Paleoredox and Environmental Conditions of Southern Neo-Tethys Deposits in South Iraq (Yamama Formation) by Geochemical Indicators

Mutadhid Al-Obaidi*, Muaiad Tahir Ahmed, Kareem Khwedim, Salah Ali Hussain
Department of Petroleum Geology and Minerals, College of Science,University of Diyala, Diyala, Iraq.

Abstract

   A geochemical and environmental study was carried out for the sediments of the Southern Neo-Tethys Ocean, represented by the Yamama Formation (Berriasian-Valaganian) in southern Iraq. The formation has a particular reservoir importance. The typical WQ-220 and WQ-280 wells were selected from the West Qurna field. Data of Gamma-ray logs were used for 30 depths of the typical well. Ten core samples were analyzed by X-Ray Fluoresces and total organic matter from both wells. The results showed that shaliness was relatively low, with an average of 16.5%, leading to a decrease in the presence of clay minerals and trace elements because the environment of the Yamama Formation is relatively far away from the coast. Qualitative evaluation of clay minerals was carried out by thorium/potassium ratio, which showed the dominance of illite and smectite. This may be due to an increase in the salinity of the ocean at that time or because potassium bonds are strong enough to resist the diagenesis processes. The origin of shale in the Yamama Formation was studied using the relationship TiO_2-MgO+Fe_2O_3; the sources were passive margin group, oceanic island arc and active continental margin. The redox potential of paleoenvironment was determined by the thorium/uranium ratio, which showed that the beginning of depositional environment was slightly oxidized, but with the increase of sedimentation, it turned into a reduced environment, which indicates a transgression phase of sea level. The results of euxinic affinity, based on the relationship between molybdenum and Total Organic Carbon (TOC), reflect dyoxic facies which is deposited in extremely low but non-zero oxygen content, while the upper was approaching anoxic facies zone. The paleoenvironment of the Yamama Formation was of restricted deep marine water (outer shelf - upper part of the benthic zone) which contained a marine transgression phase because of the opening of Southern Neo-Tethys Ocean in the Valanginian age.

Keywords: Redox Facies, Geochemistry, Paleoenvironment, Southern Neo-Tethys, Yammama Formation.

<div dir="rtl">

ظروف الاكسدة والبيئة القديمة لترسبات محيط النيوتيثس الجنوبي في جنوب العراق (تكوين اليمامة) بواسطة الادلة الجيوكيميائية

معتضد العبيدي*, مؤيد طاهر احمد, كريم حسين خويدم, صلاح علي حسين

قسم جيولوجيا النفط والمعادن, كلية العلوم , جامعة ديالى , ديالى , العراق.

الخلاصة

   تم اجراء دراسة جيوكيميائية –بيئية لترسبات محيط النيوتيثس الجنوبي والمتمثلة بتكوين اليمامة في جنوب العراق (عمر البرياسيان–الفالانجينيان), بما يشكله هذا التكوين من اهمية مكمنية نفطية , حيث تم اختيار

</div>

---

*Email: mutadhid@sciences.uodiyala.edu.iq

البئر WQ-220 النموذجي وبئر WQ-280 من حقل غربي القرنة. تم الاستعانة بمعطيات مجسات اشعة
كاما لثلاثين عمقاً من البئر النموذجي واجريت ايضاً تحليل بعض العناصر الرئيسية والنادرة لعشرة عينات لباب
صخري من كلا البئرين بواسطة جهاز مطيافية الاشعة السينية مع تحليل اجمالي المادة العضوية. أظهرت
النتائج ان نسبة السجيل في التكوين المدروس كانت منخفضة نسبياً وبمعدل (16.5). ان التقييم النوعي
للمعادن الطينية تم من خلال نسبة الثوريوم/البوتاسيوم , حيث اظهرت سيادة معدني الايلايت والسمكتايت وهذا
ممكن بسبب زيادة في ملوحة المحيط وقتها او لكون اواصر البوتاسيوم قوية كفاية لمقاومة العمليات التحويرية
في ما بعد الترسيب. تم دراسة اصل ومصدر الترسبات الفتاتية الموجودة ضمن صخور تكوين اليمامة
الكاربوناتية بأستخدام علاقة $TiO_2-MgO+Fe_2O_3$ والتي بينت ان مصدر الترسبات كان من الحافات
الصفيحية المنفعلة و القوس المحيطي و الحافات القارية النشطة. اما فيما يخص احتمالية الاكسدة للبيئة
القديمة حيث تم تحديدها بالاعتماد على نسبة Th/U حيث اظهرت النتائج انه في بداية ترسيب التكوين كانت
البيئة مؤكسدة قليلاً. تم تحديد الالفة الاختزالية السحنية بالاعتماد على علاقة عنصر المولبيديوم واجمالي
المادة العضوية حيث تبين ان تكوين اليمامة ذو بيئة شبة مؤكسدة قليلة الاوكسجين ولكن في الجزء العلوي
للتكوين تقترب سحنته من البيئة المختزلة , وهذا يدل على ان الظروف الاختزالية للمياه البحرية كانت من
وسطية الى شديدة الاختزال. ان البيئة الترسيبية القديمة لتكوين اليمامة هي بيئة بحرية للرف الخارجي الى
بداية البيئة العميقة شهدت حالة من التقدم البحري بسبب انفتاح محيط النيوتيثيس الجنوبي في عمر
الفالانجينيان.

Introduction

The lower Cretaceous period in the Middle East and Iraq included important geological events, which caused significant environmental changes because of the opening of the Southern Neo-Tethys Ocean [1]. There are several geological and stratigraphic evidences that attempted to describe these paleoenvironmental changes. In this study, we used some major and trace elements as geochemical proxies for paleoenvironmental conditions and redox facies for the Yamama Formation in the West Qurna oil field, southern Iraq, due to its economic significance as a reservoir rock. Yamama Formation belongs to Berriasian to Valaganian ages [2]. In these ages, rifting of micro continents in the north-east of the Arabian plate had took place while the drifting away formed new passive margins in almost the entire Mesopotamian basin [3]. The lithology of the Yamama Formation consists of pseudoolitic limestone, argillaceous limestones, calcareous mudstone and some sandstone [4,5]. The formation in Iraq was described by Bellen *at al*. (1959) [6] as "Yamama-Sulaiy" Formation, The upper part is assigned to the Yamama Formation according to Sadooni (1993) [7]. In the late Tithonian-Cenomanian time, major palaeogeographic changes occurred in the Arabian Plate, which formed as a result an ocean floor spreading around the northern and eastern margins of the Plate with the opening of a southern Neo- Tethys Ocean [2].

Materials and Methods

The studied area is located in Basra Governorate, Iraq, between the latitudes of 31°10′00″ - 30°45′00″N and longitudes 47°05′00″ - 47°25′00″E at the West Qurna Oilfield, as shown in Figure-1. The core samples were collected from two boreholes (WQ-220 & WQ-280). Thirty readings of selected Gamma Ray log intervals from the well WQ-220 were selected in order to assess the quantities of thorium and uranium (ppm) and the percentage of potassium according to Schlumberger log interpretation charts [6]. Some of minor and trace elements were analyzed for 10 core samples by X-Ray Fluorescence of each well, in the German laboratory of department of geology-University of Baghdad; the model of the used instrument is SPECTRO X-LAB PRO. The total organic carbon (TOC) was analyzed for quantitative evaluation of organic matter in the laboratory of Oil Exploration Company, Baghdad.

Results and Discussion

In order to find out the ancient sedimentary environment of Yamama Formation, we used some of trace elements as geochemical proxies. Most of these elements are usually within clay minerals, so it is necessary to determine the shale content in Yamama argillaceous limestones. The quantitative evaluation of shale was assessed by using data of Gamma ray well logging of WQ-220 borehole, by employing the chart of shale volume of Dresser Atlas company [8].
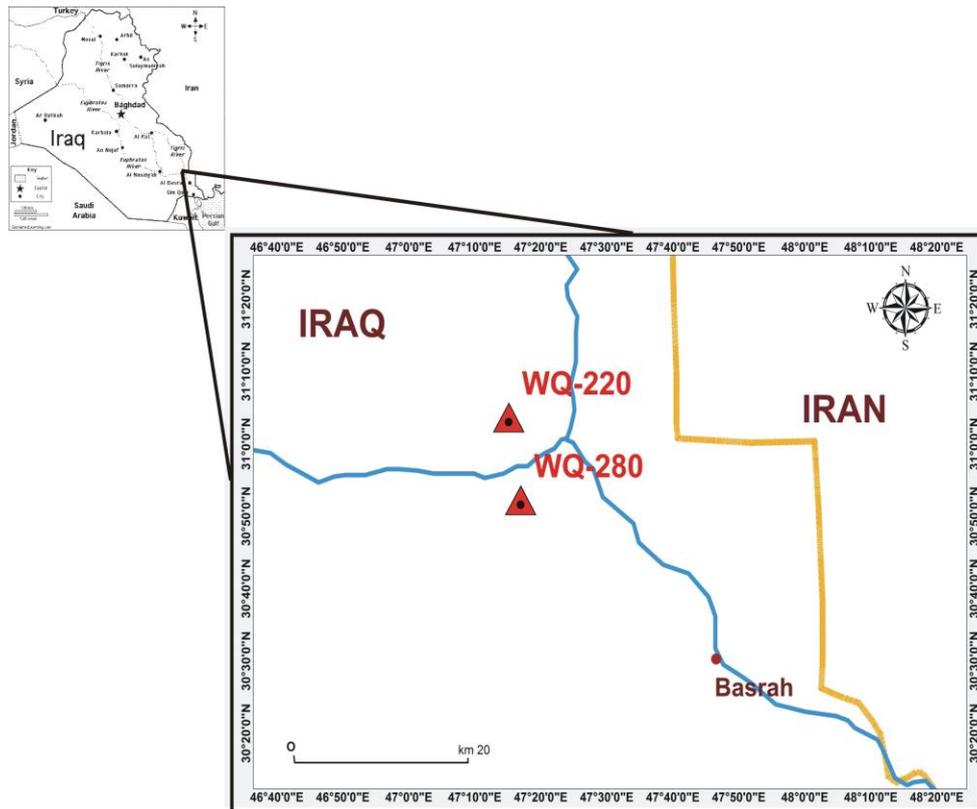
Figure 1- Map of the studied area.

The volume of shale has a range of 0-51% with an average of 16.5 %, as shown in Table-1. It is noted that the volume is low, which would affect the presence of clay minerals and thus would affect the quantities of some trace elements (Figure-2). This reflects environmental and stratigraphic indications, that the depositional environment of Yamama Formation was rather far away from the coast and, therefore, the supply of aluminsilicates was not intensive enough.

One of the indirect methods for the assessment of the quality of clay minerals is via spectral Gamma ray log, which is shown as three curves of thorium, uranium, and potassium. Thorium and uranium are reported in parts per million, whereas potassium is recorded as a percentage[9]. For clay minerals evaluation, K and Th must be used together , because reliance only on K can be an indicator of algal remains or glauconite content in carbonate rocks. Therefore, calculated gamma ray (CGR) , should be used when assessing shaliness in carbonates. Thorium is exclusively associated with aluminosilicates and, therefore, Th log is a good indicator of the volume of clay minerals [10,11].
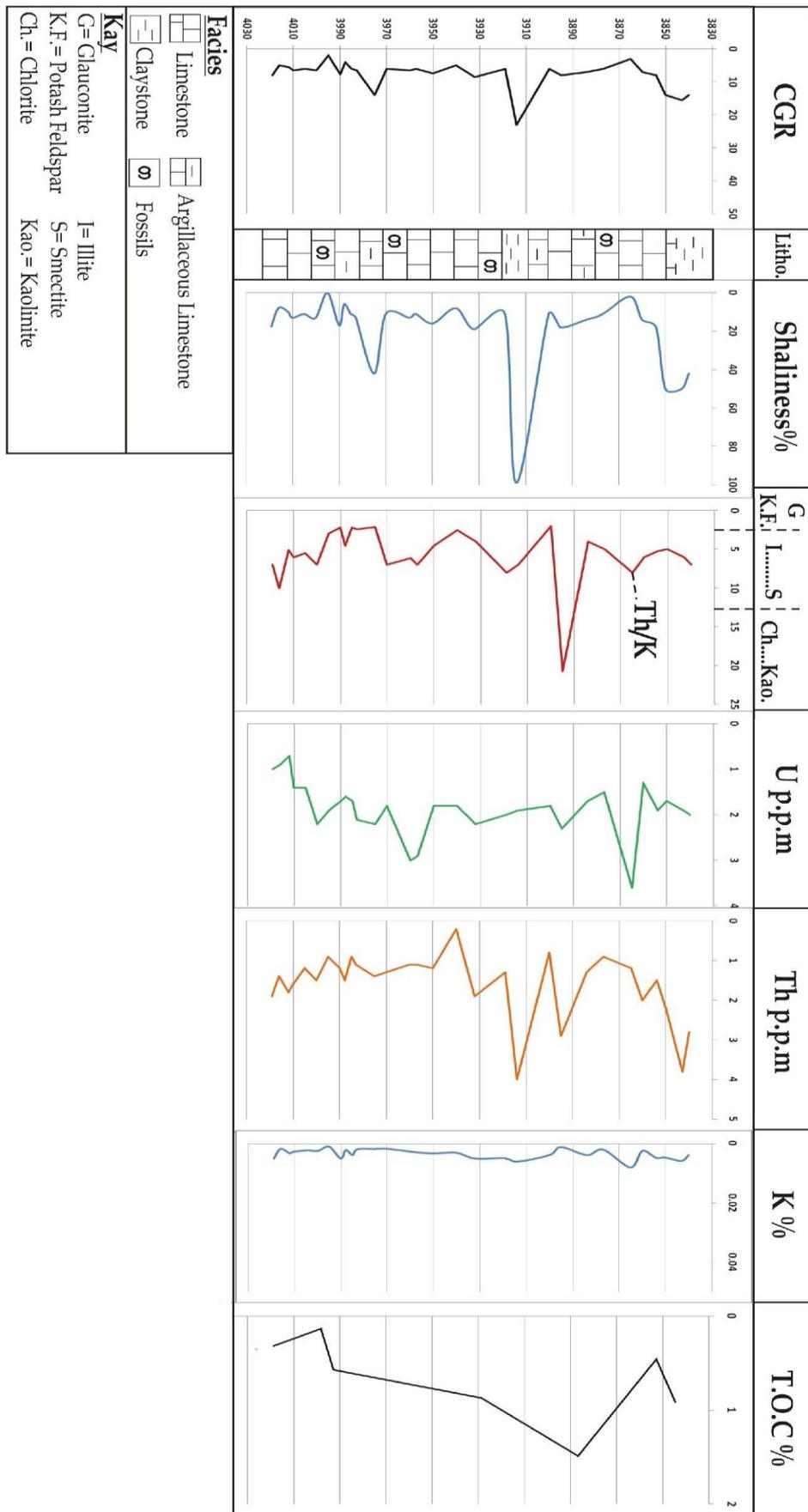
Figure 2- Geochemical log of Yamama Formation of WQ-220 borehole**.**

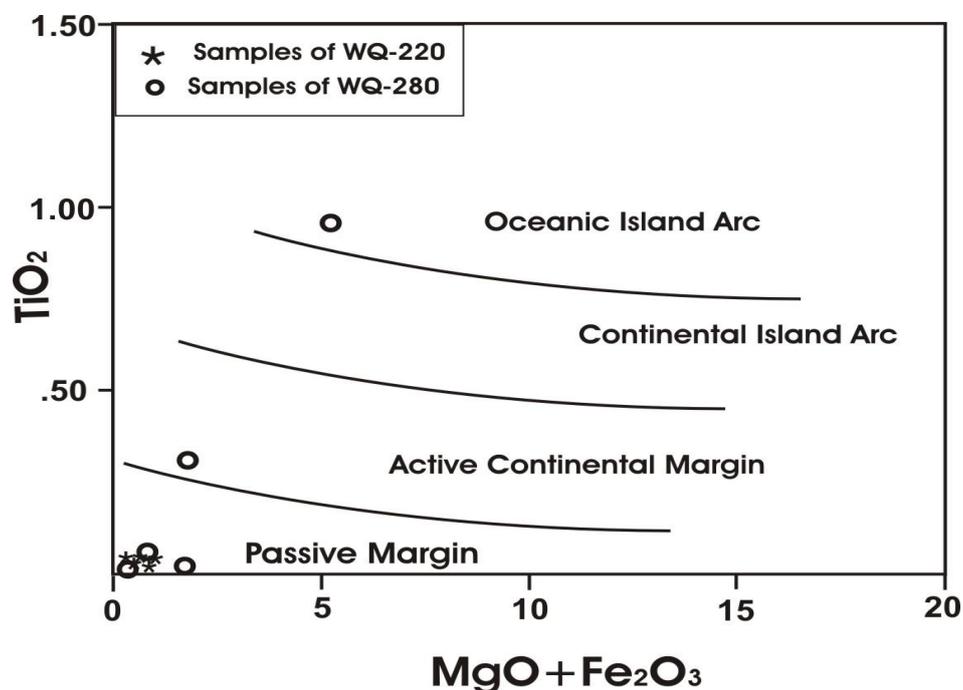**Table 1** Some minor and trace elements of Yamama Formation for WQ-220 and WQ-280 boreholes.

Depth m.	Al_2O_3	MgO	Fe_2O_3	TiO_2	Mo p.p.m	T.O.C	Shaliness %	CGR	U p.p.m	Th p.p.m	K %
\
<table with WQ-220 spanning header>											

WQ-220

Depth m.	Al_2O_3	MgO	Fe_2O_3	TiO_2	Mo p.p.m	T.O.C	Shaliness %	CGR	U p.p.m	Th p.p.m	K %
3840	0.5602	0.7331	0.2627	0.0005	32.81		42	14	2	2.8	0.0039
3843						0.471	50	15.5	1.9	3.8	0.0058
3850							50	14	1.7	2.2	0.0047
3854							18	8	1.9	1.5	0.0048
3860							14	7	1.3	2	0.0025
3865							2	3	3.6	1.2	0.008
3876.85	0.1050	0.4378	0.0407	0.0054	30.58	1.49	11	6	1.5	0.9	0.0021
3884							14	7	1.7	1.3	0.0038
3895							18	8	2.3	2.9	0.0012
3900							11	6	1.8	0.8	0.0039
3914							99	23	1.9	4	0.0061
3918.9	0.4116	0.8682	0.1964	0.0356	22.50	0.871	11	6	2	1.3	0.005
3932							19	8.5	2.2	1.9	0.0051
3940							8	5	1.8	0.2	0.0031
3950							16	7.5	1.8	1.2	0.0033
3957							11	6	2.9	1.1	0.0029
3960							13	6.5	3	1.1	0.0027
3970							11	6	1.8	1.3	0.0018
3975							42	14	2.2	1.4	0.0018
3982.9	0.1289	0.6093	0.1365	0.0006	38.76	0.568	13	6.5	2.1	1.1	0.0019
3985							11	6	1.7	0.9	0.0038
3987.8						0.137	6	4	1.6	1.5	0.0022
3990							17	7.7	1.7	1.2	0.005
3995							0	2	1.9	0.9	0.001
4000							13	6.5	2.2	1.5	0.0025
4005							11	6	1.4	1.2	0.0023
4010							13	6.5	1.4	1.6	0.0026
4012							10	5.5	0.7	1.8	0.0032
4016	0.3241	0.4705	0.1123	0.0005	30.21	0.355	8	5	0.9	1.4	0.0018
4019							17.5	8	1	1.9	0.0051
WQ-280											
3891	9.2256	0.7252	5.3108	0.9022	50.76						
3963	0.1504	0.4653	0.0769	0.0005	38.91						
4001	0.4624	0.5052	0.2984	0.0232	30.20						
4053	4.4330	0.6995	1.6229	0.3305	28.24						
4131	0.5649	1.7190	0.2745	0.0085	26.93						

It was observed that, in a depth pf 3914m of WQ-220 borehole, the value of shale was 99%. This is attributed to high U, K and Th concentrations in stylolites, which tend to accumulate uranium, organic matter, and clay minerals. The thorium/potassium ratio (Th/K) is a useful indicator for differentiating the kinds of radioactive minerals [10]. If the ratio is low, this may reflect the presence of feldspars and micas, while the values up to 3.5 appear in illite, smectite, kaolinite, and chlorite (arranged by rising ratio) [11].

The content of clay minerals of the Yamama Formation ranged from illite to smectite according to their Th/K ratio, except at the depth of 3914m which was dominated by kaolinite and chlorite (Figure-2). This majority of illite-smectite may have two explanations. The first is the non-reducing marine conditions where increasing salinity leads to the formation of illite- smectite as well as a decrease in the amount of kaolinite and chlorite formed [12].The second explanation is that the potassium bond in illite or hydrous mica is strong enough to resistant the mechanical shearing during diagenesis [13].
The geochemical composition of the clastic sediments arriving to the basin within carbonates rocks reflects different factors that include weathering, transportation, deposition and the tectonic conditions that control these factors [14,15].

Many geochemical techniques provide information about tectonic events and locations. This study used the TiO_2-MgO+Fe_2O_3 Plot suggested by Bhatia (1983) [14], which includes different tectonic settings; passive margin (PM), active continental margin, continental island arc and oceanic island arc
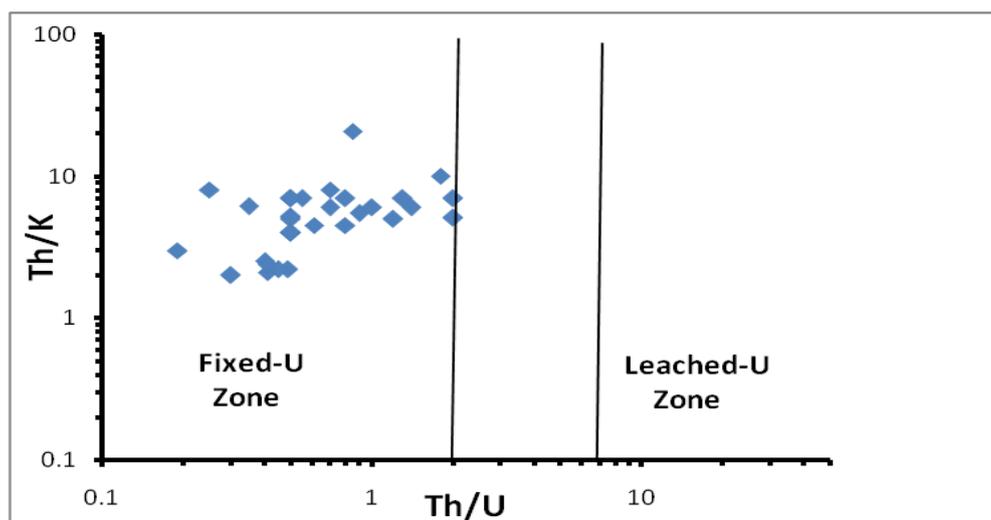
(Figure-3). Samples of WQ-220 borehole of Yamama Formation lie within the passive margin group, while samples of WQ-280 borehole lie in a diversity of groups which are the oceanic island arc, active continental margin and passive margins. This is in agreement with the idea of the new passive margins composed by carbonate ridge and rifting by the opening of the Southern Neo-Tethys Ocean [2].

Figure 3- The source of clastic sediments in the Yamama Formation according to Bhatia Diagram [14].

The redox potential of the original sedimentary environment can be assessed by the Th/U ratio and gives more information about diagenetic processes. In common, uranium is fixed and associated geochemically with organic matter because uranium has an insoluble tetravalent state under reducing conditions [9]. Uranium is mobilized and leached into solution under oxidation conditions because of its soluble hexavalent state. On the other hand, thorium is restricted to an insoluble tetravalent, according to Adams and Weaver (1958) [16]. If the Th/U ratio is less than 2, it is an indicative of reducing environment, whereas that greater than 7 represent oxidation conditions. By applying this ratio on Yamama Formation in the borehole WQ-220, we found that all samples were in the uranium fixed zone, except for two depths (3914m & 4012m) which were in the transition zone (Figure-4). However, in the beginning of the deposition of Yamama Formation, the redox of sedimentary environment had slight oxidation conditions. After the depth of 3914m and upward, the depositional redox reflected reducing conditions until the upper contact of formation. This leads to the thought that Yamama environment shows clearly a transgression phase of sea level after a simple regression state in the bottom of the formation, with an increased reduction of redox potential upward.

Trace elements have many applications to identify the ancient ecological conditions. In this research, molybdenum is used as a paleoredox indicator or proxy in restricted depositional environments. It exists in marine water as molybdate ($MoO4^{-2}$) and may be abundant within sediments with high content of organic matter, by adsorption where the sediment-water interface at the time of deposition [17].
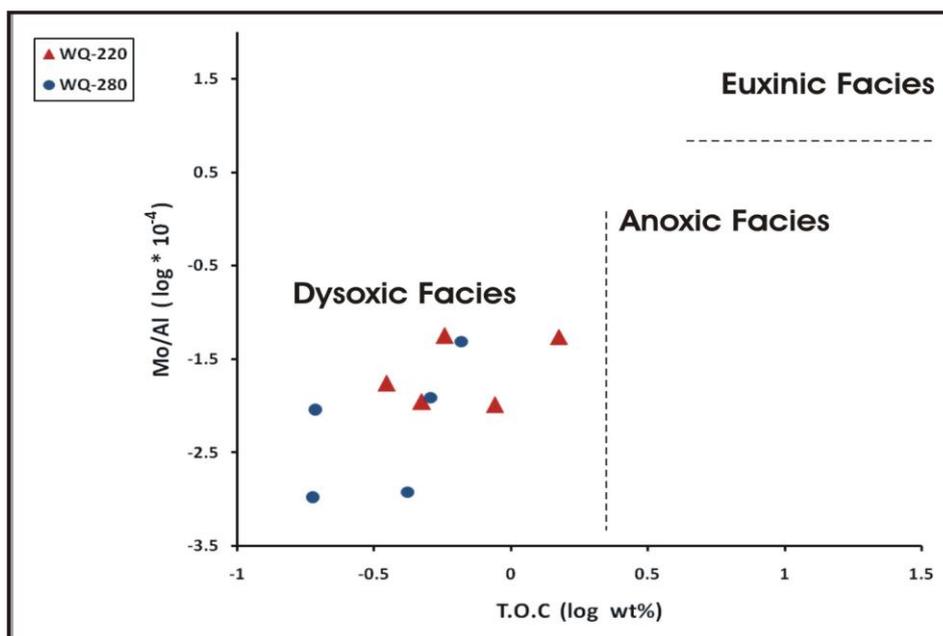
Figure 4-Assessment of redox potential by a relationship provided previously [16].

Molybdenum concentration is aluminum normalized and has units of 10^{-4} to make correction for variable dilution via organic materials and autogenic minerals [18]. The normalization process is an authentic indicator when Al concentration is in siliciclastic phases and was immobilized in diagenetic circumstances [19].

In anoxic environments , $MoO4^{-2}$ can be liberated from organic matter, via bacterial decay of sulfate, and reduced to Mo(V) or Mo(IV). Mo is adsorbed by making bonds with metal- rich minerals (especially Fe), iron sulfide and sulfur-rich organic matter [17,20]. The non-euxinic environment is characterized by limited molybdenum diffusion, and this leads to decreasing its uptake via authigenic sulfides which are based in the sediment–water surface. While, under euxinic circumstances, Mo absorption by authigenic sulfides will be increased with the aid of free H_2S in the water column [21, 22].

Redox-facies analysis is based on the relationship between TOC and trace elements, according to Alego and Maynard [23]. The studied samples are illustrated on a continuum log–log crossplot (Figure-5). The manner of euxinic affinity is shown based on the values of Mo and TOC. We have noticed that the studied samples of both wells (WQ-220 & WQ-280) fell within the dyoxic facies zone, which indicates that the rocks of Yamama Formation were precipitated in extremely low but nonzero oxygen content , almost between 0.2 and 2 mlO_2/l H_2O of O_2 concentration in the bottom of the water column. It is also noticeable that the upper part of Yamama formation in well WQ-220 was approaching the anoxic facies zone. There was also an increase in reduction conditions from moderately to strongly restricted deep marine water (outer shelf), with a clear increase in paleoproductivity of organic matter content. This signalized a marine transgression phase which was a result of the opening of Southern Neo-Tethys Ocean in the Valanginian age. The growing in the reduction conditions continues upward, where Yamama Formation grades to black shale and limestone of Ratawi Formation in the Hauterivian age [2].

Figure-5 Euxinic affinity of the Yamama paleoenvironment according to Alego and Maynard Diagram [23].

Conclusions

1- The average of shale volume in the Yamama Formation is rather low (16.5%), which leads to decreasing the quantities of clay minerals and trace elements and provides a proof that the paleoenvironment was rather distal from the coast.

2- Clay minerals for the studied formation show that the majority is of illite and smectite, which may has resulted from increasing salinity that led to the formation of illite-smectite. Another reason could be that the potassium bond in illite- smectite is strong enough to resist diagenetic processes.

3- The sources of the clastic sediments within Yamama Formation were: the passive margin group, oceanic island arc and active continental margin.

4- The estimation of redox potential of the paleoenvironment using the Th/U ratio reflected an increasing reduction potential upward and showed clearly the transgression phase of sea level after a simple regression state in the bottom of the formation.

5- According to euxinic affinity based on values of Mo and TOC, the redox facies of Yamama Formation were dyoxic, which were deposited in extremely low but nonzero oxygen content, whereas in the upper part they approached the anoxic facies zone.

6- The paleoenvironment of Yamama Formation was of moderately to strongly restricted deep marine water (outer shelf - upper part of benthic zone), due to marine transgression phase and as a result of the opening of the Southern Neo-Tethys Ocean in the Valanginian age.

References

1. Buday, T. and Jassim, S.Z. **1987**. *The Regional Geology of Iraq (Tectonism, Magmatism, and Metamorphism)*. Prague. Dolin, Prague and Moravian Museum.
2. Jassim, S. Z., and Goff, J.C. **2006.** *Geology of Iraq*. Prague. Dolin, Prague and Moravian Museum.
3. Ahmad, K. I., Hussain, S. A. and Al-Obaidi, M. **2018**. Paleoceanographic reconstruction of upper cretaceous, black shale succession, northeastern iraq using geochemical proxies to indicate paleoredox and paleoenvironment conditions. *Diyala Journal of Pure Sciences*, **14**(3): 237-264.
4. Chafeet, H.A. **2016**. Yamama reservoir characterization in the west Qurna oil field, southern Iraq. *Iraqi Journal of Science*, **57**(2A): 938-947.
5. Handhal, A.M., Al-Najm, F.M. and Chafeet, H.A. **2018**. Determination of flow units of Yamama formation in the west Qurna oil field, southern Iraq. *Iraqi Journal of Science*, **59**(4A): 1878-1898.
6. Bellen, R. C. Van, Dunnington, H. V., Wetzel, R. and Morton, D. **1959**. *Lexique stratigraphique internal Asie*. Iraq. Intern. Geol. Conger. Comm. Stratigr, 3, Fasc. 10a, 333p.

7. Sadooni, F. N. **1993**. *Stratigraphic sequence, microfacies & petroleum prospects of the Yamama Formation, lower Cretaceous, south Iraq*. AAPG Bull, 77, p. 1971- 1988.

8. Schlumberger log interpretation charts, **1988**. *Schlumberger Educational Services*, Houston, Texas, 150 p.

9. Asquith, B. G. and Gibson, C. R. **1983**. *Basic Well Log Analysis for Geologist*. Tulsa, Oklahoma USA. The American Association of Petroleum Geologists.234P.

10. Doveton, J.H. **1991**. Lithofacies and geochemical facies profiles from nuclear wire-line logs: New subsurface templates for sedimentary modeling. *Kansas Geological Survey, Bulletin*, **233**: 101-110.

11. Hassan, M., Hossin, A. and Combaz, A**. 1976**. Fundamentals of the differential gamma-ray log: Society of Professional Well Log Analysts, Transactions Paper H, 18 p.

12. Kerr, P.F. **1953**. Formation and occurrence of clay minerals : American Mineralogist, v. 1. pp. 19–32.

13. Barshad, I. **1959**. *Factors affecting clay formation. In Clays and clay minerals*, Pergamon Press. New York. pp. 110-132.

14. Bhatia, M. R. **1983**. Plate tectonics and geochemical compositions of sandstones: *Journal of Geology*, **91**: 611-627.

15. McLennan, S. M., Hemming, S., McDaniel, D. K. and Hanson, G. N. **1993**. Geochemical approaches to sedimentation, provenance, and tectonics, in Johnsson, M. J., and Basu, A., eds., processes controlling the composition of clastic sediments: Boulder, Colorado, Geological Society of America Special Paper 284, p. 21-40.

16. Adams, J. A. S. and Weaver**,** C. E**. 1958**. Thorium to uranium ratios as indications of sedimentary processes - example of concept of geochemical facies: *American Association of Petroleum Geologists, Bulletin*, **42**(2): 387-430

17. Helz, G.R., Miller, C.V., Charnock, J.M., Mosselmans, J.F.W., Pattrick, R.A.D., Garner, C.D. and Vaughan, D.J. **1996**. Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. Geochim. Cosmochim. Acta 60, 3631– 3642.

18. Morford, J.L., Russell, A.D. and Emerson, S. **2001**. Trace metal evidence for changes in the redox environment associated with the transition from terrigenous clay to diatomaceous sediment, *Saanlich Inlet, BC. Mar. Geol*. **174**: 355– 369.

19. Calvert, S.E. and Pedersen, T.F. **1993**. Geochemistry of Recent oxic and anoxic marine sediments: implications for the geological record. *Mar. Geol*. **113**: 67– 88.

20. Tribovillard, N., Algeo, T.J., Lyons, T. and Riboulleau, A.,**2006**. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chemical Geology*, **232**: 12–32.

21. Morse, J.W. and Luther III, G.W. **1999**. Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochim. Cosmochim. Acta*, **63**: 3373–3378.

22. Adelson, J.M., Helz, G.R. and Miller, C.V. **2001**. Reconstructing the rise of recent coastal anoxia; molybdenum in Chesapeake Bay sediments. *Geochim. Cosmochim. Acta*, **65**: 237–252.

23. Algeo, T.J. and Maynard, J. B. **2004.** Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chemical Geology*, **206**: 289– 318.