Paleoceanographic Reconstruction of Upper Cretaceous, Black Shale Succession, Northeastern Iraq Using Geochemical Proxies to Indicate Paleoredox and Paleoenvironment Conditions

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Abstract

Thirteen outcrop samples of lithified black shale from the North of Iraq, Gulneri Formation, were analyzed for stable carbon and nitrogen isotopes of organic matter and for trace elements distribution to assess the source of organic matter and the redox state at the time of deposition, respectively. Paleoredox-sensitive (trace) elements including ratios of Ni, V, and Co indicate fluctuations between an oxic, dyoxic, and suboxic/anoxic conditions during the deposition of the formation. Specifically V/(V + Ni) suggests generally low oxygen during the deposition of the formation. Detrital iron oxides are present in some samples. Carbon isotopic values are depleted throughout the formation ranging between -26 to -24. The nitrogen isotopic values record negative values indicative of denitrification of amino acids or nitrogen fixation in the ocean. Mineralogical observations reveal the alteration of pyrite to iron oxides in the bottom of the formation. There are two potential indicators of the deposition setting: first, the lack of pyrite except at the bottom suggests a generally oxic setting. However, fluctuations in the V/Al ratio throughout the formation, low U and Mo and the presence of planktonic foraminifera suggests that the redox conditions fluctuated and were sometimes anoxic at least in the sediment.

Key words: Stable isotope, sensitive (trace) elements, Cretaceous, black shales, paleo-productivity, paleo-oxygenation.

اعادة بناء البيئة البحرية القديمة لتتابع السجيل الاسود، الطباشيري الاعلى في شمال شرق العراق باستخدام المعطيات الجيوكيميائية لتحديد الاكسدة القديمة وظروف البيئة القديمة

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الخلاصة

ثلاثة عشر نموذج صخري اخذت من مكشف سطحي للسجيل الاسود المتصلب في شمال شرق العراق تعود لتكوين كلنيري، تم تحليل تلك العينات لقياس النظائر المستقرة للنايتروجين والكاربون للمادة العضوية وتوزيع العنصر النادرة لغرض تحديد اصل المادة العضوية والاكسدة في زمن الترسيب. العناصر (النادرة) الحساسة للاكسدة القديمة التي تتضمن النيكل، الفنيديوم والكوبالت تدل على تذبذب بين ظروف البيئة المؤكسدة وظروف البيئة المؤكسدة/غيرالمؤكسدة خلال فترة ترسيب التكوين. نسبة $V/(V + Ni)$ تدل على بيئة قليلة الاوكسجين خلال فترة الترسيب. اكاسيد الحديد الفتاتية تظهر في بعض النماذج. تنخفض قيم نظائر الكاربون على امتداد التكوين وتتراوح بين -26 الى -24 . تسجل نظائر النايتروجين قيما سالبة مما يدل على ازالة النايتروجين من الاحماض الامينية او تثبيت للنايتروجين في المياه البحرية. الملاحظات حول معدنية التكوين تشير الى تبدل البايرايت الى اكاسيد الحديد في اسفل التكوين. هنالك دليلين محتملين لوضعية الترسيب: الاولى ان فقدان البايرايت ما عدا في قاعدة التكوين تقترح بيئة مؤكسدة. الثانية تذبذب نسبة V/Al خلال التكوين، والنسبة القليلة لليورانيوم والمولبدنم وتواجد الفورامنيفرا الطافية تقترح تذبذب ظروف الاكسدة القديمة والتي كانت في بعض الاحيان تمثل نقص في الاوكسجين على الاقل في الرواسب.

الكلمات المفتاحية: النظائر المستقرة، العناصر (الحساسة) النادرة، العصر الطباشيري، السجيل الاسود، الانتاجية القديمة، الاوكسجين القديم.

Introduction

Black shales have been studied at different parts of the world; they are typically deposited slowly in deep, anoxic ocean basins [1]; [2]. This black shales are rich in organic matter and sulfides that host trace elements such as Co, Ni, V, U, Mo, Mn, P, and platinum group elements [1]; [3]; [4]; [5], [6]. Some models call for high productivity and high preservation of organic matter as the precursors for black shales [7]; [8]. Permanently stratified water column may have also contributed to the increase in preservation and accumulation of organic matter in anoxic bottom water [7]; [9]. It is likely that the presence of organic matter in black shale is controlled by a combination of several factors including redox conditions, rate of input of clastic materials, primary productivity, and degradation processes [10]; [11]; [12]; [13]; [14]; [15]; [16]. The source of organic matter in the black shales can be marine or terrestrial depending on the site [17]. For example, the sources of organic matter from Aptian-Albian black shales as well as shales at the Cenomanian-Turonian boundary were a mix of continental and marine sources [18]. Stable isotope of organic matter can also be used to identify post-deposition alteration of organic matter. This was done in oil shales from the Negev, Israel, late Cretaceous where preferential loss of nitrogen-rich organic compounds was suggested [19].

Redox sensitive elements in black shales were used to described depositional conditions in different locations in the world. For example, redox-sensitive elements indicated in Devonian–Mississippian black shales, Central Appalachian Basin (USA) along with the carbon-sulfur-iron relationships suggested anoxic conditions in the Sunbury and upper Cleveland and euxinic conditions in the Sunbury [14]. Evaluation of total organic carbon (TOC) along with molybdenum (Mo) content in Lower Ordovician black shales of the Baltica and Avalonia plates were used to understand pathways of carbon synthesis and remineralization in ancient ocean sediments [20]. Major and trace elements of Late Cenomanian- Early Turoniam organic-rich deposits from southern Tethan margin, Tunisia recorded were also used to reconstruct water redox conditions [21].

The Cretaceous black shales represent one of the most important geological units in Iraq due to the huge contents of hydrocarbons in its lithology. The climate in the cretaceous was warm [22] and the concentration of atmospheric CO_2 was high [23]. The black shales is enrich in organic matter with abundant planktonic foraminifera. The lithology of Gulneri Formation in Degala section (Figure 1) is yellowish brown shale. The lower and upper contacts with the Dokan and Kometan Formations, respectively, are conformable [24]. The purpose of this study is to reconstruct the paleoceanographic conditions during the deposition of the Gulneri Formation using geochemical analysis, including stable isotope geochemistry of bulk organic matter and major and trace elements, as well as foraminiferal assemblages. Specifically we attempt to identify the source of organic matter, shed light on paleoproductivity, and paleoxygenation of Gulneri Formation during the Cretaceous.

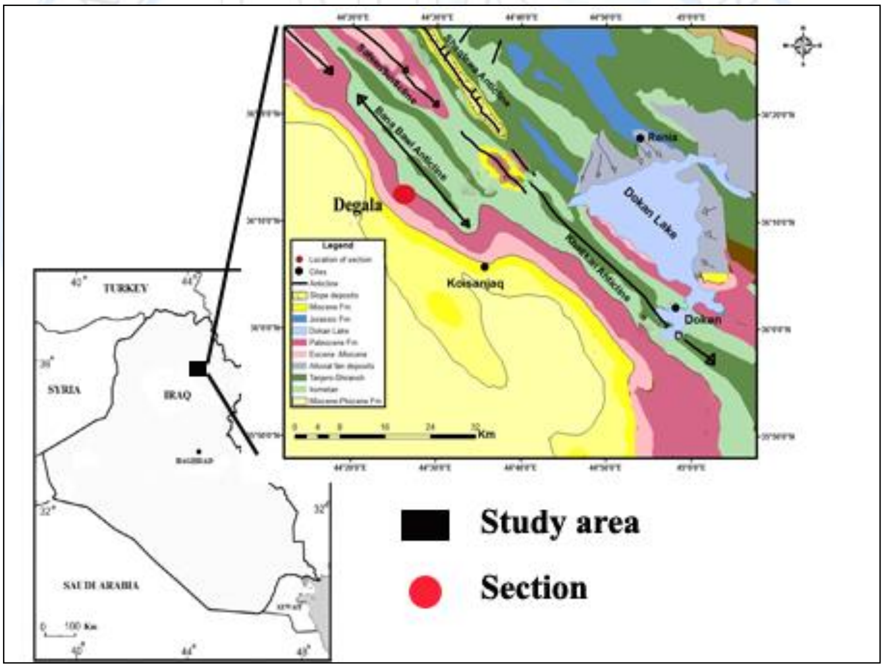

Figure 1: The study area of Gulneri Formation in Northeastern of Iraq.

Foraminiferal Assemblage

[24] described the presence of planktonic Foraminifera in the formation with absence of benthic foraminifera. The abundance of Planispiral forms like *Globigerinelloides* sp. increase during warm periods and decrease during cold periods [25], *Guembelitria* species thrived in shallow marginal marine environments and probably tolerated both salinity and oxygen variations [26]. *Whiteinella* species are typical of the latest Cenomanian OAE (Oceanic anoxic events) [27]; *Guembelitria*, *Heterohelix* have been suggested to represent shallow waters within the inner shelf [28] while *Guembelitria* indicates epicontinental settings (less than 100 m); [29]. The dominance of Heterohelicids and Globigerinellids potentially indicates shelf seas [30] and *Ticinella* characterizes shallow water condition in low latitude environments (less than 100 m) [29]. The abundance of foraminifera was obtained as revealed by table 1.

Table 1: The percentage of foraminiferal abundance in Gulneri Formation with variations in oxygen and sea-level changes based on foraminifera species.

Thickness (cm)	Foraminiferal Abundance (%)	Oxygen Tolerant	Sea-level Fluctuations
8	48	low	High Stand
48	90	low	Transgression
93	75	low	Transgression
113	55	High	High Stand
127	55	low	Transgression
147	45	low	Transgression
165	75	low	High Stand
183	90	low	High Stand
233	75	low	High Stand
272	55	moderate	High Stand
312	75	low	High Stand
352	55	low	High Stand
390	55	low	High Stand

Study Area

The study area is located in the Northeast of Iraq within the Gulneri Formation. The location of the study area is 44°26′ 23″ E and 36°12′ 43″N (Figure 1). The formation deposited in the upper part of Cretaceous. Lancaster was the first to describe the formation at the Dokan Dam site, highly folded zone of NNW Sulaimaniya Governorate, NE Iraq [31]. Lancaster describes 1.1-1.2 m of black bituminous, finely laminated, calcareous shale with some glauconite and collophane in the lower part of the formation. He describes the formation as a thin, highly condensed unit bounded by faults on the top and bottom of the formation. [32] studied the stratigraphy of the Gulneri Formation (Upper Cretaceous) in the section of Dokan area, Northeastern Iraq; the study indicated that the sediments of the Gulneri Formation consist primarily of organic–carbon rich black shale and represent a record of Ocean Anoxic Event II across the Cenomanian–Turonian boundary. The planktonic foraminiferal assemblages of the Gulneri Formation were described as being of Early Turonian age. [33] assigned Turonian age to the Gulneri formation in Zewa and Azmer, NE of Iraq based on the presence of *Helvetoglobotruncana Helvetica.* Another study by [34] suggest the Middle Turonian age to the Gulneri Formation in the north of Iraq. [24] assigned a Cenomanian age to the Gulneri Formation in the Degala section (study area of this project) based on the presence of *Guembelitria cenomana*.

Gulneri formation is a proximal to distal shelf depositional as indicated by studying palyno-facies and the ratio of palynomorphs, amorphous and phyto-clasts [35]. [33] describe the depositional environment of the Gulneri formation as being reduced with limited water circulation. [34] studied the Gulneri Formation in north Iraq and described the lithology of the Gulneri Formation as shaley limestone, rich in organic matter which was deposited in the middle-lower slope. The depositional environment of Gulneri formation in the Degala section was described as a tropical to subtropical environment, warm with an average temperature 30.3 ˚C, highly productive surface water within the continental shelf with an anoxic bottom water environment, and salinity between 34 and 37 [24]. A recent study of the Gulneri Formation by

[36] indicated that the depositional environment of the Gulneri formation was basinal deep water with slow sedimentation rate in an open sea shelf and outer shelf setting.

Sampling and Methodology

Sampling

Thirteen black shales samples were taken from the Gulneri Formation at the North East of Iraq located at 44°26′ 23″ E and 36°12′ 43″N. The outcrop belongs to the Degala section and is 4 meters thick. The samples were taken at different interval spacing between 40 cm and 20 cm. Fresh samples were taken by digging to avoid the weathered samples.

Methodology

Stable Isotope Geochemistry

Stable isotope analysis including carbon and nitrogen concentration and isotopic composition of total organic matter were determined. The thirteen samples were pre-treated using a procedure developed by the University of Kansas. Three grams of each sample were weighted and dried in an oven for overnight. 5% HCl was added to the samples and left to react overnight. The samples were rinsed after the carbonate was dissolved. The samples were dried in an oven at 45 °C overnight. The samples were weight into tin capsules and analyzed using an elemental analyzed coupled to an isotope ratio mass spectrometer at the University of California-Santa Cruz.

Trace and Major Elements

Samples were analyzed for Al, Fe, Co, Cu, V, Cr, Sr, Ca, Ba, TI, and Zn. The samples were dried in the oven over night. Then they were ground and sieved through 177 microns sieve resulting in two components: the <177 microns and >177 microns fraction. The <177 microns fraction was sent for analysis to the Australian Laboratory Services Labs (ALS) to determine the trace and major elements concentration following aqua regia digestion (ME-ICP 41).

Results

5.1 Organic Carbon Content (%C_{org}), Total Nitrogen (%N_{total}) and C/N ratios Organic carbon content varies throughout Gulneri Formation (Table 2). The average value of C_{org} was 10.2%. The highest value was 13.9 w% at 183 cm and the lowest value was 6.5 w% at 113 cm. The intermediate values ranged between 9-11% for the rest of the formation. At 93cm, 113cm, 272cm, and 312cm, the C_{org} recorded the lowest values 7.7%, 6.5%, 7.5%, and 7.6%, respectively (Table 2). Total nitrogen values were low throughout the formation. The total nitrogen ranged between 0.2% - 0.4%. Most of the samples had about 0.3% total N, except at 93cm, 113cm, and 183cm, which contained 0.2%, 0.2%, and 0.4%, respectively. C/N ratios of the Gulneri Formation were very high ranging from 26 to 39 with an average value of 34. The C/N ratios increased from the bottom to the top of the formation. A sharp decreased to a value of 29.1 occurred at 272cm (Table 2) and (Figure-2).

Table 2: Geochemical data of organic matter in Gulneri Formation

Thickness (cm)	%OC	δ^{15}N (%)	Wt %N	C/N	δ^{13}C (%)
8	12.1	-1.50	0.3	37.9	-24.45
48	12.7	-1.73	0.3	39.9	-24.56
93	7.7	-1.73	0.2	34.4	-24.35
113	6.5	-1.74	0.2	32.4	-24.47
127	10.8	-1.59	0.3	37.1	-24.46
147	11.8	-2.37	0.3	35.0	-25.54
165	10.1	-2.32	0.3	32.9	-25.57
183	13.9	-1.49	0.4	38.9	-25.71
233	11.6	-2.49	0.3	36.9	-25.79
272	7.5	-2.08	0.3	29.1	-25.40
312	7.6	-1.95	0.3	26.3	-26.26
352	10.4	-2.29	0.3	30.4	-26.38
390	10.1	-2.26	0.3	30.8	-26.29

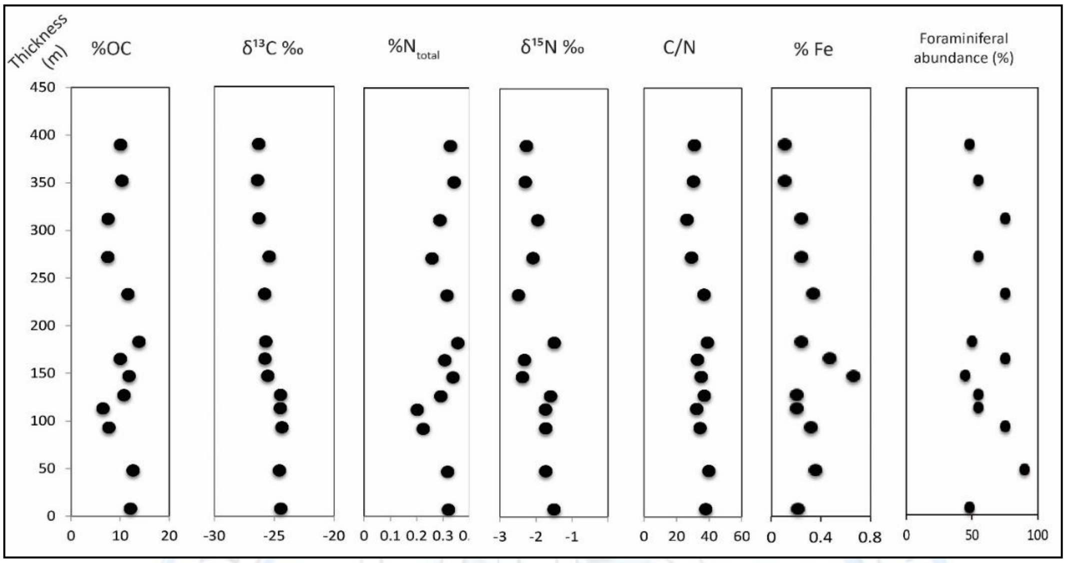

Figure 2: %OC, carbon and nitrogen isotopic compositions, C/N ration %Fe and foraminiferal abundance (%).

Carbon and Nitrogen Isotopic

Nitrogen isotopic ($\delta^{15}N_{org}$) values recorded negative values ranging from -1.49‰ to -2.37‰ with an average value -1.96‰. Carbon isotopic composition ($\delta^{13}C_{org}$) values reveals little variations ranging from -24‰ to -26‰ with an average value -25.34‰. Less negative values of $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ are seen at the bottom of the formation at 8cm, while more negative values are at the top of the formation at 390cm (Table 2) and Fig. 2.

Trace elements

The concentrations of trace and major elements in Gulneri Formation were low compared with other black shales from the Cretaceous period in other part of the world. Ca, Ba, Sr, Fe, P, V, Ni, CO, Cr were normalized to Al in order to illuminate the effect of allocanthous inputs. The general trend of the redox sensitive (trace) elements including Ni/Al, Co/Al, V/Al, and Zn/Al revealed high values between 1 and 4 meters up section except at meter 1.25 and 3 where the trend reflect a decline in the values (Table-2). A similar trend to the redox trace metals is also seen in Ba/Al, Ca/Al, an Sr/Al (Table 2). V concentrations range between 15ppm to 46ppm. Ni concentrations recorded lower values between 9ppm to 40ppm and Co concentrations are even lower between 1 to 2 ppm. Finally, Fe concentrations ranged between 0.11% and 0.48% whereas P concentrations were between 120 ppm to 1420 ppm (Table 3).

Table 3: Geochemical data of Gulneri Formation

Thick-ness	Al	Al	Ba	Sr	Ca	P	Ti	Ba\Al	Ca\Al	Sr\Al	P\Ti	Cr	Ni	Cu	V	Zn	Ni\Al	Cu\Al	Cr\Al	V\Al	Zn\Al
(cm)	%	ppm	ppm	ppm	%	ppm	ppm					ppm	ppm	ppm	ppm	ppm					
8	0.08	800	30	279	25	120	10	0.037	312.50	0.599	12	11	10	57	30	37	0.833	4.750	0.917	2.500	3.083
48	0.09	900	30	494	25	130	10	0.033	277.78	0.549	13	10	14	29	26	63	1.077	2.231	0.769	2.000	4.846
93	0.1	1000	30	522	25	210	10	0.03	250.00	0.522	21	12	16	26	31	54	0.762	1.238	0.571	1.476	2.571
113	0.09	900	30	469	25	130	10	0.033	277.78	0.521	13	9	11	53	25	39	0.846	4.077	0.692	1.923	3.000
127	0.13	1300	30	508	25	980	10	0.023	192.31	0.391	98	13	11	83	41	31	0.112	0.847	0.133	0.418	0.316
147	0.19	1900	30	382	25	1420	10	0.015	131.58	0.201	142	25	40	41	39	176	0.282	0.289	0.176	0.275	1.239
165	0.19	1900	30	356	25	1150	10	0.015	277.78	0.187	115	23	28	32	40	129	0.243	0.278	0.200	0.348	1.112
183	0.09	900	20	395	25	430	10	0.022	0.0222	0.439	43	11	13	16	46	31	0.302	0.372	0.256	1.070	0.721
233	0.11	1100	20	348	25	470	10	0.018	227.27	0.316	47	16	19	34	25	82	0.404	0.723	0.340	0.532	1.745
272	0.08	800	10	300	25	890	10	0.012	312.50	0.375	89	10	14	17	24	47	0.157	0.191	0.112	0.270	0.528
312	0.12	1200	10	226	25	1190	10	0.008	208.33	0.188	119	14	13	19	19	46	0.109	0.160	0.118	0.160	0.387

390	352
0.07	0.07
700	700
10	10
253	212
25	25
1220	1270
10	10
0.014	0.014
357.14	357.14
0.361	0.303
122	127
8	9
17	9
15	21
18	15
37	40
0.139	0.071
0.123	0.165
0.066	0.071
0.148	0.118
0.303	0.315

Discussion

Terrigenous sediment sources

In this study aluminum is used as proxy for land-derived sediments. Some major elements including Na, Mg, Si, K, Ti, and trace elements such as U, Th, Zr, and Cr have a clastic origin; variations in these elements provide information about detrital sediments influx. SI/Al and Ti/Al ratios are good indicator for Aeolian input; whereas K/Al, Mg/Al, and D* have been used to indicate the fluvial terrigenous input [37]; [38]. Generally, low aeolian input indicates humid environment and characterized by reducing Si/Al, Ti/Al, Zr/Al ratios and increasing K/Al and Mg/Al ratios[39]; [40]; [41]. In general, the Si/Al and Ti/Al ratios are low and homogenous throughout the Gulneri Formation (Figure-3). The grain size analysis indicates the presence of clay, silt and very fine sand [36]. These results reflects the lack of aeolian input deposition indicating by the very low ratios of Ti/Al. However, K/Al, Mg/Al ratios, and D* demonstrate the input if alluvial supply to the basin. Both K and Mg are part of the illite which was identified by X-ray diffraction in all samples. Also, positive relationship between K and Al (r^2: 9.4887)) (Figure-3) revealed the presence of illite. Hence, we can conclude that the climate during the formation of black shales was humid.

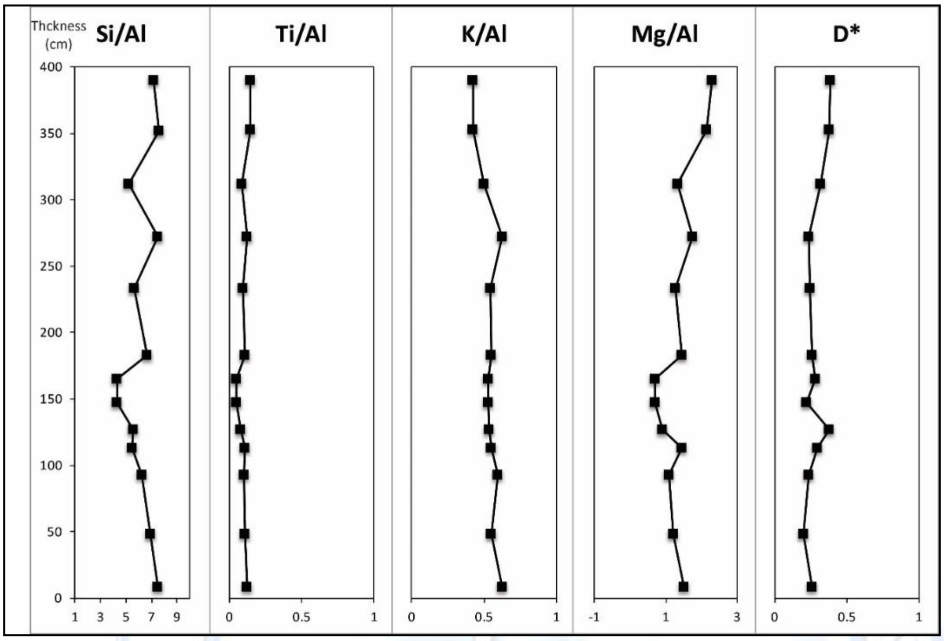

Figure 3: The Ti/Al, Si/Al, K/Al, Mg/Al ratios, and D* of Gulneri Formation.

Organic Contents %OC

Organic matter content is a good indicator of changing in surface productivity and burial processes in sediments [42]. Using total organic matter and foraminifera can aid the interpretation of surface productivity and diagenesis processes [43]. Indeed, total organic matter and foraminifera assemblages were used in the southeastern Brazilian continental shelf to determine water mass chemistry and marine productivity [44]. High organic carbon content typically indicates high paleo-productivity [45]; [46]; [47]; [48]; [49]. However organic matter can also originate from terrestrial sources. Terrestrial input is expected to also deliver minerals and hence can be identified by high Fe content. Peaks of organic carbon and Iron (%Fe) do not correlate in our sediments except at 147 cm where Fe concentration peaks with Corg (Figure 2). This supports the interpretation that the most important source of organic matter in the Gulneri Formation was from marine productivity with little input of terrestrial sources [49]. The %Corg of Gulneri Formation are high ranging from 6% to 13% and consistent with high productivity (Figure 2).The high organic input coincides with high abundance of planktonic foraminifera (Figure 2), which indicates again high surface water productivity during the deposition of Gulneri Formation. Some redox sensitive metals such as Ni, Cu, and Zn are delivered to the basin associated with weathering and input of terrigenous organic matter [50]. However, the abundance of these elements is not correlated with organic matter content. This result supports the interpretation that the source of organic matter was of marine origin. At 48cm, 147cm, and 312cm, the %C_{org} decreases although planktonic foraminifera are still abundant. This could potentially be explained by diagenesis and oxidation of the organic matter (Figure 2).

Total organic Nitrogen (TON) and Carbon/Nitrogen ratio (C/N)

TON and C/N are reliable proxies for identifying the sources of organic matter whether from algal or terrestrial origins [51]; [52]. C/N ratio over 20 reflects terrestrial organic matter; while ratios between 4-10 reflects marine sources [53]. Our records revealed high ratios of C/N throughout the formation indicating the terrestrial origin of the organic matter (Figure 2). Albian black shale from Demerara Rise also recorded high C/N ratios (20-40); the high ratios were attributed to the preferential recycling of nitrogen which increases the C/N ratio [54]. Low TON values and high C/N ratios suggest a similar process at our site thus we suggest that the degradation of nitrogen affected the C/N ratio. Thus, we potentially consider the source of organic matter is from marine origin. Another evidence that supports the interpretation that the source of organic matter is from marine origin (surface water productivity) is the positive relationship between TON and TOC with r^2 0.713 [19] (Figure 4).

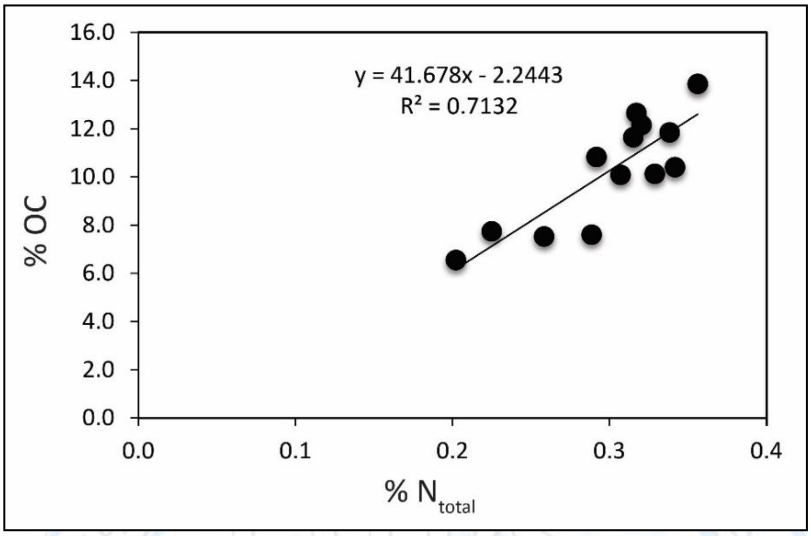

Figure 4: Illustrates the high correlation between % OC and % N_{total}, which indicates the source of nitrogen from organic origin.

Carbon Isotopic Composition (δ^{13}Corg)

Carbon isotopic composition (δ^{13}Corg) of sedimentary organic matter is a reliable proxy to distinguish between marine and terrestrial organic matter. Variations in the values of δ^{13}Corg ranging between −22‰ to −30‰ with an average −27‰ indicate terrestrial organic matter [55]; [56], whereas, marine organic matter ranging from −17‰ to −22‰ [57]. The $\delta^{13}C_{org}$ values at our section ranged from -26.38 to -24.35 (Figure 2) suggesting terrestrial origin. However, as we discussed in the previous sections, other observations suggest that the main source of organic matter was from marine algae. [58] reported low δ^{13}Corg (~−24‰) of marine organic matter in Arctic Fjord. Two processes could potentially explain the depletion of the $\delta^{13}C_{org}$; First, the $\delta^{13}C_{org}$values may be depleted as a result of digenetic effects which lead to removal of ^{13}C [53], [59]. Second, [60] suggest that the lower values of $\delta^{13}C_{org}$of marine organic matter during the Cretaceous period could be attributed to high atmospheric CO_2. [23] recorded high concentration of CO_2 during the Cretaceous period.The high atmospheric CO_2 during the Cretaceous period increased the fractionation of planktonic photosynthesis; the process caused depletion in the δ^{13}C of marine organic matter [61]. Therefore, we surmise that the organic matter in the section is of marine origin produced in a period with high atmospheric CO_2 and has undergone post depositional N mineralization (see below).

Nitrogen Isotopic Composition $\delta^{15}N_{org}$

Nitrogen isotopic composition is another proxy to determine the source of organic matter in sediments whether it is from terrestrial or marine sources. The $\delta^{15}N_{org}$ value of atmospheric N_2 is 0‰, whereas the $\delta^{15}N$ of nitrate in seawater ranges typically between +5‰ to +10‰ [62]. However, several factors including diagenesis impact the original signal of δ^{15}Norg values [19].Nitrogen cycling by bacteria in the sediment affects the signal of $\delta^{15}N_{org}$ in sedimentary organic matter and may cause depletion of $\delta^{15}N_{org}$ to negative signals [63]; [64]. The $\delta^{15}N_{org}$ values of Gulneri Formation are all negative ranging from -1.49 to -2.49 with an average -1.96 ‰ (Figure 2). These isotope values may be influenced by diagenetic processes, which in turn affect the interpretation of the data. However, the depletion of $\delta^{15}N_{org}$ values in our data coincides with a high C/N ratios hence it is not likely to be a of microbial origin (Figure 2).[62] recorded negative values of $\delta^{15}N_{org}$ for the black shale during the Cenomanian-Turonian periods and for sapropels from the Mediterranean-Pleistocene; he attributed the negative values to nitrogen fixing bacteria. [19] suggested that negative $\delta^{15}N_{org}$ values of the top phosphate member and the oil shale member, the Cretaceous period, in Israel, are due to the decomposition of amino acids via denitrification and or anammox. In our case study of the Gulneri Formation, we potentially believe that the negative values of δ^{15}Norg are due to the denitrification processes of amino acids or nitrogen fixation in the ocean. High C/N ratios and negative values of $\delta^{15}N_{org}$ support this interpretation [19] (Figure 2).

Trace elements as indicator for paleo-redox Redox-sensitive trace elements are valuable proxy to study the ancient and modern ocean [65]; [66]; [67]. Several factors impact the redox condition such as organic matter types, sediments accumulation rates, diagenetic and mineralization processes [68]. In general, the trace element concentrations in the Gulneri Formation are relatively low (Table 3) compared with other black shale samples during the Cretaceous. Enrichment of trace elements relative to Al is a useful tools to reconstruct paleo-deposition [11]; [14]; [69] Trace metals such as U, V, Mo, Cr, and Co are good indicators for paleo-redox; whereas Cu, Ni, Zn, and Cd, which are associated with organic matter, are useful for paleo-productivity [70]. High concentrations of Ni and Cu are good indicator for high organic matter influx that brings both elements to the sediments. Additionally these elements mayindicative of reduced conditions in the sediment [70].

In this study, we found high concentrations of V, Cu, Zn, Co, and Ni associated with high organic matter content. The ratios of these elements could be used to understand the redox conditions. The ratio of Ni/Co is a suitable indicator for oxygenation level [71] as is V/Cr [72]. Both these ratios were used by [66] for the same purpose. In addition, V/(V+Ni) has been used to examine the depositional environment in Pennsylvanian-age shale's [73]. Ni and V are present in prophyrin that was originally derived from chlorophyll and is typically preserved under anaerobic conditions [74]. Low Ni and V concentration reflect lower prophyrin content and could be due to the aerobic oxidation of organic matter [14]. High Ni/Co reflects anoxic conditions [66]. High V/Cr ratio above 2 indicates anoxic conditions [72] and high Ni/Co rations likewise [66]. In this project we used the ratios of Ni/Co, V/Cr and V/(V+Ni) to establish the redox condition during the deposition of Gulneri Formation (Table 3). Plotting Ni/Co down core reveals suboxic/anoxic conditions (Figure 5a). However, V/Cr ratios show the deposition environment ranged between oxic and dysoxic (Figure 5c). This result might be affected by detrital grains as demonstrated by the high correlation between Al and Cr (Figure 7). The detrital grains increase the concentration of Cr that leads to lower V/Cr ratio. Most of V/(V+Ni) ratio indicated suboxic/anoxic conditions during the deposition of the black shales except for samples 13 and 20, which show dysoxic environmental conditions (5b). This is consistent with the Ni/Co data (Figure 7a). Furthermore, the relationship between organic matter content and Ni/Co also suggests a suboxic/anoxic environment for the Gulneri Formation (Figure 7b). The fluctuations in the depositional environment between oxic, dyoxic, suboxic, and anoxic are attributed to changes in water chemistry.

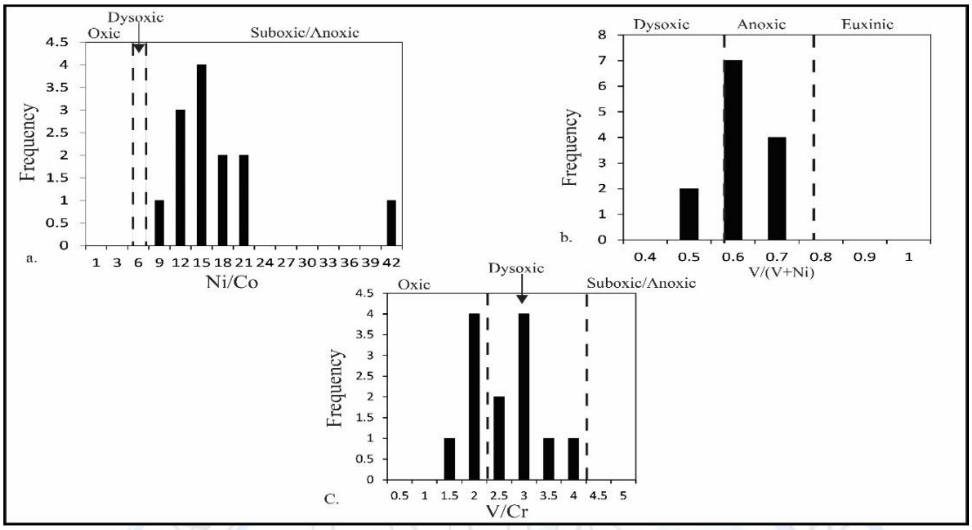

Figure 5: Plotting Ni/Co, V(V+Ni), and V/Cr with frequency shows different depositional environments in Gulneri formation.

If we assume that there is no effect of post-depositional alteration, we can see that suboxic/anoxic condition are associated with an increase in the accumulation of organic matter in the Gulneri Formation. However, in the case of a weak relationship between organic matter content and redox- sensitive elements, post-depositional processes including oxidation of organic matter post burial could modify organic matter accumulation rates. In addition to the diagenesis, changing in surface water productivity would affect the deposition of organic matter with high productivity resulting in higher organic matter burial.

Paleoproductivity and Oxygenation of the Gulneri Formation

Total organic matter (TOC) has been used to identify the paleoproductivity [75]; [76] at many time intervals and oceanic settings. TOC in sedimentary rocks reflected the surface water productivity and hence is useful for reconstruction of paleoproductivity rates [70].

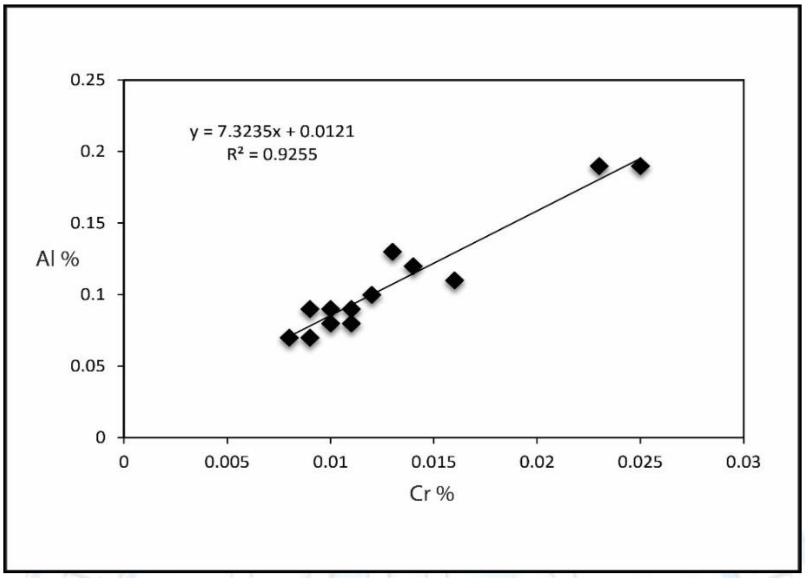

Figure 6: The high correlation between Al% and Cr%

In addition several specific elemental ratios including P/Ti [77], Ca/Al, Sr/Al [78], and Ba/Al [79]; [80]. are useful for the reconstruction of paleoproductivity rates. The ratio of P/Ti is a good indicator for the phosphate delivery to the sea bottom which does not including land derived sources [81]. Therefore, high P/Ti ratios indicate the source of phosphorous from biological activity [81]. Ca and Sr are typically associated with carbonate productivity and Ba with biogenic Barite [82]. The geochemical data of Gulneri Formation including Ca/Al, Ba/Al, Sr/Al, TOC and foraminifera abundance is used to document changes in paleoproductivity during the time the formation was deposited (Figure 9). Based on the above parameters, three periods represent high productivity; around 50cm, 200cm, and 350cm; whereas, lower productivity is seen at 150 cm and 300 cm (Figure 8). Paleo-oxygenation of Gulneri Formation was described by the following parameters: General trends ofNi/Al, Zn/Al, Cr/Al, V/Al, Cu/Al, and organic contents reveled variations in the paleo-oxygenation in the Gulneri Formation. These data provided three periods of time where the oxygen were elevated and two periods were depleted.

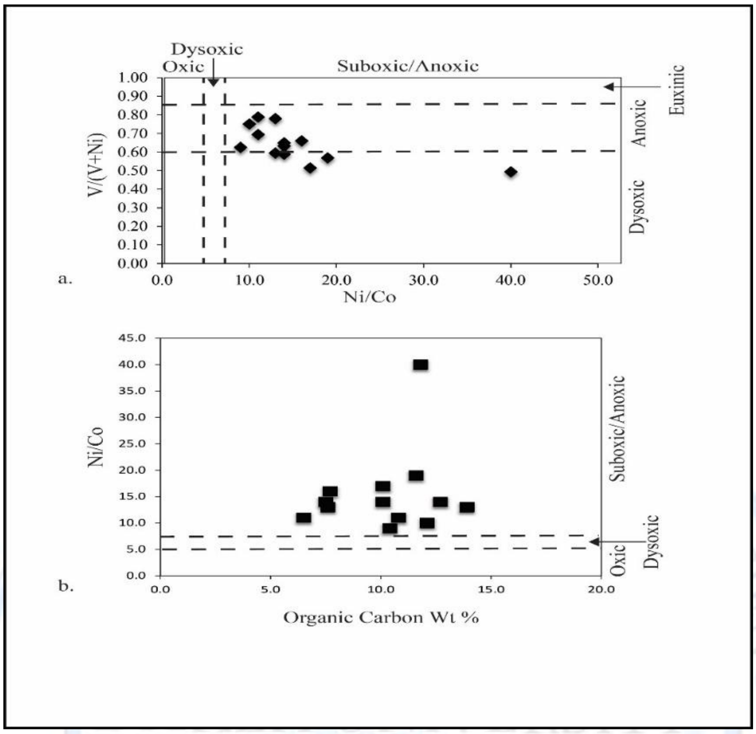

Figure 7: a. Plotting Ni/Co vs V/(V+Ni) shows anoxi and dyoxic environment for the Gulneri formation. **b**. Plotting Ni/Co vs. organic matter reveals suboxic/anoxic environment for the Gulneri Formation.

The oxygen was depleted in the following levels 8-50cm, 125-225cm, and 350-400cm supported by high concentrations of redox sensitive elements (Figure 9); however, the oxygen increased at 250-300cm and 50-125cm supporting by decreasing of redox sensitive elements and increasing Mn concentration (Figure 9). Grain size and sedimentation rate affect the oxidation of infaunal microhabitate [83]. Increase the rate of sedimentation and clay and silt particles affect the oxygenation by limit poor-water circulation [81]. The grain size analysis revealed sandy silt and silt particles in the basin. This supports our interpretation of variations of oxygen in the sea water.

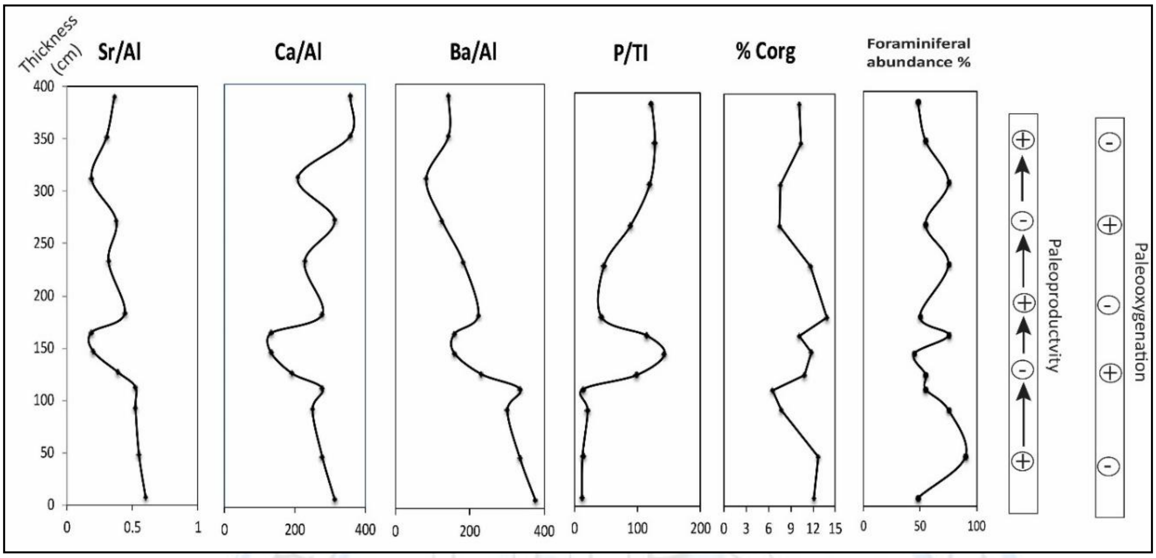

Figure 8: Plotting Sr/Al, Ca/Al, Ba/al, %OC, and foraminiferal abundance showing the paleoproductivity of Gulneri Formation.

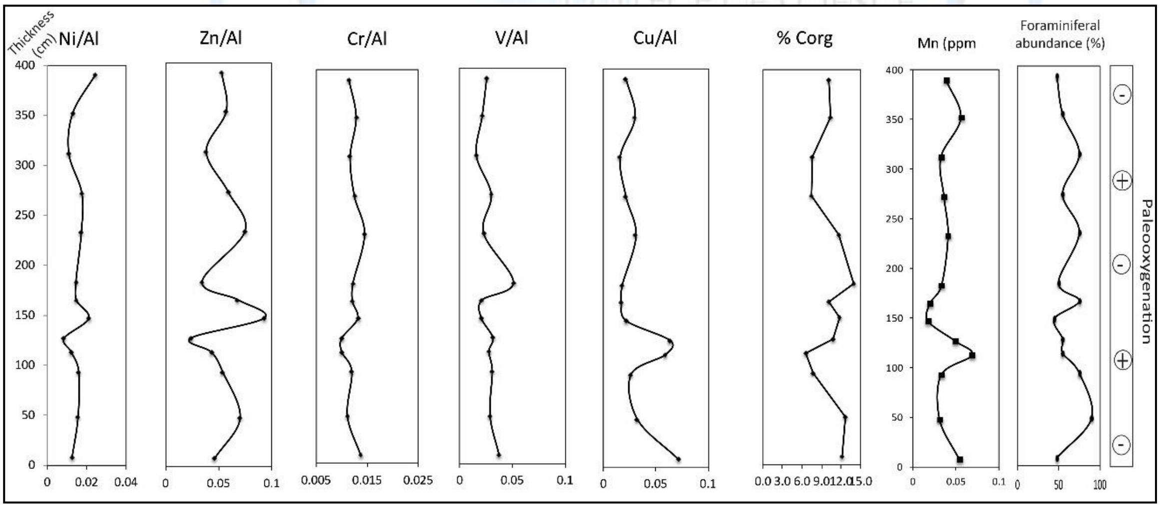

Figure 9: Plotting Ni/Al, Zn/Al, Cr/Al, V/al, Cu/Al, %OC, Mn (ppm) and foraminiferal abundance demonstrates the variation in the oxygen levels during the deposition of Gulneri Formation.

Conclusions

Variations in organic carbon contents, isotopes of nitrogen and carbon, trace elements, and foraminifera abundance provided a picture of the deposition of Gulneri Formation in Northwest/Iraq. The project provided the following findings:

1. The source of organic matter in Gulneri formation was marine with little input of land plants. Decrease in surface water productivity is reflected in the gradual decrease of organic carbon contents with times.
2. The low carbon isotopic composition values of organic matter are attributed to high CO2, which in turn increase the photosynthesis processes in the surface water.
3. Nitrogen isotopic composition values recorded negative values due to the denitrification processes of amino acids supporting by high C/N ratios and negative values of δ15Norg or by nitrogen fixation.
4. Trace elements provided information about the paleodepositon of Gulneri Formation. Fluctuations in the depositional environment among oxic, dyoxic, suboxic, and anoxic are attributed to the changes in water chemistry.
5. Paleoproductvity and paleo-oxygenation varied in the Gulneri Formation due to the surface water production and foraminiferal species.

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