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Geochemical Characteristics of the Bituminous Carbonate and Shale Rocks of the Jurassic Sequences (Sargelu, Naokelekan and Chia Gara) in the North Thrust Zone, North of Zakho, North of Iraq

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Abstract

The geochemistry and mineralogy of the three formations ; Sargelu, Naokelekan and Chia Gara are studied using XRF, XRD, SEM, and EDS-elemental map analyses. These formations represent Jurassic sequences exposed to the North of Zakho within the North Thrust Zone, and constitute bituminous carbonate and shale rocks. The average concentrations of SiO_2 and CaO in carbonate rocks are (11.7%, 7.75% and 9.16%) and (32.40%, 27.51% and 46.73%) in Sargelu, Naokelekan and Chia Gara Formations respectively, whereas in shale rocks are (27.51% and 19.48%) and (7.09% and 4.60%) in Sargelu and Naokelekan Formations. The MgO content as average in carbonate rocks is high in Sargelu (8.86%) compared to Naokelekan (0.28%) and Chia Gara (0.22%). The average contents of V, Ni, Mo and Zn in carbonate rocks are (143.2 ppm, 94.92 ppm, 96.95 ppm and 83.3 ppm) in Sargelu, (1143.3 ppm, 619.8 ppm, 588.3 ppm and 942.5 ppm) in Naokelekan and (373.4 ppm, 92 ppm, 187.4 ppm and 35.2 ppm) in Chia Gara, while in shale rocks are (661.99 ppm, 662.6 ppm, 832.8 ppm and 509 ppm) in Sargelu and (1990.8 ppm, 753.1 ppm, 324.7 ppm and 724.3 ppm) in Naokelekan.

The concentrations and geochemical relationships of the major oxides are more or less similar in both types of rocks in the three formations but their relationships with trace elements are diverse. These relationships are very compatible with the mineralogical identification. SiO_2, Al_2O_3, K_2O, TiO_2 and Zr make positive correlations with each other reflecting their existence in clay minerals, K-feldspars and are of detrital origin. CaO shows negative correlation with these oxides indicating different origin. Also CaO is related with PO_4 infers the presence of apatite. Fe_2O_3, SO_3, Mo, Zn, Ni and Cd are correlated positively due to their co-existence in sulfide minerals.

The distributions of the trace elements Zn, Ni, Cu, Cr, Cd, V and Mo are controlled by the clay minerals, oxides, phosphates, sulfides and sulfates. Mn, As, Sr and Ba distributions are mainly controlled by carbonate minerals (calcite, dolomite) and barite.

Keywords: Sargelu, Naokelekan, Chia Gara, North Thrust Zone, bituminous rocks

الخصائص الجيوكيميائية للصخور الرسوبية البتيومينية لتكاوين التتابع الجوراسي (ساركلو وناوكليكان وجياكارا) في منطقة الفوالق الزاحفة الواقعة في شمال زاخو/ شمال العراق

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الخلاصة

في هذا البحث اجريت التحاليل الكيميائية بطريقة الاشعة السينية المتفلورة (XRF) لتحديد التركيب الكيميائي (العناصر الرئيسة والنادرة) ل (65) نموذجا والفحوصات المعدنية باستخدام الاشعة السينية الحائدة (XRD) ل (49) نموذجا ، كما اجريت فحوصات (SEM-EDS elemental map) ل (17) نموذجا

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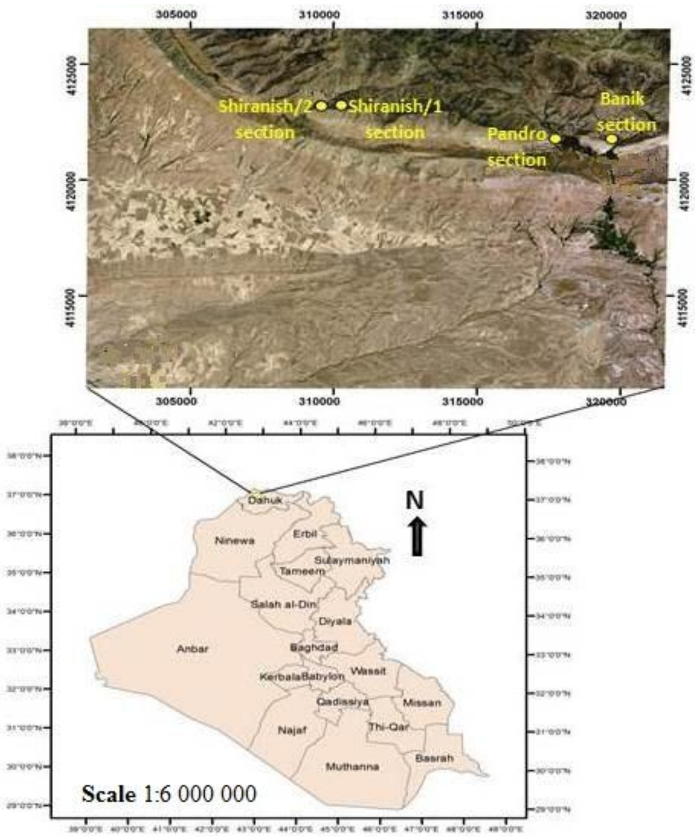
اختيرت من اصل (114) نموذجا جمعت من تكوين ساركلو (جوراسي اوسط) وتكوين ناوكليكان (جوراسي متأخر) وتكوين جياكارا (جوراسي متأخر– كريتاسي مبكر) المتكونة بشكل رئيسي من صخور الكاربونيت والشيل التي تتكشف في مقاطع الدراسة الاربعة وهي بانك وباندرو وشيرانش/1 وشيرانش/2 في منطقة الفوالق الزاحفة الواقعة شمال زاخو / شمال العراق. اظهرت التحاليل بان معدل التراكيز لكل من اوكسيد السليكون واوكسيد الكالسيوم في صخور الكاربونيت (11.7% و 7.75% و 9.16%) و (32.40% ، 27.51% ، 46.73%) للتكاوين ساركلو و ناوكيليكان و جياكارا على التوالي، بينما في صخور الشيل (27.51% ، 19.48%) و (7.09% ، 4.60%) للتكاوين ساركلو و ناوكيليكان على التوالي. ان محتوى اوكسيد المغنيسيوم كمعدل في صخور الكاربونيت يعد عاليا في تكوين ساركلو (8.86%) مقارنة بتكوين ناوكليكان (0.28%) وتكوين جياكارا (0.22%). ان معدل محتوى عناصر الفناديوم والنيكل والموليبدينوم والزنك (جزء بالمليون) في صخور الكاربونيت (143.2 ، 94.92 ، 96.95 ، 83.3) في تكوين ساركلو و (1143.3 ، 619.8 ، 588.3 ، 942.5) في تكوين ناوكليكان و (373.4 ، 92 ، 187.4 ، 35.2) في تكوين جياكارا، بينما في صخور الشيل (661.99 ، 662.6 ، 832.8 ، 509) في تكوين ساركلو و (1990.8 ، 753.1 ، 324.7 ، 724.3) في تكوين ناوكليكان. ان العلاقات الجيوكيميائية للأكاسيد الرئيسة يزداد تماثلها ويقل فيما بينها في كلا نوعي الصخور للتكاوين الثلاثة ولكن علاقاتها مع العناصر النادرة مختلفة. هذه العلاقات منسجمة ومتناغمة مع المعادن المشخصة. ان اكاسيد السليكون والالمنيوم والبوتاسيوم والتيتانيوم وعنصر الزركون تصنع علاقات موجبة مع بعضها البعض دالةً على وجودها في المعادن الطينية والفلدسبار البوتاسي ومن اصل منقول. اظهر اوكسيد الكالسيوم علاقة سالبة مع الاكاسيد انفة الذكر دالة على اصل مختلف. ان اوكسيدي الحديد والكبريت وكذلك اوكسيد الكبريت مع عناصر الموليبدينوم والنيكل والزنك ترتبط ارتباطا ايجابيا نتيجة وجودها معا في معادن الكبريتيدات (البايرايت والموليبدنايت والبنتلندايت والسفلرايت على التوالي). ايضاً اوكسيد الكالسيوم والفوسفات يتواجدان معا ليشكلان معدن الابتايت احد معادن مجموعة الفوسفايت.

Introduction

The Jurassic sequences represented by Sargelu, Naokelekan and Chia Gara Formations are located to the north of Zakho town North of Iraq within the North Thrust Zone or so-called Northern Ora Zone close to the Iraqi-Turkish border in North Iraq Figure-1. Four sections were sampled. These sections are Banik, Pandro, Shiranish/1 and Shiranish/2 comprise the outcrops of the three formations in the area. The stratigraphic successions of these formations are from older to younger are represented by Sargelu (Middle Jurassic), Naokelekan (Late Jurassic) and Chia Gara (Late Jurassic-Early Cretaceous) Figure- 2. Many workers dealt with paleontology, lithostratigraphy, and classifications. However, a relatively no detailed studies were concerned with the geochemistry and mineralogy of these rocks, and for Naokelekan there is no previous study. Sargelu Formation is composed of thin bedded black bituminous limestone, dolomitic limestone, black papery shale with streak of thin black chert in the upper part. The thickness in the outcrops varies from 20-125 m, the age is Bajonian-Bathonian according to paleontological evidences [1-3]. The Naokelekan Formation comprises laminated bituminous limestone alternate with bituminous shale, highly bituminous dolomite with thickness ranges from 10-30 m [2]. The age of the formation is reported to be Upper Oxfordian-Lower Kimmeridgian [1, 3]. Chia Gara Formation defined at Chia Gara anticline south of Amadia town in High Folded Zone, North Iraq. The thick of this formation varies from 30-300 m [2] but in the type locality it is 230 m. The lithology is rather uniform consists of thin bedded limestone and calcareous shale. According to paleontological evidences the age is proposed to be Middle Tithonian-Berriasian [1]. The main target of the present work is to study in detail the geochemical characteristics of the Jurassic sequences Sargelu, Naokelekan and Chia Gara and to shed light on the relationships between major and trace elements as a clue to enhance their mineralogy composition. Many statistical parameters are employed in order to give a clear view for the abundance and enrichment of each element via using the geochemical data toolkit (GCDkit version 2.2, Czech Geological Survey) program, Histograms and correlation coefficient.



Section	Bottom		Top	
Banik	38S UTM	0319704 4121879	38S UTM	0319705 4121772
Pandro	38S UTM	0317829 4121833	38S UTM	0317742 4121786
Shiranish/1	38S UTM	0310240 4123268	38S UTM	0310271 4123230
Shiranish/2	38S UTM	0309562 4123201	38S UTM	0309565 4123185

Figure 1- Location map of the study area shows the sites of the studied sections.

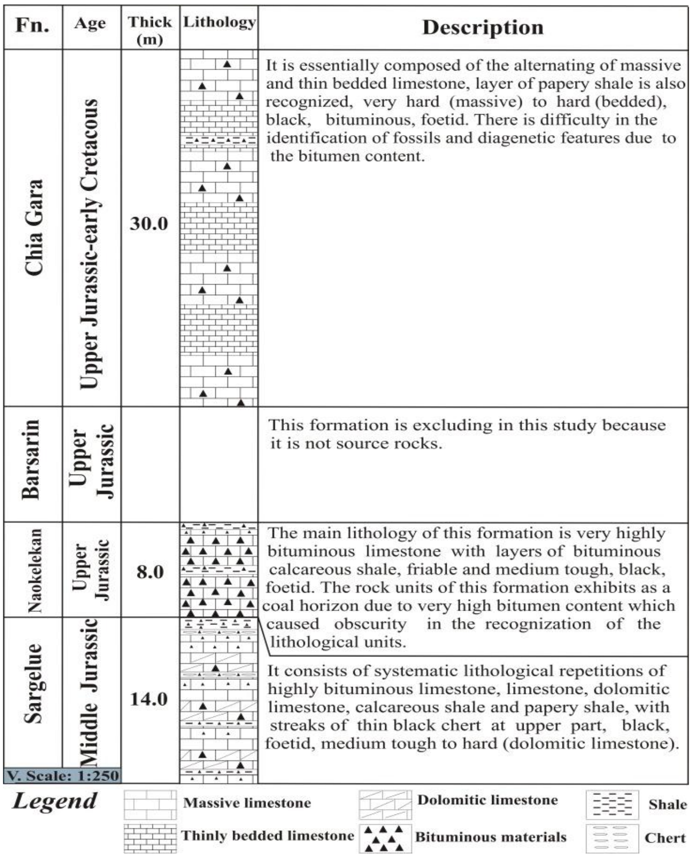


Figure 2- lithostratigraphic section of the studied formations at Northern Zakho/Northern Iraq (Sargelu, Naokelekan and Chia Gara/Banik section).

Material and Methods

For geochemical and mineralogical analyses, the total number of collected fresh samples (point samples) from all sections is 114 samples distributed in the three formations according to thickness and lithologic variations. Sixty five (65) representative bulk powder samples from the three studied formations were chosen for chemical analyses by XRF technique, the model of the used instrument is SPECTRO X-LAB 2000. Thirty four (34) bulk powder samples from the three studied formations were examined by XRD technique on an EQUINOX 1000/2008 X-RAY DIFFRACTOMETER (radiation X-ray Co-Ka1, wavelength 1.788970 A^o). These analyses were carried out at Ankara University/Department of Geology/Turkey. Fifteen (15) selected samples were treated with acetic acid (0.3 molar) at room temperature to dissolve calcite without affecting other minerals and studied by XRD technique, the model of the used instrument is XRD 7000/2008 MAXIMA-X/SHIMADZO JAPAN Type (radiation Cu-Ka1, wavelength 2.03 A); these analysis were done in the Iraqi Geological Survey. The sample were crushed and taken into a small mill type (FRITSCH/pulverisette 7) to get the size of granules less than or equal to five microns (≤ 5). Then the homogeneous mixture of 4 grams of each powder sample with 1 gram of wax were taken into a pellet-making machine type (PE-EL/pressure 15-20*10^4 N). To determine mineral phases, seventeen (17) polished sections from the three studied formations were performed using scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) analyses at the University of Western Australia-Scanning Electron Microscopy Center, tool machine type Teskan Vega 3-USA and at Hacetapa University in Ankara/Turkey, tool machine type ZEISS EVO 50 .

Results and Discussion

In the three studied formations, the dominant carbonate minerals are calcite and dolomite, silicates are represented by quartz, clay minerals (kaolinite, illite, montmorillonite and palygorskite) and K-feldspar. Sulfides are mainly pyrite with sphalerite, pentlandite and molybdenite. Oxides are represented by hematite and goethite. Fluorapatite apatite is one of the phosphate minerals found in these rocks as well as gypsum and barite are the dominant sulfate minerals. The range and average of the selected major oxides and trace elements of the three formations for the carbonate and shale rock samples are listed in Tables 1, 2 and 3.

Table 1- Range and average of major and trace elements of the carbonate and shale samples in Sargelu Formation

Value / Element	carbonate rocks		shale rocks	
	Range	Average	Range	Average
SiO_2%	2.257-22.98	11.70	16.08-41.1	27.51
Al_2O_3%	0.414-7.242	3.22	4.368-14.52	7.66
K_2O%	0.011-3.326	0.929	1.76-6.667	3.81
TiO_2%	0.0236-0.3405	0.14	0.3209-0.7397	0.46
Fe_2O_3%	0.093-3.032	0.88	2.787-5.58	4.30
SO_3%	0.2574-3.513	1.499	3.734-16.02	8.85
MgO%	0.18-17.63	8.86	0.664-4.046	2.59
CaO%	18.33-55.47	32.40	0.8727-14.88	7.09
MnO%	0.00065-0.0165	0.0084	0.0068-0.0096	0.00769
P_2O_5%	0.0045-0.394	0.0899	0.1316-0.5434	0.34
V_2O_5%	0.009-0.0723	0.0255	0.0788-0.1942	0.118
Cr_2O_3%	0.00073-0.0121	0.00438	0.01071-0.0286	0.0187
Ni ppm	1.0-250.6	94.92	345.4-1037.0	662.61
Mo ppm	3.4-545.7	96.95	132.4-1739.0	832.82
U ppm	8.1-46.9	24.43	34.6-110.8	62.91
Zn ppm	1.0-303.3	83.31	204.5-1076.0	509.01
As ppm	1.0-40.5	10.52	36.4-108.5	64.94
Ba ppm	11.3-226.4	41.07	47.8-455.9	152.65
Y ppm	1.0-19.8	8.31	15.4-66.3	33.3
Sr ppm	12.0-235.4	110.85	50.8-136.4	83.07
Cd ppm	0.5-5.6	3.23	7.1-40.8	25.28
Zr ppm	9.4-82.6	25.61	48.0-248.5	118.77
Cu ppm	1.0-158.8	35.34	82.3-373.2	230.64

Table 2- Range and average of major and trace elements of the carbonate and shale samples in Naokelekan Formation.

Value / Elem.	carbonate rocks		shale rocks	
	Range	Average	Range	Average
SiO_2%	2.998-14.04	7.75	15.5-29.87	19.48
Al_2O_3%	0.727-2.659	1.757	3.526-10.33	5.49
K_2O%	0.336-1.365	0.824	1.835-3.942	2.45
TiO_2%	0.0693-0.2686	0.1699	0.336-0.807	0.49
Fe_2O_3%	0.429-1.88	1.267	2.481-6.526	4.01
SO_3%	6.798-13.82	10.89	6.53-18.47	15.31
MgO%	0.091-0.499	0.282	0.52-1.631	0.97
CaO%	14.78-37.72	27.51	1.448-6.264	4.60
MnO%	0.0034-0.0058	0.0044	0.0042-0.011	0.008
P_2O_5%	0.1196-0.2897	0.2142	0.2708-0.548	0.35
V_2O_5%	0.0829-0.3721	0.2040	0.266-0.474	0.35
Cr_2O_3%	0.0064-0.0327	0.0139	0.013-0.044	0.031
Ni ppm	240.1-895.4	619.87	357.0-1047.0	753.18
Mo ppm	192.2-1082.0	588.35	195.1-602.7	324.74
U ppm	48.2-90.3	71.52	47.2-91.1	69.5
Zn ppm	305.3-1528.0	942.56	195.8-1018.0	724.38
As ppm	14.7-48.5	32.22	46.6-88.6	68.64
Ba ppm	69.5-1932.0	706.2	95.3-1977.0	485.96
Y ppm	21.2-53.2	35.07	19.5-106.2	66.36
Sr ppm	105.1-327.9	246.34	53.0-75.2	68.7
Cd ppm	7.8-50.9	39.0	17.5-62.3	33.3
Zr ppm	13.4-44.1	25.63	62.5-180.4	92.18
Cu ppm	34.0-80.6	52.03	94.5-163.2	120.4

Table 3- Range and average of major and trace elements of the carbonate samples in Chia Gara Formation.

Value / Elem.	range	average
SiO_2%	1.692-18.0	9.164
Al_2O_3%	0.657-7.35	3.489
K_2O%	0.084-2.066	0.675
TiO_2%	0.039-0.515	0.236
Fe_2O_3%	0.183-4.801	1.465
SO_3%	0.744-9.149	2.611
MgO%	0.029-0.449	0.220
CaO%	27.84-55.93	46.734
MnO%	0.0039-0.0161	0.0074
P_2O_5%	0.0141-0.4448	0.08519
V_2O_5%	0.0089-0.2668	0.0666
Cr_2O_3%	0.00206-0.0182	0.00629
Ni ppm	13.1-443.2	92
Mo ppm	27-760.3	187.41
U ppm	9.9-81.5	27.39
Zn ppm	0.8-140.2	35.27
As ppm	0.8-34.3	11.48
Ba ppm	13.2-649.1	80.68
Y ppm	0.7-24.6	6.57
Sr ppm	140.5-501.9	258.39
Cd ppm	0.5-15.5	3.31
Zr ppm	11.2-129.0	41.56
Cu ppm	2.1-202.7	41.68

Geochemistry of Major Elements

Correlation coefficient of each pair of the major elements for carbonate and shale samples of Sargelu, Naokelekan and Chia Gara Formations are illustrated in Figures-3, 4, 5, 6 and 7, respectively.

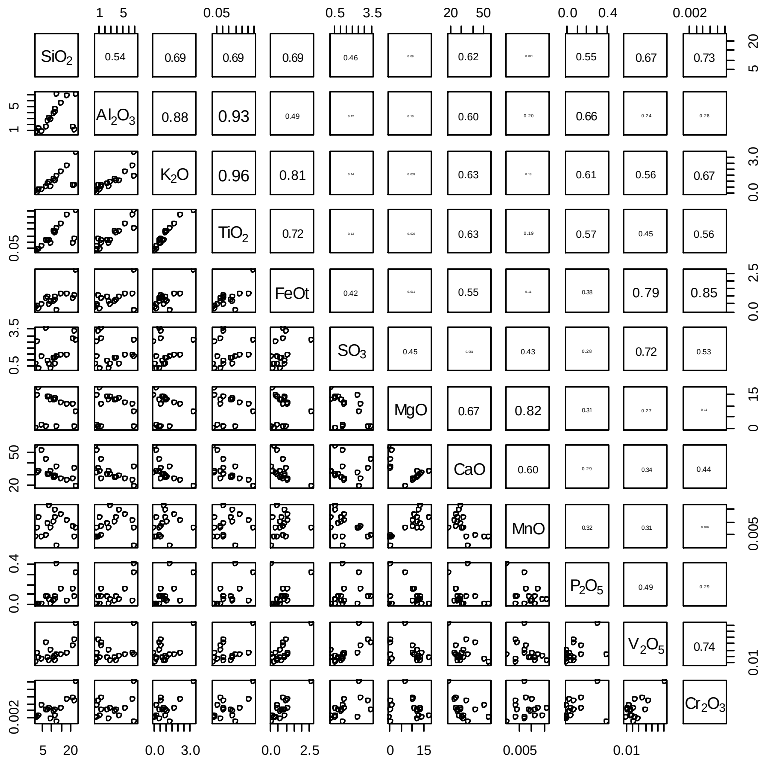


Figure 3- Correlation coefficient of the major elements of carbonate samples in Sargelu Formation. (n=17)

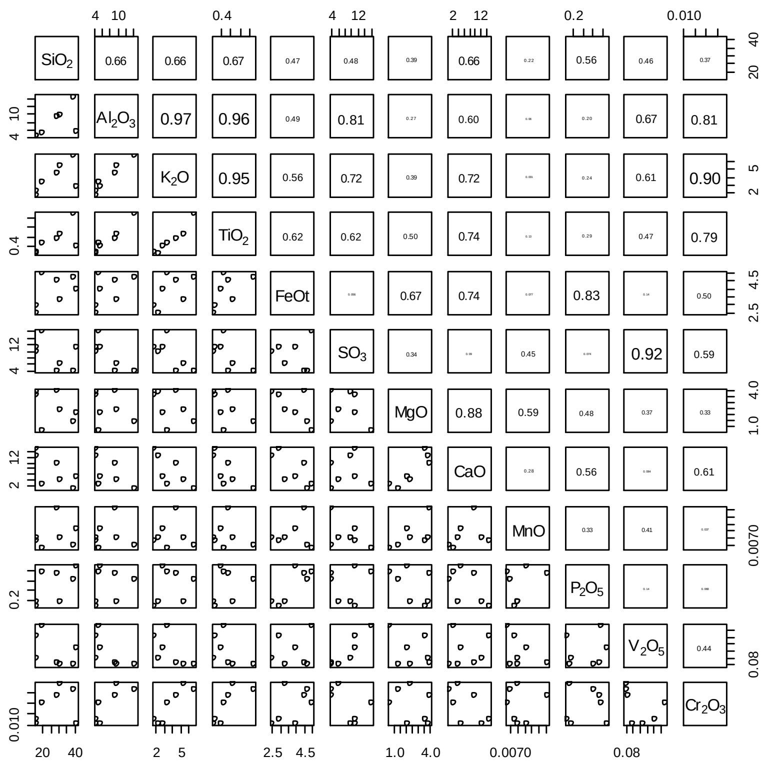


Figure 4- Correlation coefficient of the major elements of shale samples in Sargelu Formation. (n=7)

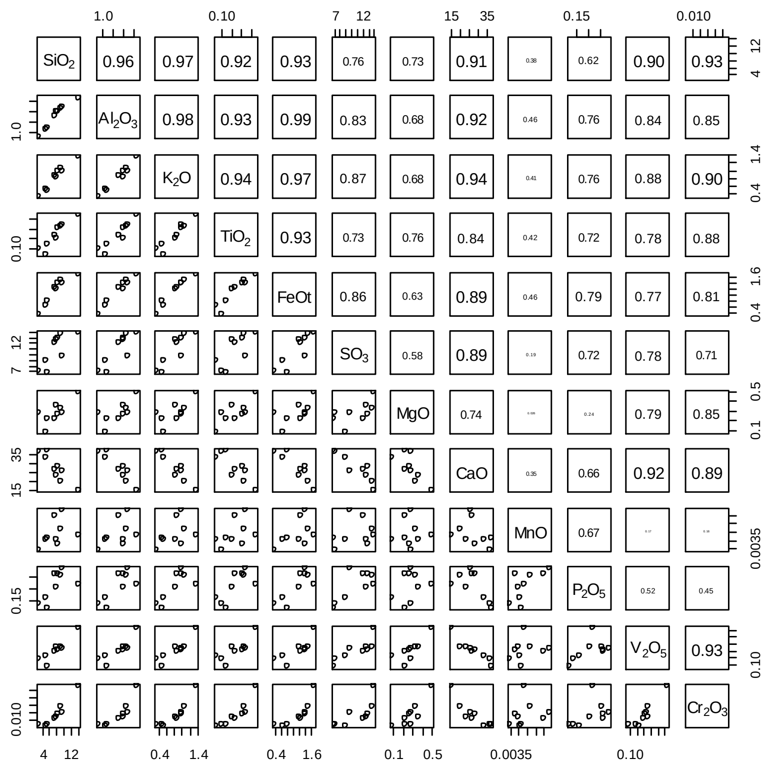


Figure 5- Correlation coefficients of the major elements of carbonate samples in Naokelekan Formation. (n=9)

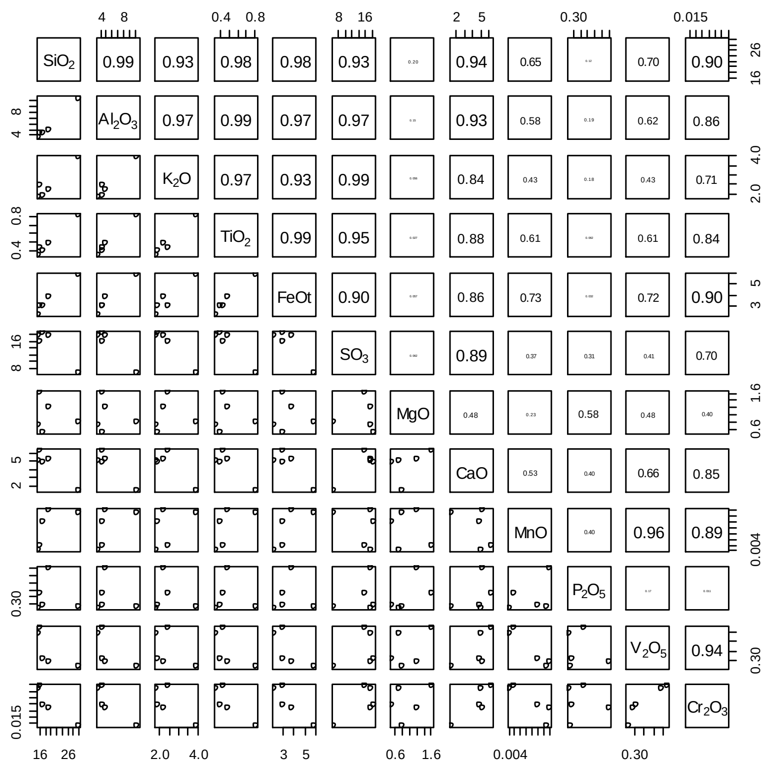


Figure 6- Correlation coefficient of the major elements of shale samples in Naokelekan Formation. (n=5)

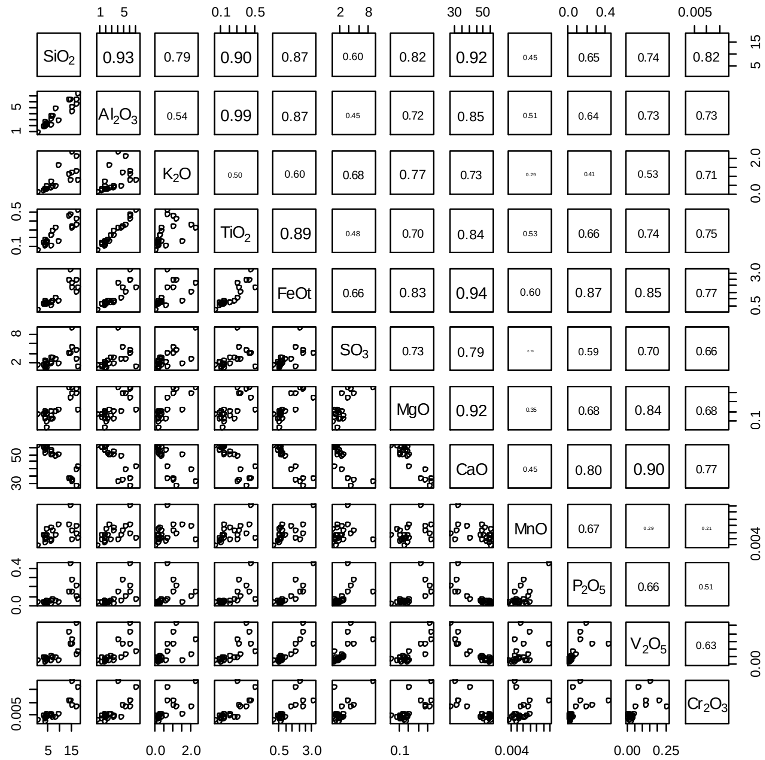


Figure 7- Correlation coefficient of the major elements of carbonate samples in Chia Gara Formation. (n=22)

SiO_2*, *Al_2O_3*, *K_2O*, *TiO_2* and *Fe_2O_3

There are positive correlations between SiO_2 and Al_2O_3, K_2O and TiO_2 suggesting the occurrence of these oxides in common phases of combined silica such as clay minerals and K-feldspar in addition to the existence of free silica as quartz. Al_2O_3 concentration is thought to be a good measure of detrital influx. This is evident from its positive trend with SiO_2, K_2O, TiO_2 and Zr which explain their terrigenous origin (e.g. the point chemical analyses in the sample of Sargelu Formation sample: Si and O concentrations up to 30.53% and 36.73%, respectively, both K and Al concentrations up to 9.4% and 12.22% respectively, and the concentration of Ti up to 0.5%, ….

TiO_2 shows binary style reflecting the presence of Ti-bearing minerals such as anatase or its polymorph (rutile).

Fe_2O_3 as total iron is mainly concentrated in sulfide minerals mainly pyrite and its oxidation products such as hematite and goethite

CaO and MgO

CaO is mainly represented by calcite and dolomite in carbonate and shale rock samples. Also, very little quantity of CaO is related to P_2O_5 and SO_3 indicating that the Ca exists in the form of phosphate (apatite) and sulfate (gypsum), respectively.

MgO content is mainly related to the presence of the mineral dolomite due to dolomitization process. This is supported by the negative correlation between MgO and CaO. Also, Mg is related to clay minerals (palygorskite and montmorillonite). Derver [4] mentioned that under reducing environments, Mg associates with clay minerals.

SO_3

SO_3 is detected in the carbonate and shale rocks. The mineralogical observation and the positive correlation between SO_3 and Fe_2O_3, Mo, Zn and Ni indicate the existence of sulfide minerals such as pyrite, sphalerite and pentlandite in addition to sulfate (gypsum).

P_2O_5

P_2O_5 is found in both carbonate and shale rocks of the studied formations. The mineralogical investigations (SEM and EDS) are represented by the spectra including (e.g. the point chemical analyses in the samples of Sargelu, Naokelekan and Chia Gara Formations: CaO=48.24%, PO4=35.77%, F=10.13%, …; CaO=45.78%, PO4=36.77%, F=7.28%, …; CaO=49.77%, PO4=36.27%, F=5.55%, …, respectively), as well as the positive correlation of P_2O_5 with Al_2O, SiO_2, K_2O, and TiO_2 indicating that the source of P_2O_5 is mainly apatite and clay minerals, where $(PO_4)^{3-}$ has ability to be absorbed by clay minerals or substitutes OH^{1-} [5].

MnO

MnO shows negative correlation with CaO in the carbonate rocks. This is attributed to substitution of Ca^{2+} by Mn^{+2} under reducing sea water conditions [6]. The positive correlation between Mn^{2+} and Mg^{2+} as well as the similarity in their ionic radii and electric charges indicate that there is merging of Mn^{2+} in the dolomite lattice during diagenetic process (dolomitization), in other words, Mn concentration in dolomite infers that it is incorporated from dolomitizing solution rather than the parent rocks [7]. Also, the positive correlation of Mn with Ca suggests the co-existence of Ca and Mn, where Rubio et al.[8] postulated that Mn can form rhodochrosite ($MnCO_3$) inside calcite structure under co-precipitation of a calcite-manganese phase. The positive correlation of MnO with SiO_2, Al_2O_3 and K_2O denotes its relation with clay minerals. Amin [9] referred to the adsorption of Mn on the surfaces of clay mineral.

V_2O_5* & *Cr_2O_3

V_2O_5 has the ability to form complex components in bituminous rocks under reducing conditions [10]. The mobile vanadate anion $(VO_4)^{3-}$ is formed during weathering processes and remains dissolved in solution until it precipitates under reducing conditions as vanadium components (V_2O_3, $V(OH)_3$, $VO(OH)_2$) [10]. Hirst [11] reported the association of vanadium in clay minerals especially the kaolinite and illite, and also it has the ability to be adsorbed by iron oxides and hydroxides [12]. This is supported by the many spectra of EDS point chemical analyses (in the samples of Sargelu Formation: Fe_2O_3=79.10%, V_2O_5=1.23%,... ; Fe_2O_3=79.82%, V_2O_5=1.21%, …; Fe_2O_3=83.10%, V_2O_5=0.95%, …; and in samples of Naokelekan Formation: Fe_2O_3=68.54%, V_2O_5=5.15%, …; Fe_2O_3=65.76%, V_2O_5=6.20%, …).

The positive correlation of Cr_2O_3 with Al_2O_3, SiO_2, and K_2O could be attributed to its association with clay minerals where Cr has the tendency to concentrate in clay minerals [13]. The positive correlation of Cr with Fe_2O_3 and SO_3 reveals its contribution in iron-minerals (pyrite and its weathering products). Sulfide minerals play a critical role in the geochemical cycling of trace elements, among them, pyrite is the most common which acts as natural reluctant to reduce Cr^{6+} to Cr^{3+} [14], and also pyrite acts as an efficient Cr^{6+} reducing agent [15]. Thus, Cr may occur associated with pyrite and its weathering products (iron-oxides hydroxides).

Geochemistry of trace elements

Tables-4, 5, 6, 7 and 8 show the correlation coefficients of each pair of major with trace elements of carbonate and shale rock samples for the three formations.

Table 4- Correlation coefficient (r) between major with trace elements of carbonate lithology of Sargelu Formation. (n= 17, sig. level= 0.412)

	Ni	Mo	U	Zn	As	Ba	Y	Sr	Cd	Zr	Cu
SiO_2	0.7	0.53	0.24	0.61	0.64	0.58	0.57	-0.20	0.53	0.57	0.69
Al_2O_3	0.13	-0.17	-0.07	0.27	0.25	0.64	-0.09	-0.63	0.11	0.85	0.60
K_2O	0.47	0.07	0.18	0.63	0.61	0.89	0.21	-0.42	0.42	0.95	0.90
TiO_2	0.43	0.06	0.12	0.55	0.50	0.79	0.18	-0.44	0.32	0.92	0.80
Fe_2O_3	0.81	0.41	0.51	0.86	0.91	0.87	0.57	-0.04	0.69	0.78	0.93
SO_3	0.74	0.66	0.63	0.70	0.55	0.30	0.64	0.34	0.67	0.13	0.32
MgO	-0.21	-0.40	-0.56	-0.19	-0.20	-0.08	-0.26	-0.64	-0.19	-0.04	0.05
CaO	-0.35	-0.02	0.18	-0.37	-0.34	-0.46	-0.17	0.71	-0.29	-0.51	-0.59
MnO	-.09	-0.34	-0.40	-0.12	-0.14	-0.03	-0.17	-0.50	-0.36	0.06	0.17
P_2O_5	0.23	0.12	0.28	0.30	0.37	0.50	0.002	-0.42	0.31	0.61	0.40
V_2O_5	0.84	0.62	0.67	0.89	0.86	0.74	0.74	0.13	0.88	0.57	0.69
Cr_2O_3	0.76	0.44	0.41	0.82	0.80	0.77	0.57	0.01	0.69	0.61	0.87

Table 5- Correlation coefficient (r) of major with trace elements of shale lithology of Sargelu Formation. (n= 7, sig. level= 0.669)

	Ni	Mo	U	Zn	As	Ba	Y	Sr	Cd	Zr	Cu
SiO_2	-0.32	-0.31	-0.12	-0.64	-0.08	0.29	-0.18	-0.62	-0.71	0.58	0.58
Al_2O_3	-0.78	-0.78	-0.31	-0.34	-0.45	0.55	-0.40	-0.73	-0.92	0.98	0.93
K_2O	-0.68	-0.81	-0.22	-0.38	-0.38	0.55	-0.32	-0.84	-0.91	0.98	0.97
TiO_2	-0.61	-0.65	-0.15	-0.28	-0.25	0.39	-0.16	-0.68	-0.82	0.96	0.87
Fe_2O_3	0.04	-0.14	0.66	-0.13	0.52	0.38	0.50	-0.43	-0.29	0.57	0.54
SO_3	0.97	0.79	0.62	0.33	0.76	-0.73	0.82	0.58	0.88	-0.74	-0.76
MgO	-0.35	-0.03	-0.47	0.13	-0.50	0.31	-0.65	0.32	0.08	-0.34	-0.26
CaO	0.02	0.38-	-0.27	0.47	-0.19	-0.07	-0.30	0.72	0.48	-0.65	-0.61
MnO	-0.28	-0.16	0.01	-0.25	-0.11	0.78	-0.41	-0.20	-0.25	0.04	0.20
P_2O_5	0.23	0.08	0.71	-0.43	0.62	0.27	0.50	-0.31	-0.08	0.21	0.20
V_2O_5	0.90	0.83	0.70	0.59	0.86	-0.57	0.87	0.66	0.78	-0.59	-0.61
Cr_2O_3	-0.56	-0.76	-0.14	-0.10	-0.33	0.61	-0.28	-0.77	-0.79	0.89	0.95

Table 6- Correlation coefficient of major with trace elements of carbonate lithology of Naokelekan Formation. (n= 9, sig. level= 0.582)

	Ni	Mo	U	Zn	As	Ba	Y	Sr	Cd	Zr	Cu
SiO_2	0.60	0.33	0.03	-0.23	0.79	-0.18	0.70	-0.59	0.50	0.89	0.97
Al_2O_3	0.68	0.53	0.06	-0.18	0.82	-0.07	0.80	-0.45	0.56	0.88	0.94
K_2O	0.77	0.54	0.18	-0.06	0.87	-0.11	0.75	-0.38	0.61	0.94	0.98
TiO_2	0.67	0.49	-0.09	-0.05	0.86	-0.38	0.73	-0.43	0.63	0.93	0.92
Fe_2O_3	0.72	0.60	0.10	-0.17	0.81	-0.08	0.76	-0.36	0.51	0.89	0.92
SO_3	0.92	0.77	0.44	0.16	0.89	0.26	0.58	-0.03	0.63	0.82	0.84
MgO	0.48	0.23	-0.34	0.02	0.81	-0.33	0.38	-0.56	0.65	0.73	0.76
CaO	-0.76	-0.54	-0.18	0.02	-0.88	-0.06	-0.67	0.35	-0.66	-0.89	-0.93
MnO	0.11	0.24	0.01	-0.15	0.15	-0.02	0.67	-0.04	0.13	0.28	0.31
P_2O_5	0.73	0.76	0.38	0.25	0.67	0.07	0.89	0.14	0.63	0.68	0.65
V_2O_5	0.68	0.31	0.19	0.06	0.86	-0.04	0.60	-0.46	0.70	0.85	0.93
Cr_2O_3	0.63	0.26	-0.01	-0.07	0.84	-0.33	0.50	-0.56	0.60	0.93	0.94

Table 7- Correlation coefficient (r) of major with trace elements of shale lithology of Naokelekan Formation. (n= 5, sig. level= 0.805)

	Ni	Mo	U	Zn	As	Ba	Y	Sr	Cd	Zr	Cu
SiO_2	-0.93	-0.57	-0.64	-0.90	-0.72	-0.25	-0.64	-0.88	-0.62	0.98	0.11
Al_2O_3	-0.88	-0.46	-0.63	-0.89	-0.69	-0.24	-0.70	-0.89	-0.52	0.99	-0.01
K_2O	-0.75	-0.24	-0.47	-0.81	-0.55	-0.38	-0.72	-0.84	-0.30	0.97	-0.16
TiO_2	-0.84	-0.41	-0.52	-0.83	-0.59	-0.31	-0.61	-0.83	-0.46	0.98	0.05
Fe_2O_3	-0.85	-0.48	-0.52	-0.79	-0.57	-0.22	-0.50	-0.77	-0.53	0.95	0.19
SO_3	0.79	0.29	0.57	0.87	0.66	0.36	0.81	0.91	0.35	-0.98	0.23
MgO	0.51	0.70	0.85	0.49	0.78	-0.56	0.33	0.44	0.77	-0.19	-0.08
CaO	0.97	0.65	0.84	0.99	0.90	0.11	0.78	0.97	0.72	-0.95	0.02
MnO	-0.67	-0.68	-0.40	-0.42	-0.35	0.19	0.10	-0.32	-0.72	0.53	0.74
P_2O_5	0.22	-0.00	0.65	0.44	0.61	-0.28	0.76	0.53	0.10	-0.26	0.76
V_2O_5	0.79	0.82	0.62	0.57	0.57	-0.28	0.06	0.47	0.88	-0.58	-0.66
Cr_2O_3	0.91	0.74	0.70	0.78	0.69	-0.09	0.36	0.71	0.81	-0.83	-0.42

Table 8- Correlation coefficient (r) of major with trace elements of carbonate lithology of Chia Gara Formation. (n= 22, sig. level= 0.36)

	Ni	Mo	U	Zn	As	Ba	Y	Sr	Cd	Zr	Cu
SiO_2	0.74	0.74	0.67	0.81	0.82	0.46	0.82	0.52	0.74	0.81	0.72
Al_2O_3	0.61	0.63	0.59	0.70	0.73	0.51	0.71	0.42	0.62	0.83	0.65
K_2O	0.74	0.65	0.56	0.69	0.67	0.20	0.77	0.42	0.68	0.53	0.56
TiO_2	0.64	0.63	0.62	0.72	0.74	0.54	0.74	0.46	0.65	0.85	0.66
Fe_2O_3	0.83	0.85	0.86	0.89	0.92	0.74	0.86	0.64	0.87	0.97	0.88
SO_3	0.92	0.85	0.77	0.77	0.81	0.35	0.84	0.33	0.87	0.66	0.76
MgO	0.83	0.88	0.78	0.77	0.89	0.46	0.80	0.39	0.81	0.76	0.82
CaO	-0.88	-0.93	-0.84	-0.88	-0.96	-0.57	-0.87	-0.52	-0.89	-0.88	-0.90
MnO	0.28	0.35	0.55	0.56	0.47	0.77	0.35	0.53	0.34	0.60	0.42
P_2O_5	0.69	0.80	0.90	0.89	0.87	0.92	0.65	0.70	0.79	0.90	0.83
V_2O_5	0.81	0.91	0.73	0.67	0.89	0.43	0.75	0.39	0.81	0.77	0.91
Cr_2O_3	0.83	0.64	0.61	0.78	0.71	0.36	0.92	0.61	0.81	0.75	0.61

Strontium (Sr) & *Arsenic (As)*

Sr commonly makes positive correlation with CaO in the studied samples confirming its accommodation in the lattice of the mineral calcite. Sr shows negative correlation with MgO. This could be explain by the expulsion of Sr from the lattice of dolomite during dolomitization process due to its large ionic size [7, 16]. The difference of ionic radii between strontium (Sr^{2+}=1.12 A°) and magnesium (Mg^{2+}=0.66 A°) leads to a limited substitution of Sr for Mg in dolomite [17]. Therefore, there are two sources for Sr; carbonates which is considered the main source and gypsum evident by the positive correlation between Sr and SO_3. Sr shows negative and positive correlations with CaO and MgO, respectively; this indicate the predominance of recrystalization diagenetic process effect [18]. The positive correlation of Sr with SiO_2, Al_2O_3, K_2O and TiO_2 supports its relation with clays. Hirst [11] and Goldschmidt [10] mentioned that Sr combines with clay minerals structurally when they enter to the basin of deposition.

Arsenic is founded in both carbonate and shale rocks in the studied samples of the three formations. It is related to dolomite supported by SEM and EDS analyses. Spectra (spot chemical analyses) clearly show that arsenic is combined with dolomite (e.g. in the samples of Sargelu Formation: CaO=63.08%, MgO=34.75%, As=2.16%; CaO=62.86%, MgO=34.48%, As=2.65% and in the sample of Naokelekan Formation: CaO=51.66%, MgO=32.57%, As=9.95%, ... Also, it is related to clay minerals supported by positive correlation of As with SiO_2, Al_2O_3, K_2O and TiO_2.

Nickel (Ni), Zinc (Zn) and Molybdenum (Mo)

Nickel makes positive correlation with SO_3 indicating its accommodation in sulfide minerals and its positive correlation with SiO_2, Al_2O_3, K_2O and TiO_2 is related to clay minerals, due to the ability of Ni to be adsorbed on clay mineral surfaces [19].

Zinc has a strong association with sulfide minerals, could be adsorbed by iron hydroxide, or incorporates in illite lattice, and also may present in small amounts in carbonate minerals forming tiny crystals of sphalerite by diagenetic recrystallization [9, 10, 20, 21]. In carbonate and shale rocks of the studied formations, Zn shows positive correlation with SO_3; SiO_2, Al_2O_3, K_2O, TiO_2 and Fe_2O_3 indicating the existence of this trace element in iron oxides/hydroxides and in clay minerals (illite), as well as in sulfide minerals; pyrite and sphalerite although the correlation between Zn and SO3 is weak positive; this could be attributed to the alteration of Zn-sulfide to Zn-carbonate (smithonite ZnCO3). The spot chemical analyses in the sample of Naokelekan Formation (SO_3=42.32, Fe_2O_3=45.03, Zn=1.36, …) reflects the contribution of Zn in pyrite and the presence of tiny crystals of sphalerite in carbonate minerals.

Molybdenum in carbonate rocks of Naokelekan and Chia Gara Formations is related to sulfide minerals and clay minerals. This is supported by positive correlation of Mo with SO_3, Fe_2O_3, SiO_2, Al_2O_3, K_2O and TiO_2. Regarding the carbonate rocks of Sargelu Formation, Mo shows positive correlation with Fe_2O_3, SO_3 and SiO_2 . These are explained by Mo-captured in Fe-sulfide, Mo-sulfide and adsorption on quartz grains. These relationships are enhanced by the EDS point chemical analysis in the sample of Sargelu Formation (SiO_2=96.26%, Mo=2.83%). Also, Mo relates to carbonate minerals by its positive correlation with CaO. This is based on the point EDS analyses in the sample of

Sargelu Formation (CaO=85.02%, Mo=2.15%, …), reflecting the co-precipitation of Ca and Mo. In shale rocks of the three formations, Mo is related to Mo-sulfide as indicated from the positive correlation between Mo and SO_3. The EDS analyses show pronounce association of Mo with pyritic oxidation products and iron oxides; this is supported by the EDS point chemical analyses in the sample of Sargelu Formation (Fe_2O_3=75.73%, SO_3=9.42%, Mo=1.24%, …). Under reducing conditions, Mo is taken up in the presence of HS^- [22, 23], as soluble Mo which is converted to particle reactive thiomolybdates $MoO_xS_{4-x\ (x=0\ to\ 3)}$; thiomolybdates are scavenged from solution via sulfidized organic material or via Mo capture by Fe-S phases [24, 25]. The positive correlation of Mo with SO_3 and its negative correlation with Fe_2O_3 could be attributed to the possibility of formation of Mo-sulfide mineral, this suggestion is based on the fact that under high sulfidic conditions, the uptake of Mo may occur as a metal sulfide (e.g. MoS_4^{-2} …..) in the absence of dissolved Fe [24, 26, 27].

Copper (Cu) & Cadmium (Cd)

Usually, copper follows Zn in its chemical behavior and distribution. It could be incorporated in the lattice of the clay minerals, mostly illite, associates in the lattice of pyrite and adsorbed by iron-oxides/hydroxides [17, 18, 28]. Cu shows positive correlation with SiO_2, Al_2O_3, K_2O, TiO2, Fe_2O_3 and SO_3 which indicating the association of this trace element with clay minerals, iron-oxides/hydroxides and pyrite. Also, Cu could be adsorbed on the surfaces of quartz grains [29]. This is supported by the positive correlation of Cu with SiO_2.

Cadmium in carbonate and shale rocks of the three formations shows positive correlation with SiO_2, Al_2O_3, K_2O, TiO_2, SO_3, Fe_2O_3, Ni, and Zn. This indicates its occurrence in clay and sulfide minerals. Rankama and Sahama [13] and Goldshmidt [10] mentioned that Cd has a strong affinity for sulfur to form sulfide minerals in reducing environments. This is clear in this study, strongly supported by the EDS-point chemical analyses in the sample of Naokelekan Formation (Zn=55.47%, S=31.54%, Cd=1.2 %, …). Cd could also be precipitated on the clay minerals surfaces and it could substitutes for Ca which is attributed to the similarity in the ionic radii of Cd (0.97A^o) and Ca (0.99A^o) [18, 30, 31].

Uranium (U)

U presents in the analyzed samples of carbonate and shale rocks of the three formations . In these rocks, U is found related to the phosphate mineral fluorapatite from its positive correlation with P_2O_5. In general, U is strongly associated with the phosphate minerals and commonly presents in the structure of fluorapatite partially substituting for Ca (ionic radii of U=0.97Å and Ca^{2+}=0.99Å) [32-34]. In carbonate rocks, U may adsorbed on some forms of organic matters that are deposited simultaneously with the carbonate sediments [35].

U in the phosphate mineral (apatite), could be precipitated from sea water and incorporated by ionic substitution for Ca [36]. This is clearly by its positive correlation with P_2O_5 and its negative correlation with Ca. The positive correlation of U with SO_3, Fe_2O_3, Ni and/or Zn in carbonate and shale rocks is explained by its association in sulfide minerals. The positive correlation of U with SiO_2, Al_2O_3, K_2O, TiO_2 is attributed to the association of U with clay minerals. Also, U is occurs in carbonate minerals which is indicated from the positive correlation with CaO. The precipitation of U is attributed to the reduction of dissolved U^{6+} to undissolved U^{4+} under reducing conditions [30]. U is accumulated by direct precipitation from seawater by the action of hydrogen sulfide H_2S (pH about 6.5) [36]. This explains the positive correlation of U with sulfide minerals.

Barium (Ba), Yttrium (Y) and Zirconium (Zr)

Barium in both carbonate and shale rocks of the studied formation has common relationship with SO_3, Al_2O_3, SiO_2, K_2O, and TiO_2, making positive correlation with these oxides. This indicates occurrence of sulfate minerals; barite ($BaSO_4$) supported by EDS-point chemical analyses in sample of Naokelekan Formation (BaO=59.02% and SO_3= 34.32%, …), In addition, Ba could be contributed in clay minerals [10, 11, 13]. The negative correlations of Ba with MgO could be attributed to the loss of Ba during dolomitization process [10].

Yttrium in both carbonate and shale rocks of the three formations is closely associated with the phosphate mineral (apatite) expressed by its positive correlation with P_2O_5. The positive correlation between Y and SiO_2, Al_2O_3, K_2O, and TiO_2 is related to its association with clay minerals. Also, Y is related to sulfide minerals as shown from the positive correlation between SO_3, Fe_2O_3, Ni, and Zn and Y. Goldschmidt [10] reported the possibility of Y to be associated with clay minerals during weathering, erosion, and deposition processes. Also, Rankama and Sahama [13] referred to the presence of Y with low concentrations in sulfide minerals and its weathering products iron oxides and hydroxides.Zirconium in carbonate and shale rocks of the three formations shows positive correlation with clay mineral components; SiO_2, Al_2O_3, K_2O and TiO_2. Hirst [11] suggested that Zr has the capability to enter the crystal lattice of the clay minerals.

Conclusion

- The study revealed the occurrence of carbonates (mainly calcite and dolomite), silicates (free quartz, K-feldspar and clay minerals), sulfides (mainly pyrite), sulfate minerals, apatite and iron oxides and hydroxides.
- The geochemical characteristics and relationships of the major oxides and trace elements are compatible with the mineralogical identification: SiO_2, Al_2O_3, K_2O, TiO_2, $Fe_2O_3$and Zr are positively correlated reflecting the existence of clay minerals and K-feldspar and mostly of detrital origin. Fe_2O_3 is mainly incorporated into the iron oxides and hydroxides as well as sulfides and clay minerals. CaO makes negative correlation with these oxides implying different source and relates with SO_3 and PO_4, indicating the existence of gypsum and apatite.
- The distribution patterns of the trace elements (Ni, Zn, Cu, Cd and Mo) are controlled by the mineral phases present such as clay and sulfide minerals, whereas Sr, As and U are mainly contributed in the carbonate and phosphate minerals.

References

1. Bellen, R.C. van, Dunnington, H.V., Wetzel, R. and Morton, D.M. **1959**. *Lexique stratigraphique international*. Paris, Asie, Fascicule 10a Iraq, III, pp:333.
2. Buday, T. **1980**. *The Regional Geology of Iraq*, Volume 1, Stratigraphy and Paleogeography, Dar Al-Kutub publishing house, University of Mosul, Iraq.
3. Jassim, S.Z. and Goff, J. **2006**. *Geology of Iraq*, Published by Dolin, Prague and Moravian Museum, Brno.
4. Derver, J. I. **1971**. Early diagenesis of clay minerals, Rio American Basin, Maxico , *J. Sedi. Petrol.*, 41, pp: 982-994.
5. Degens, E. T. **1965**. *Geochemistry of sediments*. A brief survey. Prentice-Hall, New Jersey, p:342.
6. Bencini,A. and Allesandro,T. **1974**. Mn distribution in the Mesozoic carbonate rocks from lima valley , *J. Sed. Petrol*., 44, pp: 774-782.
7. Atwood, D.K. and Fry, H.M. **1967**. Strontium and manganese content of some coexisting calcites and dolomites: *American mineralogist*, 52, pp: 1530-1535.
8. Rubio, B. Nombelam.A. and vilas, F. **2000**. Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): An assessment of metal pollution. *Marine Pollution Bulletin*, 40, pp: 968-980.
9. Amin, M. A. **1979**. Geochemistry and Mineralogy of Namurian sediments in the Pennine basin, England, Unpublished Ph. D. thesis, University of Sheffield.
10. Goldschmidt, V. M. **1962**. *Geochemistry*. 3^{rd} ed., London, Oxford University Press.
11. Hirst, D. M. **1962**. The geochemistry of modern sediments from the Gulf paria-I, the relationship between mineralogy and the distribution of major elements, *Geochim. et Cosmochim . Acta*., 26, pp: 309-334.
12. Krauskopf, K. B. **1956**. Factors controlling the concentrations of thirteen rare metals in sea water. *Geochim. et Cosmochim . Acta*, 10, pp: 1-26.
13. Rankama,K. and Sahama,T.G. **1950**. *Geochemistry*. University of Chicago Press, Chicag , USA.
14. Frederic, D., Mullet, M., Bernard, H., and Michot, L. **2005**. Pyrite oxidation by hexavalent chromium :solution species and surface chemistry , *Environmental Science Technology*, 39, pp: 8747-8751.
15. Houda, Z., Wang, Q., Wu, Y. and Xu, X. **2007**. Reduction remediation of hexavalant chromium by pyrite in the aqueous phase, *J. of Applied Sciences*, 11, pp: 1522-1527.
16. Shearman, D. J. and Shirmuhammad, N. H. **1969**. Distribution of Strontium in dolomites from the French Jura, *Nature*. 223, pp: 606-608.
17. Al-Hashimi, W. S. **1976**. Significance of Strontium distribution in some carbonate rocks in the carboniferous of North-Umberland, England, *Journal of Sedimentology and Petrology*, 46 (2) pp: 369-376.
18. Al-Marsumi, A. H. **1980**. Geochemistry and Petrology of Lower Fars evaporates in selected sections-NE Iraq (in Arabic) Unpublished M. Sc. thesis University of Baghdad.
19. Krauskopf, K. B. **1967**. *Introduction to Geochemistry*, McGraw-Hill Book Co., New York.

20. Krauskopf, K. B. **1959**. Sedimentary deposition of rare metal. *Economic Geol*. 50th Anniversary, pp: 411-463.

21. Hem, J. D. **1977**. Reaction of metal ions at surfaces of hydrous iron oxide. *Geochim. Cosmochim. Acta*., 41, pp: 527-538.

22. Bertine, K.K. **1972**. The deposition of molybdenum in anoxic waters: *Marine Chemistry*, 1, pp: 43-53.

23. Calvert, S.E. and Pedersen, T.F. **1993**. Geochemistry of recent oxic and anoxic marine sediments: implications of the geological record. *Marine Geology* 113, pp: 67-88.

24. Tribovillard, N., Riboulleau, A., Lyons, T. and Baudin, F. **2004**. Enhanced trapping of molybdenum by sulfurized organic matter of marine origin as recorded by various Mesozoic formations: *Chemical Geology*, 213, pp: 385-401.

25. Vorlicek, T.P., Kahn, M.D., Kasuza, Y. and Helz, G.R. **2004**. Capture of molybdenum in pyrite-forming sediments: role of ligand-induced reduction by polysulfides: *Geochimica et Cosmochimica Acta*, 68, pp: 547-556.

26. Wilde. P, Lyons, T.W. and Quinby-Hunt, M.S. **2004**. Organic carbon proxies in black shales: molybdenum. *Chem. Geol*., 206, pp: 167-176.

27. Algeo, T. J. and Lyons, T. W. **2006**. Mo-total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. *Paleoceanography* 21, PA1016 .

28. Steele, K. F. and Wanger, G. H. **1975**. Trace metal relationships in bottom sediments of a fresh water stream the Buffalo River. Arkansas, *Jour. Sedi. Petrol*., 45, pp: 310-319.

29. Richardson, P. W. and Hawkes, H. E. **1958**. Adsorption of copper on quartz. *Geochim. et Cosmochim. Acta*., 15, pp: 6-9.

30. Goldschmidt, V. M., **1954**. *Geochemistry*, London. Oxford Univ. Press.

31. Bruland, K.W. **1980**. Oceanographic distributions of cadmium, zinc, nickel and copper in the North Pacific. *Earth Planet. Sci. Lett*. 47, pp: 176-198.

32. Swanson, V. E. **1960**. Oil yield and uranium content of black shales. U.S. Geological Survey Professional Paper 356-A, United States Government Printing Office, Washington. USA, 44p.

33. McClellan, G.H. and Van Kauwenbergh, S.J. **1990**. Mineralogy of sedimentary apatites. In: Phosphorite Research and Development, Notholt, A.J.G. and Jarvis, I. Eds. Geological Society Special Publication, 52, pp: 23-31.

34. Al-Bassam, K. **2007**. Uranium in the Iraqi Phosphorites, *Iraqi Bulletin of Geology and Mining*, 3 (2), pp: 13-31.

35. Bell, K. G. **1963**. Uranium in carbonate rocks, Geological Survey Professional Paper 474-A, United States Government Printing Office, Washington. USA, p:29.

36. Swanson, V. E. **1961**. Geology and geochemistry of uranium in marine black shales-A review. US Geological Survey Professional Paper 356-C, United States Government Printing Office, Washington. USA, p:112.