limestone and marly limestone (15m).

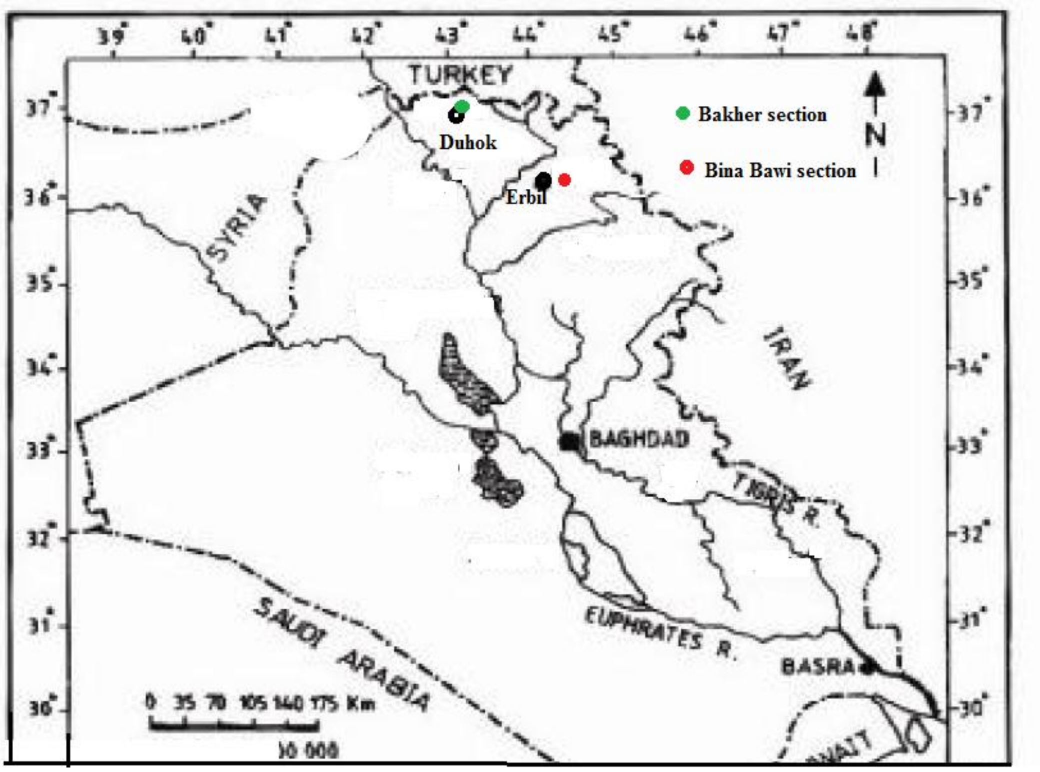

Figure 1- Location map of studied area.

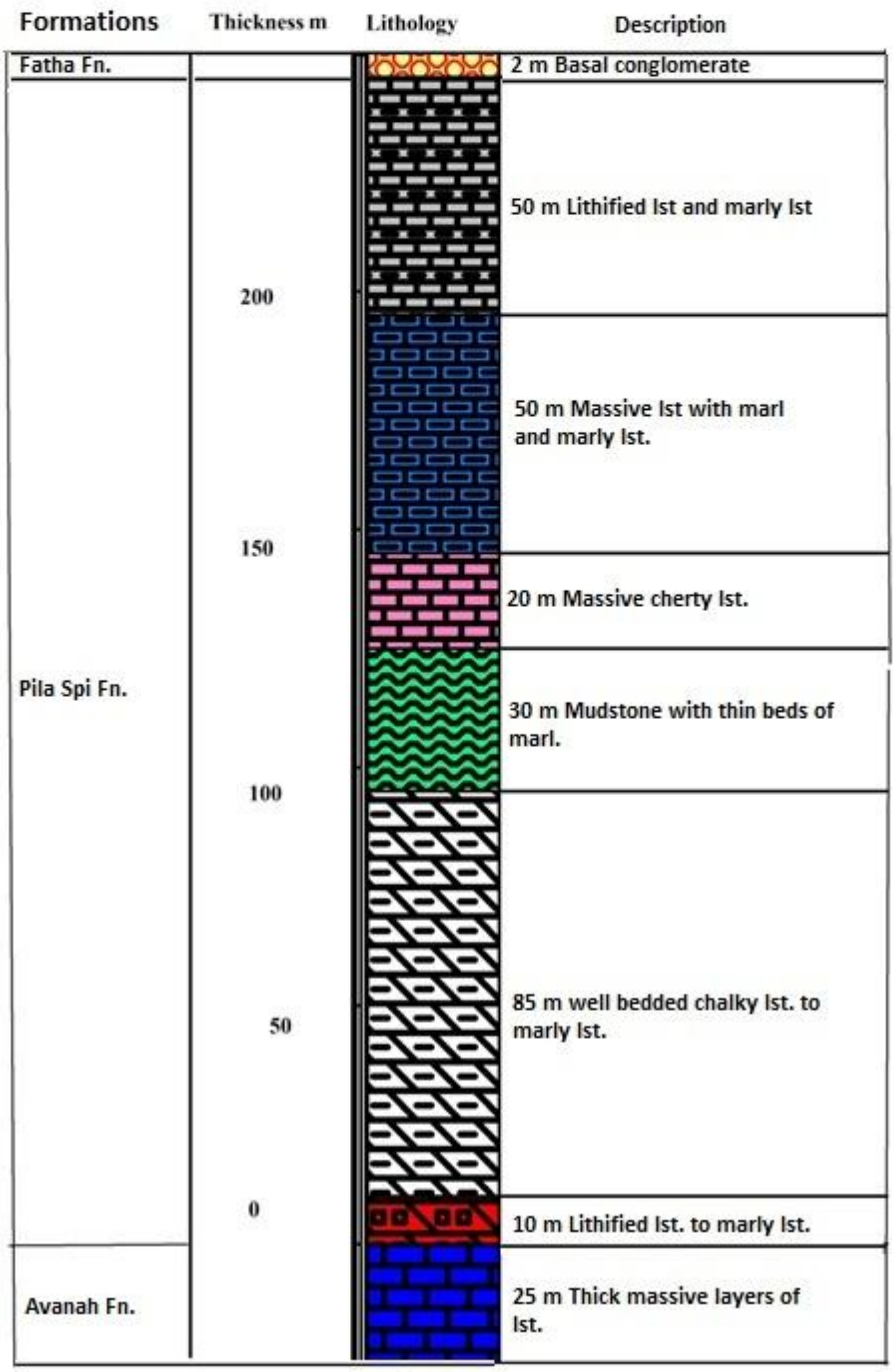

Figure 2- Stratigraphic column of the Pila Spi formation at NE limb of Bakhar anticline, Duhok area.

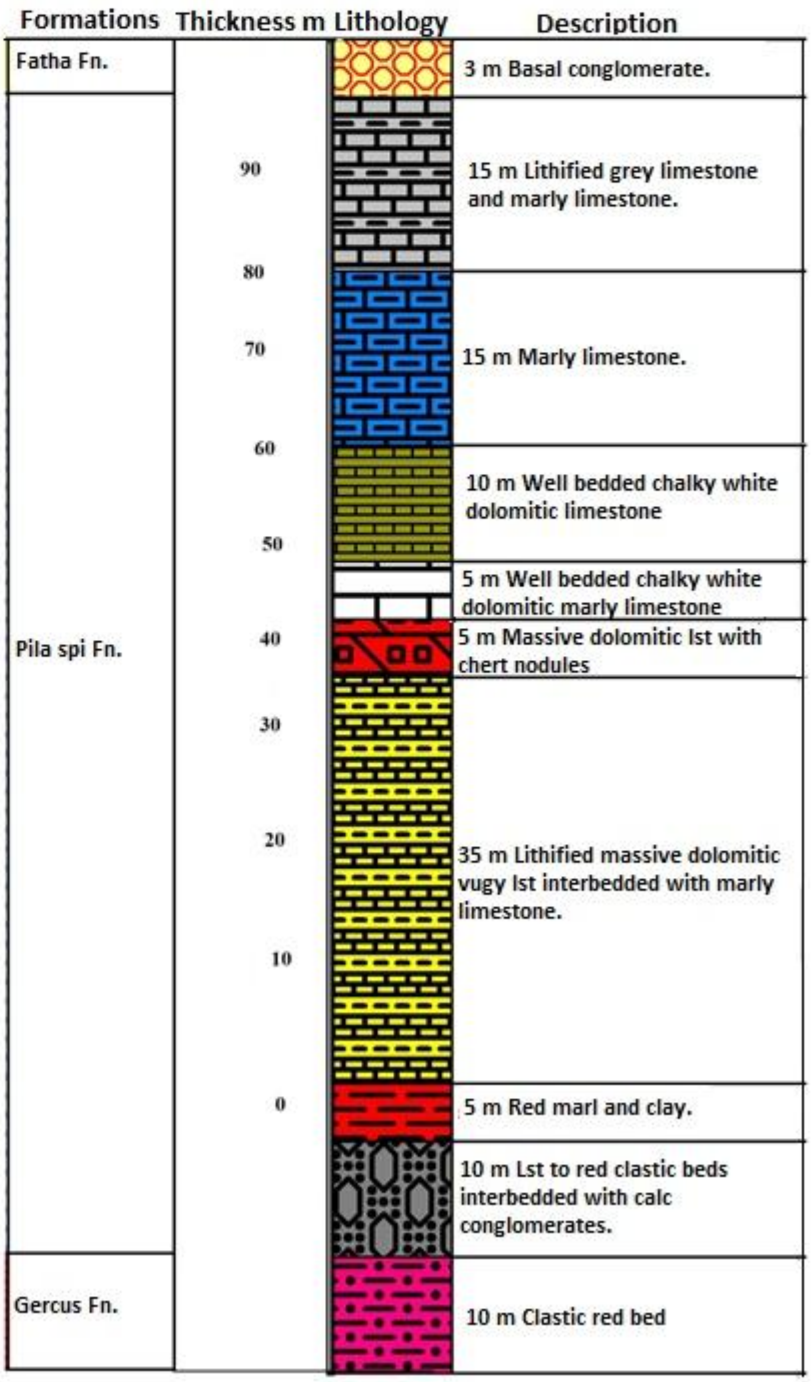

Figure 3- Stratigraphic column of the Pila Spi formation at SW limb of Bani bawy anticline, Erbil area.

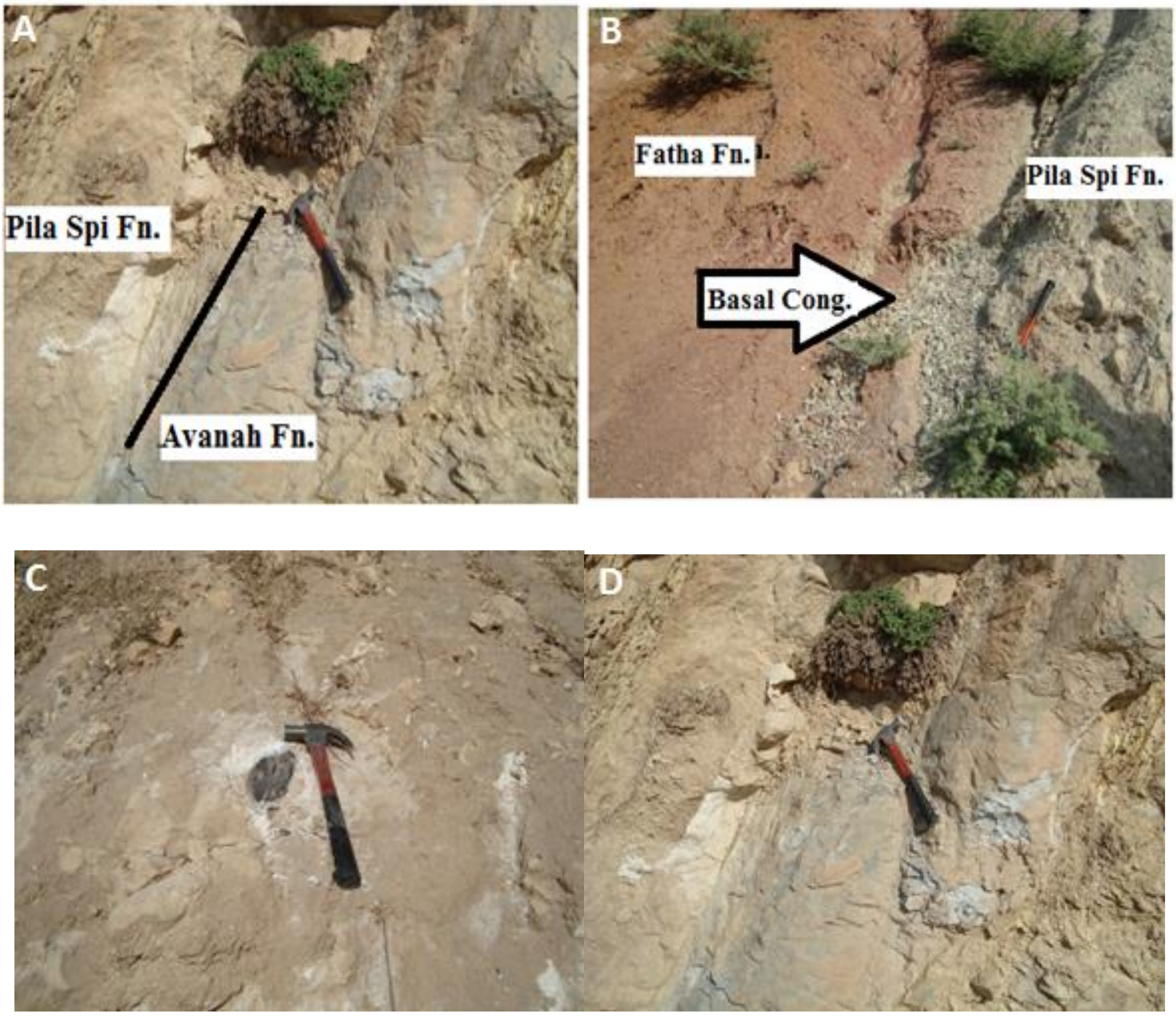

Plate 1- Field photographs shows the lithologic units in Bakhar section at Duhok area.

- **A.** The contact between Avanah and Pila Spi Formations.
- **B.** The contact between Pila Spi and Fatha Formations.
- **C.** Chert nodules with massive limestone.
- **D.** Massive limestone.

Plate 2- Field photographs shows the lithologic units in Bani bawy section

- **A.** The contact between Gercus and Pila Spi Formations.
- **B.** The contact between Pila Spi and Fatha Formations.
- **C.** Chert nodules with lithified limestone.
- **D.** Massive limestone

Petrography:

The petrographic studies are very important in the description of mineralogical components of carbonate rocks and used for the indication and identification of these rocks and leads to construction of the environment of deposition and their conditions, also it is important in the description and establishing of the microfacies and grouping them in facies assemblage which depend on the discrimination of grains, fabrics, biocontents and microscale sedimentary structures coupled with diagenetic effect and kind of matrix which are intimately related to the depositional conditions and sea-level fluctuations [8].

The petrographic study of Pila Spi carbonate rocks is carried out for 17 thin sections collected from Bakhar locality and 15 thin section from Bani bawy locality, employing the polarizing microscope for studying the stained thin sections. The examined samples have been selected according the change of physical and field characters.

Carbonate rocks consist mainly of groundmass and grains. The grains are regarded as important constituents for finding out the depositional environments and texture types. According to [8], the constituents of carbonate are divided into skeletal grains include fossils and their clasts and non-skeletal grains.

The skeletal grains of Pila Spi carbonate represent mainly preserved hard parts of fossils assemblages with the fragmented particles or bioclasts. In general both studied sections are highly effected by dolomitization and diagenetic processes and most of skeletal grains have been destroyed.

From the petrography of Duhok section it was found from the base to the top, the lower part of the section composed mainly of micrite or mudstone according to [9] classification which contains fossils mostly benthonic types highly effected by diagenetic and dolomitization processes (Plates-3A, B). The diagenetic processes represented by the formation of spary calcite and microspar growth in the cavities and replaced the micrite (Plate-3A, C).

Dolomite phenocrystals indicate protodolomite type also present in the middle part of the section indicating hypersaline diagenetic conditions (Plate-3B); in addition to the presence of patches of iron oxides or organic remains with rims of silica (Plate-3D). Also the middle part of the section is rich in chert with patches of iron oxides in aggregate may be precipitated during the late digenetic processes.

High porosity and neomorphism with high degree of recrystallization and formation of microspar in the cavities which represent removing or destroying of benthonic fossils (Plate-3A), also elongated fractures replaced by microspar and formation of dolomite euhedral grains have been recognized (Plate-3E). The upper part of Duhok section are mostly formed of mudstone with fossils and intraclasts. The presence of iron oxides is common. The rocks mostly with high porosity; also fossils of benthonic foraminifera filled with spary calcite have been recognized (Plate-3A). The upper part of Pila Spi Formation in Duhok section is mostly chetry limestone classified as mudstone according to [9] with euhedral grains of dolomite (Plate-3F) it seems that dolomite formed at late stages of diagenesis processes.

The field observations and petrographic studies of Bani bawy section in Erbil area, reveals that the lower part of this section are mostly formed of mudstone according to [9], often marly limestone was effected by diagenetic processes with fractures filled by microspar or spary calcite which forming the cementing materials, few intraclasts and benthonic foraminifera replaced by microspar also present, highly effected by diagenetic processes such as recrystallization (Plate-3E).

The middle part of Bani bawy section contain shells (10-20%) mostly is benthonic forams and classified as wackestone [9], as well as most of mudstone in this part contains phenocrystals of drusy calcite filling the fractures (Plate-3C). The rocks of this part is highly porous dolomitic and chalky limestone with nodules of chert, and sometime patches of iron oxides were observed.

The upper part of the Bani bawy section are mainly composed of mudstone to wackestone according to [9], the carbonate grains are mostly of different benthonic types of foraminifera and intraclasts (Plat-3E) also highly effected by recrystallization, with high porosity, patches of iron oxides and organic remains are present.

The layers of the carbonate near the upper contact with Fatha Formation are rich in benthonic forams and classified as wackestone according to [9]. Fractures and highly broken layers filled by microspar and spary calcite. Carbonate balls with uncertain origin of spary calcite or drusy calcite was observed.

The occurrence of chert with limestone have been discussed by many authors such as [10] who considered that the chert in limestone dominantly microcrystalline or cryptocrystalline with a lesser amount of fibrous quartz (chalcedony). He also stated that chert may formed as epigenetic concretions by metasomatic processes operating during diagenesis and involving the aggregations of silica that originally have been deposited through the host rocks. [11] summarized that the origin of chert creation related to replacement of carbonate host rocks, and [10] referred that the evidence of replacement are including the occurrence of chert along fissures in limestone, the very irregular shape of some nodules and the association of silicified fossils in some chert. In thin-section studies, replacement origin was displayed by 1) the presence of relict masses of host rock (carbonate rocks) inside the nodules; 2) the presence of pseudomorphs after single crystals or aggregates of crystals; 3) the presence of pseudomorphs after host-rock structures; and 4) the growth of authigenic carbonate minerals of a composition different from those of the host rock in and near nodules [10]. In present study silica filling cavities was identified in mudstone as chalcedonic silica (Plate-3G), and the chert nodules are considered as replacement type.

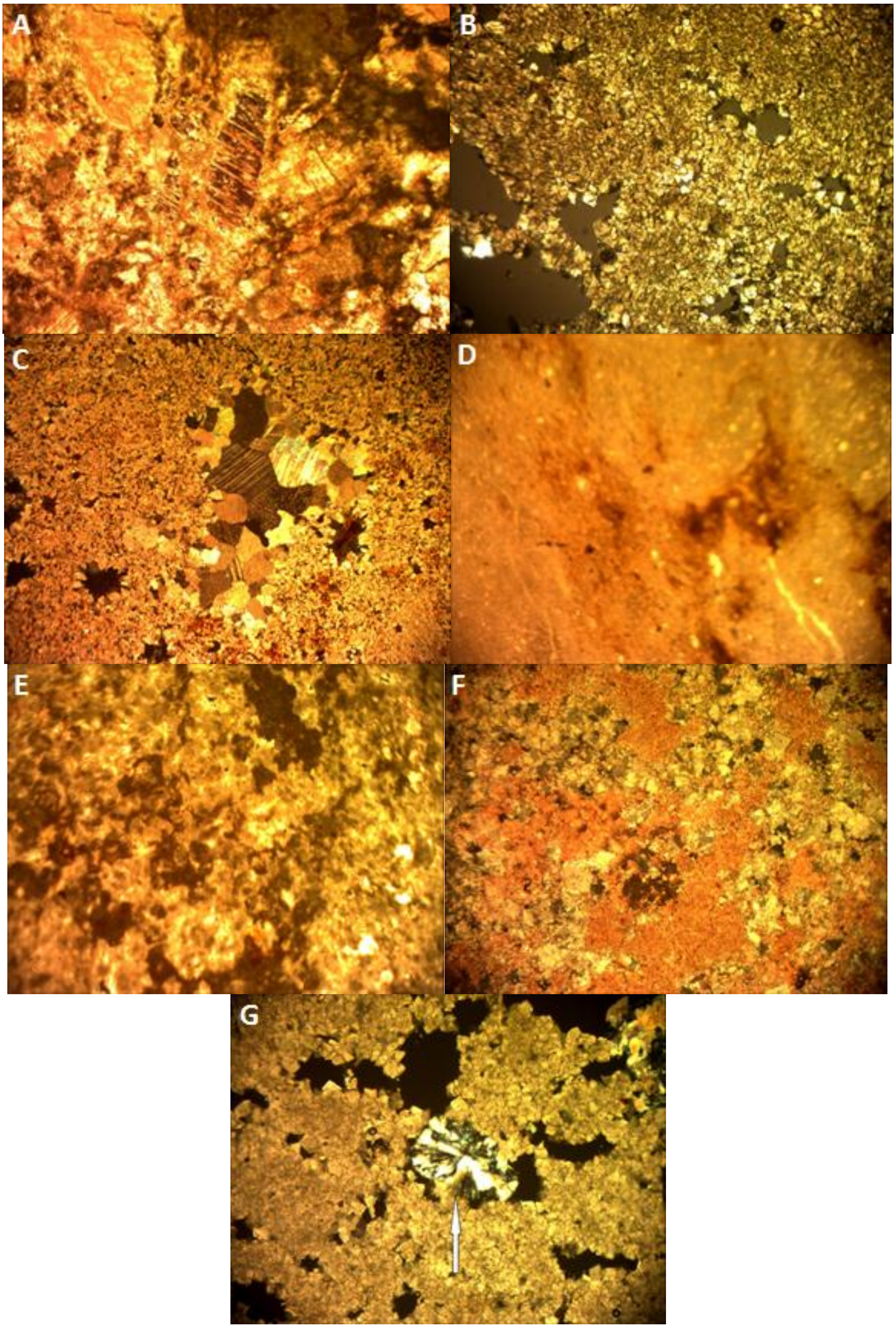

Plate 3- Petrographic features in Bakhar and Bani bawy thin sections.

- **A.** Fractured fossils in mudstone with spary calcite (CNx100X).
- **B.** Euhedral dolomite grains (PPx40X).
- **C.** Drusy sparite calcite as cement with microsparite(CNx100X).
- **D.** Mudstone with patches of iron oxide (PPx40X).
- **E.** Intraclasts and benthonic fossils replaced by microspar and dolomite (CNx40X).
- **F.** Microspar patches and euhedral dolomite (PPx100X).
- **G.** Chalcedonic silica with mudstone (CNx100X).

Geochemistry:

Geochemical investigations were achieved to determine the geochemical composition of the Pila Spi Formation at Bakhar and Bani bawy sections and interpret their depositional and digenetic conditions, as well as to evaluate their suitability for cement industry. Five samples were selected from Bakhar section and four from Bani bawy section for chemical analysis, all the chemical analysis were carried out in Central Laboratories Department of Iraq Geological Survey. Wet chemical analysis method was used and atomic absorption spectrometer devices was employed in order to analyze the major oxides CaO, MgO, SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MnO, and trace elements Sr, Ni, Cu. Loss on ignition (LOI) was determined by burning the samples powder at 1000°C. The results, range, average of geochemical analyses of the samples from Pila Spi Formation at Bakhar and Bani bawy sections are presented in the Table-1.

Table 1- The results of geochemical analyses of Pila Spi Formation in Bakhar and Bani bawy sections.

S. N		CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	LOI	Total	Sr	Ni	Cu	Ca/Mg	Sr/Ca
		%									ppm				
P1	Bani bawy section	29.68	20.0	3.12	0.9	0.26	0.04	0.009	44.96	99.03	58	26	6	1.76	0.00027
P4		21.84	14.18	29.74	0.36	0.19	0.01	0.008	32.79	99.18	48	25	6	1.82	0.00030
P11		28.56	20.4	2.66	1.29	0.44	0.04	0.011	44.86	98.33	70	37	8	1.66	0.00034
P14		30.24	19.0	3.44	1.18	0.6	0.04	0.007	44.29	98.86	54	35	6	1.88	0.00025
Min.		21.84	14.18	2.66	0.36	0.19	0.01	0.007	32.79	98.33	48	25	6	1.66	0.00025
Max.		30.24	20.4	29.74	1.29	0.6	0.04	0.011	44.96	99.18	70	37	8	1.88	0.00034
Avg.		27.58	18.39	9.74	0.93	0.37	0.032	0.009	41.72	98.85	57.5	30.75	6.5	1.78	0.00029
D5	Bakhar section	30.5	20.8	0.96	0.07	0.06	0.006	0.002	46.37	98.84	60	25	6	1.74	0.00027
D10		26.4	17.46	16.36	0.2	0.23	0.006	0.006	39.2	99.93	51	25	6	1.79	0.00027
D13		21.28	18.0	16.76	4.74	2.45	0.18	0.011	36.98	100.38	45	75	13	1.40	0.00029
D16		30.8	20.4	1.9	0.19	0.06	0.006	0.002	46.24	99.66	81	25	6	1.79	0.00036
D21		29.86	18.8	2.85	1.88	1.0	0.04	0.005	44.02	98.52	65	80	8	1.88	0.00030
Min.		21.28	17.46	0.96	0.07	0.06	0.006	0.002	36.89	98.52	45	25	6	1.40	0.00027
Max.		30.8	20.8	16.76	4.74	2.45	0.18	0.011	46.37	100.38	81	80	13	1.88	0.00036
Avg.		27.77	19.09	7.77	1.42	0.76	0.05	0.005	42.54	99.47	60.4	46.0	7.8	1.71	0.00030

In the present study insignificant correlation coefficient was observed between most components (oxides and trace element), According to correlation coefficient schedules of [12], as a result of very limited data, where the number of analyzed samples is very little, consequently very high significant level more than 0.95 required to indicate reliable relationship.

CaO

The CaO content of Pila Spi Formation in Bakhar section range from 21.28% to 30.8% with an average of 27.77% and Bani bawy section ranges between (21.84% -30.24%) with an average of 27.58% Table-1. In both sections its average is less than the reference value of carbonate rocks (42.32%) documented by [13], due to the intense effect of dolomitization process, were calcium replaced by magnesium ions. According to the classification of limestone purity stated by [14] Table-2, most of analyzed samples of Pila Spi Formation were classified as impure limestone Table-3.

Table 2- Classification of limestone purity according to the $CaCO_3$%, after [14].

Purity	Percentage of $CaCO_3$
Very high purity	>98.5
High purity	97.0-98.5
Medium purity	93.5-97.0
Low purity	85.0-93.5
Impure	<85.0

Table 3- Purity of limestone in Pila Spi Formations according to $CaCO_3$%.

Sample No	CaO %	$CaCO_3$ %	Limestone purity	Sample No	CaO %	$CaCO_3$ %	Limestone purity
Bakhar section				Bani bawy section			
D5	30.5	54.46	impure	P1	29.68	53	impure
D10	26.4	47.14	impure	P4	21.84	39	impure
D13	21.28	38.00	impure	P11	28.56	51	impure
D16	30.8	55.00	impure	P14	30.24	54	impure
D21	29.86	53.32	impure				

MgO

MgO% in Bakhar and Bani bawy section are varies from 17.46% to 20.8% with average 19.09% and14.18% to 20.4% with average of 18.39% respectively (Table-1). It is much higher than those averages of the international standard of carbonate rocks (7.79%) reported by [13]. The higher magnesium content is believed by [15] when he studied the Mississippian Joana limestone to be indicative of shallower and warmer water. Therefore in present research high content of MgO attributed to intensive dolomitization process, in shallow and relatively warm water. The Ca/Mg and Sr/Ca Molar ratios in Pila Spi Formation of analyzed samples are used in order to evaluate the depositional environment, assess the configuration of the depositional basin and the distance from shore line in both sections. [16, 17] observed that in some localities there is an increase in Ca/Mg ratios of the calcareous sediments with increasing depth and distance from shore line. [18] referred to the importance of Ca/Mg ratio in evaluation of the configuration of the depositional basin. The very low Ca/Mg average ratio in Bakhar and Bani bawy sections (Table-1), may indicate near shore and shallow marine environment. General slight decrease in Ca/Mg ratio from the bottom toward the top in both sections (Table-1), may indicate considerable shallowing in Pila Spi Formation basin in upwards. On the basis of Ca/Mg ratio, and according to [15] classification of carbonate rocks (Table-4), the carbonate rocks of Pila Spi Formation are classified to three main rock types: Slightly calcareous dolomite, dolomite and magnesian dolomite Table-5.

Table 4- Classification of carbonate rocks after [15].

Rocks types	Ca/Mg %
Magnesian dolomite	1-1.5
Dolomite	1.5-1.7
Slightly calcareous dolomite	1.7-2.0
Calcareous dolomite	2-3.5
Highly dolomitic limestone	3.5-16
Dolomitic limestone	16-60
Slightly dolomitic limestone	60-105
Calcitic limestone	>105

Table 5- Classification of carbonate rocks in Pila Spi Formation at Bakhar and Bani bawy sections on the basis of Ca/Mg ratio, after [15].

Sections	Samples no	Ca/Mg ratios	Types of carbonate rocks
Bakhar	D 5	1.74	Slightly calcareous dolomite
	D 10	1.79	Slightly calcareous dolomite
	D 13	1.40	Magnesian dolomite
	D 16	1.79	Slightly calcareous dolomite
	D 21	1.88	Slightly calcareous dolomite
Bani bawy	P 1	1.76	Slightly calcareous dolomite
	P 4	1.82	Slightly calcareous dolomite
	P 11	1.66	Dolomite
	P 14	1.88	Slightly calcareous dolomite

In order to evaluate the suitability of these rocks for the manufacturing of cement, Limy Saturation Factor (LSF) and Silica ratio (SR) was determined Table-6. [19] determined the LSF When the amount of MgO is more than 2%:

$$LSF=\frac{100(CaO\%+1.5\ MgO\%)}{2.8SiO_2\%+1.2Al_2O_3\%+0.65Fe_2O_3\%}$$

The LSF represent the proper content of free lime of mixed raw material required to react with SiO_2, Al_2O_3 and Fe_2O_3 without leaving any access free lime [19]. The lower abundance of CaO% and less LSF value in analyzed samples of both section as compared to the range of the international reference values of carbonate rocks utilized in cement industry was reported by [20], Table-6, bring about to decrease the proportion of Tricalcium silicate $3CaO.SiO_2$ (C_3S) phase and increase the Dicalcium silicate $2CaO.SiO_2$ (C_2S) phase in clinker, which cause to reduce the compression strength of the concrete [21,22]. The far more abundance of MgO than the range of reference values of carbonate rocks listed by [20] Table-6, which leads to many operational problems through the production of cement. The access in proportion of MgO in raw material leave part of it un combined with clinker phases, and through the un proper burning condition it crystallized as free magnesia MgO (periclase), and during the preparation of concrete it react slowly with water and produce $Mg(OH)_2$ (brucite) phase via hydration of cement, which expand and cause fractures in concrete bring about to damage the constructions [23,21,24].

Table 6- Shows the average CaO, MgO, LSF and SR in Bakhar and Bani bawy sections as compared with the references values of carbonate rocks used in cement industry, after [25,20].

Components of rocks	The accepted range of Wt% in ordinary and Portland cement	Bakhar section	Bani bawy section
CaO	44-52	27.77	27.58
MgO (Max)	3.5	19.09	18.39
$SiO_2+Al_2O_3+Fe_2O_3$	According to the values of (LSF) and (SR) of raw mixture		
Na2O+K2O	<0.6		
$S^{-2}+SO_3$	<0.6		
Free silica	<0.8		
LSF		804.48	450.005
SR	1.9-3.2	11.21	15.06

SiO_2 and Free Silica

The wide range of SiO_2 content in both sections (0.96% -29.74%) of carbonate in Pila Spi Formation, as well as their higher average contents as compared to the reference values of carbonate rocks (5.14%) reported by [13] Table-1, may be interpreted to the concentration of silica in certain sites within the limestone rather than the others, as a result of digenetic processes. The silicification of carbonate rocks is a diagenetic process that involves the replacement of carbonate by silica minerals. The required silica for this process may be obtained locally from siliceous components included within the carbonate rock (mainly siliceous microfossils, siliciclastic grains, clays and volcanic ash), or it may be transported from remote sites, generally by phreatic or hydrothermal water [26]. The diffusion and movement of intrastratal solutions are the most important dynamic factor for transferring silica in the form of H_2SiO4 [27,28] confirmed the replacement and displacive origins of chert nodules in Kometan Formation of Dokan area, NE - Iraq.

In present study probably late diagenetic replacement process involved in the development of chert nodules, where the groundwater transferred the dissolved silica throw the porosity of mostly slightly calcareous dolomite rocks. [29] pointed out that the chert nodules of Drunka Formation (Lower Eocene) in Egypt are mostly formed after moderate alteration of limestone by meteoric water and the replacement of carbonate mud by microcrystalline quartz was the dominant chertification process.

To estimate the potentiality of cement industry exploitation of the carbonate rocks, silica ratio (SR) must determined:

$$SR = \frac{SiO_2\%}{Al_2O_3\% + Fe_2O_3\%}$$

It is a measure of liquid phase in the course of clinker preparation [30]. The elevated average values of the silica ratio (SR) in Bakhar and Bani bawy section Table-6, as compared to the international values of SR (1.9-3.2), indicate unsuitability of these rocks for cement industry, because it decrease the burnability of the raw mixture, due to reduction of the liquid phase, bring about to increase in the content of free lime [30]. The higher average proportion of coarse free silica more than 7-8%, and the abundance of chert nodules in carbonate rocks, cause some operational problems, such damages of the kiln lining, or corrosion of crushers and mills, due to the higher hardness of quartz and chert [25].

Al_2O_3

Al_2O_3 content in the samples of Bakhar section ranged from 0.07% to 4.74% with an average 1.42% greater than its reference values of carbonate rocks (0.79%), and in Bani bawy section it is ranged from 0.36% to 1.29%, with an average of 0.93%, Table-1 which it is slightly more than its average in the published values determined by [13]. It could be related to increment in clay minerals proportion in Bakhar section, as a result of relatively enhanced supply of terrigenous sediments in that site of deposition in contrast to the Bani bawy site.

Fe_2O_3

The range of Fe_2O_3 concentration in Bakhar section is 0.06% -2.45% of 0.76% average, whereas it is greater than its range 0.19-0.6% and average 0.37% in Bani bawy section (Table-1), and more than its average content in published values of carbonate rocks 0.54% reported by [13]. This increment is probably due to increase in the abundance of insoluble residue, as a result of enhanced rate of terrigenous sediments supply in Bakhar site of deposition. The strong significant positive correlation coefficient of Fe_2O_3 with Al_2O_3 (0.998) suggest the association of iron with clay minerals. [31] pointed out that iron may exist as substitution for Al in octahedral positions of clay minerals e.g. in montmorillonite, or as a coat of ferric oxides surrounding clay minerals particles such as kaolinite. The common form of iron in supergene deposits is hydrated ferric oxide [32]. The relative elevated Fe_2O_3 concentration in Bakhar section as compared to Bani bawy section, may indicate slight increase in the pH of the depositional environment of the former relative to the later one. The oxidation potential of iron greatly affected by hydrogen ion concentration of natural water. It is drop greatly with increased pH [32].

TiO_2

The range and average of TiO_2 contents in the studied samples of Bakha and Bani bawy rsections are 0.006%-0.18%, 0.05% and 0.01%-0.04%, 0.032% respectively (Table-1), generally in both sections they are lower than its average content of reference values in carbonate rocks (0.067%) [13], due to the poverty or diminished proportion of insoluble residue in the carbonate rocks On the other hand Bakhar samples have slight excess in TiO_2 content relatively to Bani bawy samples, as a result of little increment in insoluble residue proportion in Bakhar samples. Significant strong positive correlation of TiO_2 with Al_2O_3 (0.98) and Fe_2O_3 (0.98) in Bakhar section, suggest its association with clay minerals and/or accommodation in some heavy minerals such as ilmenite. [33] Pointed out to the occurrence of Ti^{4+} in clay minerals, which replace Al^{3+} and Fe^{3+} in octahedral positions. Titanium oxide constitutes some heavy minerals, where it is combined with ferrous oxide to form the ilmenite mineral [34].

SO_3

Pila Spi Formation is characterized by very little or negligible amount of SO_3 which are in both section less than 0.07%, and much lower than its average content of the reference published values in carbonate rocks 0.3% listed by [13], certainly as a result of the poverty in sulfate minerals such as anhydrite, gypsum, and celestite. The diminished content of SO_3 and insignificant correlation with Sr, may indicate low salinity of depositional condition at back reef environment. [35] referred to significant association of Sr with sulfates in the near shore facies at Makhmour area, and they expected relatively high salinity of depositional environments. [5] studied the new facies in the Pila Spi formation (middle – upper Eocene), at sulaimanyia area, NE Iraq, and referred to the gradual facies change and absence of significant grainstone and oolitic high energy facies, he concluded a carbonate ramp depositional environment with low topographic patchy reef, back reef. The diminished content of SO_3 in carbonate rocks considered as effective and encouraging feature in cement industry [36]. Nevertheless in present research it opposable with other factors.

MnO

The range and average of MnO in the samples of Bakhar and Bani bawy sections are 0.002% - 0.011%, 0.005% and 0.007% - 0.011%**,** 0.009% respectively (Table-1). Their averages are much less than those of reference published values in carbonate rocks 0.142% reported by [13]. The depletion of MnO in Pila Spi samples may be attributed to relatively shallow marine environments of these sediments. The abundance and distribution of manganese in carbonate sediments, considered as a significant indicator utilized to recognize deep marine sediment from shallow, where Mn content is higher in the lithofacies of deep marine environment than the facies of shallow environment [37]. This depletion may be related to the mineralogy of Pila Spi Formation, which probably is originally formed of aragonite deposited in shallow marine environment. Shallow-water aragonitic carbonate sediments do not show significant amount of Mn, whereas the high Mn content in deep-water lithofacies reflects the original calcite mineralogy [38]. On the other hand the diminished concentration of MnO in the Pila Spi sediment may be related to the arid climate of the provenance and very less supply of terrigenous materials. The significance of manganese as paleoclimates indicator was demonstrated by [39], where the lower MnO contents indicate an arid climate in source area during the deposition.

Strontium (Sr) and Sr/Ca ratio

The lower average concentration of strontium in analyzed samples of Bakhar and Bani bawy sections 60.4 ppm and 57.5 ppm respectively Table-1 as compared to the reference results of carbonate rocks (610%), reported by [13], may indicate a near shore shallow marine environment, of low salinity, probably in back reef environment. [40] pointed out that the carbonate facies of low Sr content indicates a shallow near shore, low salinity environment. The depletion of Sr content could be attributed to either the intense impact of dolomitization process, where the Sr^{2+} ions in part removed with the aqueous solution. [41] and [42] pointed out to the replacement of Mg for Ca and Sr in calcite crystal lattice, and release of Sr from the system. [43] referred to the decreasing of Sr content through the dolomitization process. The lower Sr content may also interpreted as a result of early digenetic processes which contribute in the conversion of primary aragonite to calcite and removal of strontium. [42] and [44] pointed out to the influence of the diagentic processes (recrystallization and inversion) on the content of Sr in carbonate rocks.

The very low average Sr/Ca ratio in the samples of Bakhar and Bani bawy sections 0.00030 and 0.00029 respectively (Table-1), as compared to Sr/Ca ratios of deep-sea carbonate (0.00525) reported by [45], indicating shallow marine environment of Pila Spi Formation, and probable the effect of diagenetic processes such as recrystallization, inversion and dolomitization which remove Sr from originally precipitated carbonate minerals.

Nickel (Ni) and copper (Cu)

The range of Ni contents in Bakhar and Bani bawy studied samples are (25-80 ppm, 25 -37 ppm) with average (46, 30.75, ppm) respectively (Table-1). The averages contents are more than its mean in published values of carbonate rocks (Ni: 20 ppm; Cu: 4 ppm). Likewise the average of Cu concentration in both section is also greater than the reference value, with range and average are (6-13 ppm, 7.8 ppm) in Bakhar and (6-8 ppm, 6.5 ppm) in Bani bawy samples respectively. The little excess in concentration of Ni and Cu in Bakhar compared to Bani bawy samples, may interpret the relatively increased the rate of terrigenous supply. Generally the lower abundance of trace elements such as Cr, Ni and Cu indicates the minimal contribution of mafic components in the source rocks [46]. In present study these elements may occurs in carbonate rocks with the minor amount of clay minerals and/or associated with Fe oxides and hydroxides. [35] concluded that Cr, Ni and Cu are present mainly in clay minerals and/or associated with Fe-Mn oxides and hydroxides. Cu was structurally combined with clay minerals and transported to the basin of deposition [47].

Conclusions:

Field observations, petrography and geochemical studies conclude the following:

1. The Pila Spi formation mostly formed of massive lithified beds of limestone, marly limestone and dolomitic limestone with chert nodules in both studied sections.
2. The limestone is commonly of mudstone and few beds of wackestone and is mostly highly effected by dolomitization and diagenetic processes which leads to destroy most of the skeletal grains. Replacement, recrystallization, high porosity are common in both studied sections. Dolomite phenocrystals indicate late diagenetic secondary dolomite in the Bakhar section, indicating hypersaline diagenetic conditions.
3. The geochemical studies show that the SiO_2, Al_2O are higher than standards while CaO is lower than the reference standards, whereas MgO is higher than reference values that may be due to dolomitization and diagenetic processes as well as to the shallow environment of deposition. The little amount of Sr also indicates shallow environment of low salinity. The rocks are classified as impure limestone, mostly of slightly calcareous dolomite.
4. The diminished content of Mno, may reflect shallow environment and arid climate of source area while the relatively elevated abundance of Fe_2O_3 may entails relatively high alkaline condition.
5. The relatively higher contents of Al_2O_3, Fe_2O_3, TiO_2, Ni and Cu in Bakhar section as a compared to the Bani bawy section, indicate the increase rate of terrigenous supply in Bakhar, may be due to its relatively approach to the source area.
6. Ca/Mg and Sr/Ca ratios indicate that the carbonate deposited at near shore of shallow marine environment, and the basin become shallower upward in both sections.

7. The high percentage of SiO_2, MgO, and the lower abundance of CaO and LSF, indicate that the under consideration carbonate rocks are not suitable for the cement industry processes, as well as the presence of chert nodules inside the carbonate rocks cause some operational problems.

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