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Paleoceanographic Conditions of Neo-Tethys Deposits in Northeast Iraq (Shiranish Formation) by Geochemical Proxies

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Abstract
Geochemical proxies provide detailed information on depositional environment and diagenetic processes. The main objectives of the present study are the evaluation of the paleoenvironment and diagenetic conditions of selected three sections of the Shiranish Formation (Late Campanian-Maastrichtian) in Dokan-Sulaymaniyah, Kurdistan Region, northeast of Iraq. The major and some trace elements were analysed by X-Ray Fluoresces. These geochemical results showed a positive correlation of SiO_2, Al_2O_3, Fe_2O_3, MgO and TiO_2 between each other due to the influence of detrital influx from the active oceanic margins and thrust belts of the northeast Arabian Plate. The terrigenous supply of silicates (K-feldspar) and clay minerals (Illite) caused a positive correlation between K_2O values and Al_2O_3. In general, there is a low abundance of SiO_2 and Al_2O_3 contents, referring to the deepening of the Neo-Tythus ocean basin in the formation's lower part. The Mn* factor of the lower and middle part of the formation exhibited anoxic conditions while oxic- suboxic conditions at the upper part. The Mn/Sr ratios were less than one, which means that Shiranish marly limestone was well preserved out of diagenetic processes. The paleoredox proxies {Th/U, V/Cr &V/(V+Ni)} confirmed that the lower part of the Formation was deposited in a relatively anoxic deep-outer shelf environment with a rising in paleoproductivity. In contrast, the upper part was characterised by dyoxic-oxic redox. Due to the inner shelf environment, this redox fluctuation reflects a regression phase of sea level, which is compatible with the closure events of the Neo-Tethys in the Eocene epoch.

Keywords: paleoredox, geochemical proxies, paleoenvironment, Neo-Tethys, Shiranish Formation.

ظروف البيئة البحرية القديمة لترسبات محيط النيوتيثس في شمال شرق العراق (تكوين شيرانش) بوساطة المعطيات الجيوكيميائية

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الخلاصة
ان المعاملات الجيوكيميائية توفر معلومات قيمة عن البيئة الترسيبية والعمليات التحويرية, كانت اهداف الدراسة الحالية هي تقييم ظروف البئية القديمة والعمليات التحويرية لثلاثة مقاطع مختارة من تكوين شيرانش (الكمباني

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المتأخر– الماسترختيان) في السليمانية , شمال شرق العراق. تم تحليل العناصر الرئيسية وبعض العناصر النادرة بواسطة جهاز مطيافية الاشعة السينية. اظهرت النتائج الجيوكيميائية علاقة الترابط الموجبة بين SiO_2, Al_2O_3, Fe_2O_3, MgO,TiO_2 وبعضهم البعض وهذا بسبب ترسيب الرواسب الفتاتية القادمة من الحافات المحيطية النشطة والاحزمة الزاحفة من شمال شرق الصفيحة العربية.

ان التجهيز بالرواسب الفتاتية الحاوية على معادن السليكات (الفلدسبار البوتاسي) وايضاً المعادن الطينية (أيلايت) ادى الى علاقة ارتباط موجبة بين قيم K_2O و Al_2O_3 . بصورة عامة كان هناك تواجد قليل لمحتوى SiO_2 و Al_2O_3 في الجزء السفلي من التكوين وهذا يعود على زيادة عمق الحوض لمحيط النيوتيثس. اظهر معامل *Mn في الجزء الوسطي والسفلي من التكوين, ظروفاً اختزالية بينما كانت مؤكسدة الى شبه مؤكسدة في الجزء العلوي من التكوين. ان نسب Mn/Sr كانت اقل من واحد , وهذا يعني ان صخور الجيرية الطينية للتكوين كانت محفوظة جيداً بعيداً عن العمليات التحويرية. اكدت معاملات جهد التأكسد القديمة {Th/U,V/Cr, V/(V+Ni)} ان الجزء السفلي من التكوين قد ترسب بيئة الرف المختزلة العميقة نسبياً الى بيئة الرف الخارجي مع زيادة في الانتاجية القديمة للمادة العضوية, بينما تميز الجزء العلوي من التكوين ببيئة شبه مؤكسدة الى مؤكسدة والتي تعود على بيئة الرف البحري الداخلي, هذا الانقلاب في جهد التلأكسد يعكس حالة من التراجع البحري في مستوى سطح البحر والذي يكون منسجماً مع احداث انغلاق محيط النيو تيثس في فترة الايوسين.

Introduction

The geochemical applications afford sensitive indicators for evaluating the depositional environment and stratigraphic correlation. The upper Cretaceous period in Iraq included significant geological events that caused ancient environmental changes [1]. The emphasis of the present study is on Late Campanian-Maastrichtian sediments represented in the Shiranish Formation in the Kurdistan Region, northeast of Iraq. This Formation was defined by [1] in the High Folded Zone of Northern Iraq, consisting of thin-bedded argillaceous limestones overlain with blue pelagic marls. The lower contact of the Shiranish Formation is unconformable with the Kometan Formation (Turonian-Santonian age), and the upper contact is gradated to Tanjiro Formation (Maastrichtian age) [2]. The sequences of Late Campanian-Maastrichtian were affected by the obduction zone and closure of the Southern Neo-Tethys, and flysch derived from erosion of the Arabian plate flanking thrust belt [3]. The studied area is located in the high fold zone of an unstable shelf of the northeast Arabian plate [4]. This study focused on determining the concentrations of major and some trace elements in carbonate rocks because of their importance in knowing the paleoenvironmental conditions and diagenetic processes.

Materials and Methods

The studied outcrops of the Shiranish Formation are located in Dokan, Sulaymaniyah Governorate, in the Kurdistan Region, northeast of Iraq, between the latitudes of 35°58′17″ - 35°58′5.13″N and longitudes 44°53′35.36″ - 44°54′18.85″E, as shown in Figure-1. Three sections from the Shiranish Formation were selected to collect samples for geochemical evaluation. The major and some trace elements were analysed via X-Ray Fluorescence, model SPECTRO X-LAB PRO, in the German laboratory, Department of Geology at the University of Baghdad. Many statistical parameters are employed to provide a clear view of the abundance and enrichment of each oxide and element, including; minimum, maximum and average values to give a scale for the variability of the obtained data. In addition to the correlation coefficient (r) to determine the linear association between pairs of data, which ranges from -1.0 to +1.0, the negative value indicates a negative correlation. In contrast, the positive value refers to a positive correlation and no correlation for zero value [5].

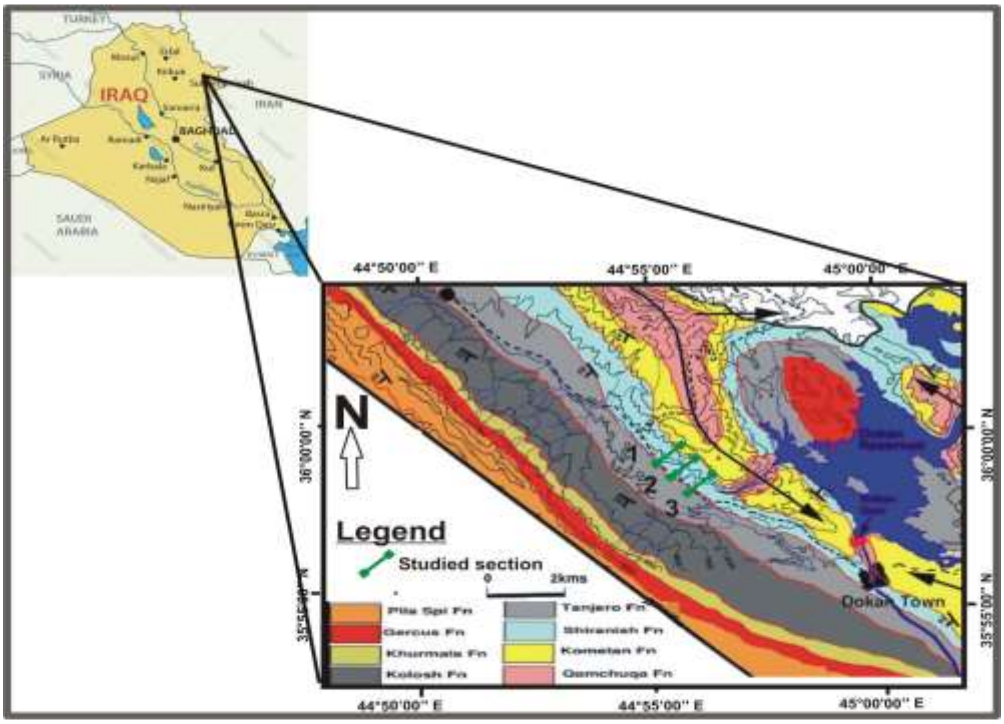

Figure 1- The map of the studied area, modified from [6].

Results and Discussion

The geochemical investigation was performed by chemical analysis of major oxides and some trace elements of the Shiranish Formation samples, which are listed in Table 1. It was noticed that SiO_2 content ranges from 10.9 to 31.6%, with an average of 19.6. The higher concentrations of SiO_2 may be due to the influence of terrigenous influx and silicification processes as a result of deposition of authigenic quartz from the radiolarian re-crystallization in argillaceous limestones of Shiranish. The low concentrations of SiO_2 at the beginning of the formation precipitation indicate the deepening of the basin of the Neo-Tythus ocean in this area. The Al_2O_3 content ranges from 2.8 to 5.9%, with an average of 4.0; the higher concentrations of Al_2O_3, especially in the middle and upper part of the formation, are linked with the influx of detrital sediments and feldspars or of in the depositional basin [7]. This could explain the strong positive correlations between SiO_2, Al_2O_3 and Fe_2O_3, and MgO values referring to clay minerals content as shown in Table 2. The CaO content ranges from 52.6 to 81%, averaging 70.1. The high concentrations of CaO are due to approaching the central part of the basin. Relatively low CaO concentration is related to the dolomitization process to forming dolomite minerals. Therefore, CaO negatively correlates with MgO. Also, CaO negatively correlates with SiO_2, Al_2O_3, Fe_2O_3 and TiO_2 because of the insolubility of silicate minerals largely during the detrital influx [8]. The MgO content ranges from 0.55-2.1%, with an average of 1%; as we have mentioned above, the occurrence of MgO due to dolomitization action and the content of clay minerals such as palygorskite and montmorillonite, and its lowest values indicate the diffusion of freshwater or less saline water by leaching during later stages of diagenesis [9].

In the present study, Fe_2O_3 values range from 1.6-5.2 %, on average, 2.6. The high abundance of Fe^{2+} in Shiranish marly limestone is related to the increasing sedimentation rate of detrital materials from continental sediments and the active oceanic margins of the northeast Arabian plate. This is obvious from the positive correlation of Fe_2O_3 with SiO_2, Al_2O_3, MgO and TiO_2. A minor amount of Fe^{2+} may also substitute for Ca^{2+}or Mg^{2+} to form ferroan calcite in reducing conditions of the diagenetic process. Fe_2O_3 makes a weak negative correlation with SO_3, indicating that iron oxides and hydroxides are composed of the oxidation of pyrite [10].

Na_2O is suitable as a paleosalinity indicator during marine carbonate precipitation, this can be notable from adsorbed and trapped sodium into (Ca, Mg) CO_3 lattices [11]. Na_2O content ranges from 0.75-1.06% on average 0.88%, showing moderated positive correlation with CaO reflecting co-precipitation in carbonate structures. The K_2O values range from 0.5 to 1.7%, with an average of 1.09; K_2O positively correlates with Al_2O_3 due to the terrigenous supply, especially silicates (K-feldspar) and clay minerals (Illite) in argillaceous limestones of the Shiranish Formation. P_2O_5 is found in studied samples in average 0.13%, but we noted in sample No.S12 has a relatively high concentration (0.96%). It may be referred to as chemisorption uptake of dissolved phosphate on the surface of calcium carbonate by near-surface leaching and enrichment [12], and

Table 1-Major and minor oxides of the Shiranish Formation

Sections	Sample No.	SiO2%	Al2O3 %	Fe2O3 %	CaO%	MgO%	Na2O %	K2O%	TiO2%	P2O5%	SO3%
Section 1	S1	10.911	3.156	1.602	81.099	0.557	0.884	1.092	0.211	0.128	0.136
	S2	14.769	3.467	1.821	77.311	0.595	0.822	1.643	0.263	0.165	0.264
	S3	18.641	4.783	2.338	70.014	0.721	0.784	1.643	0.334	0.196	0.310
	S4	27.825	4.987	3.741	63.803	1.678	0.841	1.327	0.357	0.196	0.513
	S5	31.634	5.917	5.222	53.300	2.183	0.833	1.095	0.457	0.113	0.153
	S6	31.231	5.841	5.155	52.620	2.156	0.822	1.081	0.451	0.111	0.151
Section 2	S7	11.408	3.490	1.709	79.879	0.729	0.812	1.153	0.232	0.139	0.204
	S8	14.211	3.518	1.853	78.947	0.704	0.847	1.773	0.242	0.127	0.199
	S9	13.695	3.580	1.940	77.271	0.612	0.903	1.269	0.210	0.134	0.167
	S10	26.582	3.830	2.239	61.352	0.893	0.796	1.229	0.312	0.153	0.762
	S11	28.156	4.040	3.774	59.728	1.825	0.760	0.713	0.343	0.115	0.927
	S12	18.082	2.846	2.243	73.844	0.693	0.955	0.505	0.249	0.963	0.119
Section 3	S13	18.208	2.971	2.314	73.264	0.814	0.988	0.527	0.228	0.128	0.207
	S14	14.631	4.252	1.671	75.162	0.643	1.027	0.947	0.314	0.156	0.898
	S15	15.389	4.139	2.288	73.967	0.681	0.995	0.969	0.321	0.134	0.522
	S16	18.590	4.168	2.503	71.352	0.702	0.944	0.928	0.318	0.084	0.131
	S17	20.019	3.606	2.782	69.526	0.884	1.065	0.780	0.285	0.104	0.653

Table 2-Correlation coefficient of Major and minor oxides of the Shiranish Formation

Elements	SiO2%	Al2O3%	Fe2O3%	CaO%	MgO%	Na2O%	K2O%	TiO2%	P2O5%	SO3%
SiO2%	1									
Al2O3%	0.722	1								
Fe2O3%	0.906	0.816	1							
CaO%	-0.983	-0.779	-0.920	1						
MgO%	0.904	0.779	0.969	-0.904	1					
Na20%	-0.367	-0.332	-0.296	0.352	-0.413	1				
K2O%	-0.147	0.223	-0.150	0.153	-0.115	-0.536	1			
TiO2%	0.847	0.939	0.880	-0.895	0.838	-0.277	0.009	1		
P2O5%	-0.071	-0.328	-0.127	0.126	-0.164	0.142	-0.339	-0.190	1	
SO3%	0.236	0.048	-0.008	-0.228	0.098	0.087	-0.170	0.175	-0.200	1

This indicates a noticeable change in an environment representing the beginning of the lower part of the Tanjiro Formation.

The trace elements are considered very important to specify the environmental conditions and include much evidence about the diagenetic processes of carbonate rocks. Local variations in Eh can be inferred by determining Mn concentrations in carbonates because of the reduction of high Mn-oxide minerals in the rock [13]. The accepted hypothesis is that the decay of organic matter in sediments after burial produces a reducing environment, and that causes a reduction of Mn^{+4} solid case to Mn^{+2} in solution. After that, the Mn^{+2} solution migrates upward of the sedimentary column with the availability of free oxygen to reprecipitate as Mn^{+4} solid case again. Therefore, this process could be a good indicator of the oxidation potential Eh and pH condition of the sediments [14]. Mn redox cycling is important in suboxic–anoxic systems because it can start and accelerate the transfer of Mn from seawater to sediments and remobilise trace elements within the sediments [15] [16]. The Mn values range from 80-1635ppm with an average of 400ppm, the high concentrations of Mn concentrated in the middle and upper part of the Shiranish Formation. The paleo-oxygenation condition was evaluated via Mn* indicator, which has been used by many authors [17],[18]. The Mn* factor was obtained from the application of the following equation:

$$Mn^* = \log \frac{(\text{Mn sample} / \text{Mn shales})}{(\text{Fe sample} / \text{Fe shales})}$$

-where Mn shales = 600 ppm & Fe shales = 46150 ppm.

The Mn* of studied samples shows a negative values range (-0.003 to -0.54), indicating anoxic conditions in the lower and middle part of the Shiranish Formation. Then Mn* values were changed to a positive range (+0.23 to +0.67), indicating oxic conditions in the upper part of the formation and the beginning of the lower part of Tanjiro Formation. This paleoredox fluctuation reflects a regression phase of the sea level of Neo-Tethys ocean. In contrast, the depositional basin tends to become more shallow, coinciding with the events that led to the closure of the Neo-Tethys in the Eocene epoch.

Another of the most important trace elements is strontium due to its mobility during diagenesis and replacement with Ca in aragonite and calcite because of the similarity in standard electrode potential. The Sr content decreases with increasing alteration in carbonate rocks by continental waters [19]. The Sr values range from 1061-1594 ppm with an average of 1267 ppm. It is obvious the Sr content extends from medium to high values. The high Sr concentrations are due to the dissolving Sr & Ca by dissolution, and reprecipitation progresses under a closed diagenetic system [20],[21]. This is represented in section No.3 and the upper part of section No.2 of the Shiranish Formation, where relatively high Sr content indicates the least alteration of diagenesis processes. According to [22], the Mn/Sr ratio considers a good indicator of diagenetic alteration of limestone, this ratio for the formation ranges from 0.05 to 1.2. The values less than one indicate well-preserved limestones; rather, they are getting closer to original marine carbonate rocks.

The paleoredox proxies {Th/U, V/Cr &V/(V+Ni)} were applied for paleoenvironmental reconstruction with studied samples (Figure-2). It was noticed that the paleoenvironment at the beginning of the Shiranish precipitation was anoxic non-shallow marine water (outer shelf) and continued on this redox whole the lower part of the Formation. This leads to higher paleoproductivity during organic matter accumulation mainly resulting from an anoxic water column [23],[24].

Table 3-Some minor and trace elements of the Shiranish Formation

In the upper part of the Formation, a remarkable change happened to dyoxic-oxic redox, which indicates a sort of oxygenated shallow marine water (inner shelf). The oxic conditions led to weak paleoproductivity and poor organic matter retention in the sediments [25,26,27].

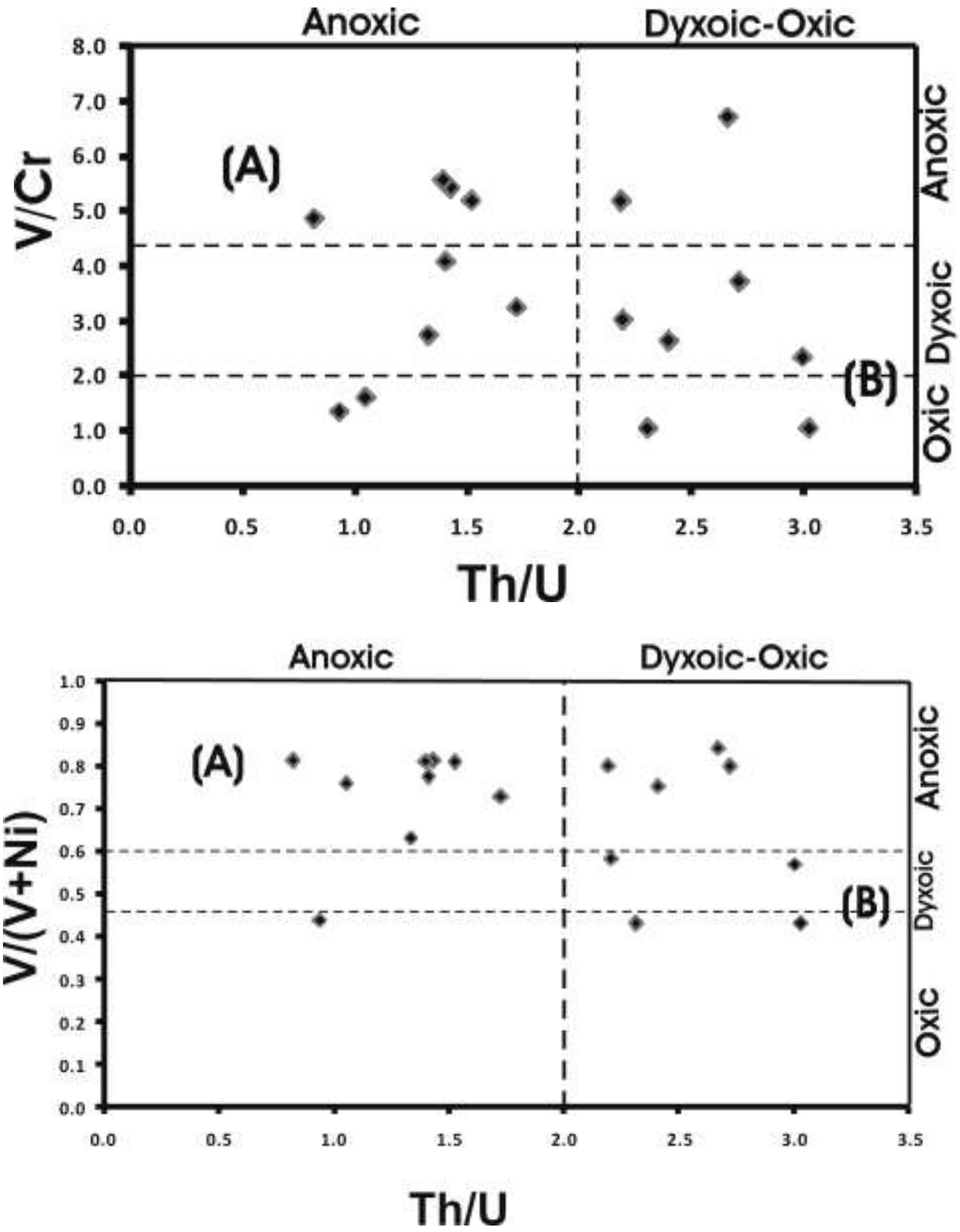

Figure 2- The paleoredox proxies of Shiranish Formation. (A) the lower part of Shiranish and (B) in the upper part of the formation in both graphics.

Conclusions

This study is based on the distribution of major oxides and some trace elements. The positive correlation of SiO_2, Al_2O_3, Fe_2O_3, MgO and TiO_2 between each other refers to the increasing detrital flux rate from the active oceanic margins of the northeast the Arabian Plate. The K_2O content positively correlated with Al_2O_3 refers to the terrigenous supply by silicates (K-feldspar) and clay minerals (Illite) in the marl of the Shiranish Formation. The low concentrations of SiO_2 and Al_2O_3 in the lower part of the formation indicate the deepening of the basin of the Neo-Tythus ocean at that time. The Mn* value showed anoxic conditions in the lower and middle part and oxic- suboxic conditions in the upper part of the Shiranish Formation. The Sr values range from medium to high, which indicates the slightest alteration of diagenesis processes in section No.3 and the upper part of section No.2 of the Shiranish Formation. Almost Mn/Sr ratios were less than one, can be inferred that Shiranish marly limestone was well preserved out of diagenetic alteration. The geochemical redox proxies {Th/U, V/Cr & V/(V+Ni)} are compatible with Mn*value, confirming that the formation's lower part is an anoxic outer shelf environment with higher paleoproductivity. The upper part was dyoxic-oxic redox of the inner shelf environment; this redox fluctuation reflects a regression phase of sea level, coinciding with the Neo-Tethys' closure events in Eocene.

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