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# Anoxic Marine Conditions Recorded from the Middle Paleozoic Black Shales (Kaista and Ora formations), Northern Iraq: A multi-Proxy Approach

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# Abstract

The shale units of the Late Devonian to Early Carboniferous successions of the Kaista and Ora formations from extreme northern Iraq have been studied for their geochemical and mineralogical features to reconstruct paleoenvironmental conditions. The Chemical Index of Alteration (CIA; high values ~93-99), high, Plagioclase Index of Alteration (PIA ~92– 98), and the A-CN-K plot indicate the studied shales have undergone intense weathering at the source area. Also, high kaolinite content and predominance of kaolinite over illite in the studied shale support this conclusion. The Rb/K and Sr/Ba ratios of the Kaista and Ora formations indicate freshwater to brackish water during deposition. Geochemical investigations, using redox-sensitive trace elements ratios such as V/ (V + Ni), Th/U, and U index suggest deposition of the Ora black shales under anoxic marine conditions, thus recording an ocean anoxic event in the region. Geochemical variations in the concentrations of some major and trace elements and their elemental ratios such as an increase in the Rb, K<sub>2</sub>O, Th, K/Al, and TOC values and a decrease in the Zr/Al, Ti/Al, Mo, P, Zn, and Zr, from the Kiasta upward to the Ora Formation indicate the transgressive systems tract (TST) of the Kaista-Ora sequence. Paleo-productivity indicators (P content, P/Ti, and P/Al ratios) suggest lower productivity and the paleoredox conditions in the Ora shales play an important role in the preservation of organic matter. The ternary diagram of Co–Zn–Ni, Co/Zn, U/Th, and Ba/Sr ratios indicates that there was hydrothermal activity in the basin during the deposition.

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#### 1. Introduction

Anoxic event.

Shale (mostly calcareous) represents one of the main lithofacies in the succession of Devonian-early Carboniferous Kaista and Ora formations from extreme northern Iraq intercalated with sandstones, siltstones, and limestone (dominantly dolomitic). The studied succession is hydrocarbon-promising in the northern part of Iraq (Al-Hadidy, 2007; Aqrawi et al., 2010; Abdula et al., 2020) and prospective in the western desert near Jordan, Saudi Arabia, and Syria.

A combination of the mineralogical and chemical composition of siliciclastic rocks (sandstones and shales) commonly is used as a tool to determine the paleoenvironmental conditions and provenance history of these rocks (Armstrong-Altrin et al., 2004; Jafarzadeh and Hosseini-Barzi, 2008; Dostal and Keppie, 2009; Armstrong-Altrin, 2009; Armstrong-Altrin et al., 2015, Khazaei et al., 2018, Akkoca et al., 2019 ) and to evaluate weathering processes and paleogeography (Absar et al., 2009; Ranjan and Banerjee, 2009; Zimmermann and Spalletti, 2009; Armstrong-Altrin et al., 2013; Tobia and Mustafa, 2019; Akkoca and Karatas, 2019).

formations did not get enough attention in the geologic studies of the study area. Most of the studies were focused on the middle Paleozoic sequence in terms of sequence stratigraphy (Al-Juboury et al, 2012), facies and depositional environment (Al-Juboury and Al-Hadidy, 2008), palynostratigraphy (Sherwani et al., 2010), oil and gas generation based on palynology (Abdula et al., 2020).

The present work aims to address the paleoenvironmental conditions, including paleoclimate, paleosalinity, paleoredox conditions, transgressive system tract, paleoproductivity, and hydrothermal activity of the middle Paleozoic (Devonian-Carboniferous) shales in the Kaista and Ora formations.

#### 2. Materials and Methods

Shale samples were collected from the Middle Paleozoic Kaista and Ora formations of the Ora type section, northernmost Iraq, representing various mineralogical and geochemical characteristics to achieve the goals of the present study.

These samples were studied as follows:

#### 2.1. X-ray diffraction (XRD)

Twenty-one samples from the Kaista (5 samples) and

The middle Paleozoic shale of the Kaista and Ora

Ora (16 samples) were selected and analyzed by XRD to identify the mineralogical composition. The investigation was carried out on bulk rock samples at the Premier Laboratory in Houston, Texas, USA., using a Bruker D8 Advance XRD instrument. Quantification of mineral phases in the bulk diffraction pattern is accomplished using the TOPAS software package.

#### 2.2. Scanning electron microscopy (SEM)

Eight samples were selected for SEM analysis to identify the clay minerals' main detrital and diagenetic elements, as well as mica, feldspar, quartz, and carbonate minerals. The analysis was conducted using a Camscan MV 2300 SEM with a calibrated energy dispersive X-ray analysis system on gold-coated samples at the Institut für Geowissenschaften-Geologie, University of Bonn, Germany.

# 2.3. X-ray fluorescence (XRF)

The Geochemical analysis of major and trace elements for 21 shale samples (5 and 16 from the Kaista and Ora formations respectively) was done using the portable Bruker Tracer 5i Energy-Dispersive X-Ray Fluorescence (ED-XRF) instrument. Analyses were performed at the Premier Laboratory in Houston, Texas, USA.

## 2.4. Total organic carbon (TOC) content

Twenty-one samples of shales from the Kaista (5 samples) and Ora (16 samples) were analyzed for their Total Organic Carbon using the LECO C230 instrument, which requires decarbonization of the rock sample by treatment with hydrochloric acid (HCl). This is accomplished by soaking weighted samples for two hours in concentrated HCl. The acid is then removed by rinsing the samples with water and flushing them through filtration equipment. The filter is then removed, placed into a LECO crucible, and dried in a lowtemperature oven (110°C) for 4 hours. Samples were weighed after this process to obtain a percent carbonate value based on weight loss. The Leco instrument is calibrated with a standard of known carbon values. Furthermore, the standard is analyzed as an unknown for every 10 samples to check the variation and calibration of the analysis. Random and selected reruns are done to verify the data. The acceptable standard deviation for TOC is a 3% variation from the established value.

# 3. Geological Setting and Paleogeography

Iraq lies in the border area between the major Phanerozoic units of the Middle East, i.e., between the Arabian part of the African Platform (Nubio-Arabian) and the Asian branches of the Alpine tectonic belt. The platform part of the Iraqi territory is divided into two basic units, i.e., a stable and an unstable shelf (Fig. 1). The stable shelf is characterized by a relatively thin sedimentary cover and a lack of significant folding. The unstable shelf has a thick and folded sedimentary cover and the intensity of the folding increases toward the northeast (Buday,1980).

The Devonian-Early Carboniferous time was interpreted

as a period of extension and compression that resulted from the Hercynian orogeny and development of the intracratonic basin (Tectonic Megasequence AP4; Sharland et al., 2001). At that time, widespread marine shales and limestones were deposited in intracratonic basins throughout the central part of the Arabian Plate in Iraq, Syria, and Turkey (Jassim and Goff, 2006). The wide shelf sea of this basin was located between tropical and subtropical regions of the southern hemisphere and their areal extent changed in response to succeeding transgressions and regressions (Beydoun, 1991).

The middle Paleozoic (Late Devonian-Early Carboniferous) sedimentary succession of Iraq is represented by the Kaista, Ora, and Harur formations. They extend from the western part of Iraq to the Ora area of northernmost Iraq (Fig. 1). This succession is composed of siliciclastic-carbonate facies and was considered to be deposited in a subsiding basin with a wide geographic distribution reflecting epicontinental or epeiric seas setting in a homoclinic ramp in a transgressive system tract (TST) (Al-Hadidy, 2007; Al-Juboury and Al-Hadidy; 2008, 2009; Al-Juboury et al., 2012).

The Kaista Formation is about 70 m thick (Fig. 2). It consists of heterogeneous clastics of sandstones intercalated with siltstones and calcareous shale and represents the transition between the continental-fluvial deposition of Pirispiki Formation and those of shallow-marine deposits of the Ora Formation. The depositional environment of the Kaista Formation is interpreted to be a mixed fluvial-marine system (Al-Juboury and Al-Hadidy, 2008).

The Ora Formation is more than 220 m thick and characterized by its shale lithofacies that intercalate with subordinate sandstones, siltstones, and dolomitic units (Fig. 2). It represents the transition between the mixed (fluvialmarine) clastics of the Kaista Formation and the carbonates of the Harur Formation. The black micaceous and calcareous shales of the Ora Formation were deposited in a subtidal shelf environment Sharland et al. (2001). The Harur Formation represents the termination of the overall transgressive Late Devonian-Early Carboniferous sequence, in which the facies are dominantly carbonates, alternated with dolomitic shale and thin sandstones. These carbonates are commonly dolomitized and are similar to other Paleozoic carbonates in the geologic record (Wilson, 1975). The Harur Formation was deposited in a shallow-marine environment and is a continuation of the ramp setting of the Ora Formation.

The studied formations are recorded in wells Akkas- 1, Key Hole KH 5/1, and Khleisia-1 with a thickness ranging from 45-104 m for the Kaista Formation and from 100–300 m for the Ora Formation (Al-Hadidy, 2001; Gaddo and Parker, 1959; Al-Haba et al. 1991, 1994). These formations crop out in the Kaista and Harur areas, near the Khabour Valley, and in the Geli Sinat and Derashish areas northwest of Shiranish, Amadia district of extreme northern Iraq (Fig. 1).



**Figure 1.** A- Structural provinces of Iraq modified after Jassim and Goff (2006) showing the location of wells referred to in the text. The location of map C- is indicated by the black box. B- Inset map shows countries neighboring Iraq; the location of map A is indicated by the red box. C- Geological map of northern Iraq modified after Sissakian (2000) showing the location of the Ora type section.



Figure 2. Lithological section of the studied formations at Ora type section of northernmost Iraq with sample locations and geochemical parameters indicative of transgressive system tract (TST), see Tables 2 and 3 for values and ratios.

## 4. Results

## 4.1. Mineralogical study

# 4.1.1. XRD analysis

Mineral compositions of the shale samples from XRD analyses have revealed that they consist mainly of clay minerals represented by mixed layered Illite/smectite (I/S), followed by varying amounts of illite/mica (I/M), pyrophyllite, kaolinite, and chlorite (Fig. 3). Other non-clay minerals include quartz, feldspars (k-feldspar and plagioclase), calcite, Fe-dolomite (ankerite), goethite, rutile, and a few pyrite (Table 1).

The main carbonate mineral phases are calcite and a few Fe-rich dolomites (ankerite). In general, the studied shales are carbonate-rich.  $CaCO_3$  ranged from 1.5-16.8 wt% in the Kaista shale, and 5.8-34.8 wt% in the Ora shale (Table 2).

# 4.1.2. SEM study

SEM study shows that shale is composed mainly of hexagonal degraded kaolinite plates (Fig. 4A-B). Illite is commonly found in the form of fibers or platy illite as intergrown on kaolinite grains and mica (Fig. 4A-B). Illite/ smectite (I/S) is present in the form of interlocked fibers (Fig. 4C). Fractures and vugs/pores are commonly present in the studied samples (Fig. 4A-D). Carbonates are dominated by calcite and/or dolomite and occur as fine grains and/or lumps either filling fractures and pore space or distributed randomly throughout the matrix (Fig. 4B).

# 4.2. Elemental Geochemistry

The major and trace element analysis results of the shale from the middle Paleozoic (Kaista and Ora) formations are presented in Tables 2 and 3 respectively.

## 4.2. 1. Major elements

The average concentration of major element oxides of shale samples from Kiasta is enriched in the absolute abundances of SiO<sub>2</sub> (53.02%), Al<sub>2</sub>O<sub>3</sub> (18.18%), Fe<sub>2</sub>O<sub>3</sub> (7.06%), K<sub>2</sub>O (4.216%), CaO (2.69%), MgO (2.25%), TiO<sub>2</sub> (1.21%), Na<sub>2</sub>O (0.17), P<sub>2</sub>O<sub>5</sub> (0.11%) and MnO (0.05%). In contrast, the major element oxide concentrations of shales from Ora are characterized by narrow compositional variations and are enriched in the absolute abundances of SiO<sub>2</sub> (52.01%), Al<sub>2</sub>O<sub>3</sub> (20.36%), Fe<sub>2</sub>O<sub>3</sub> (8.45%), K<sub>2</sub>O (2.98%), MgO (1.59%), CaO (1.39%), TiO<sub>2</sub> (1.39%), Na<sub>2</sub>O (0.77%), P<sub>2</sub>O<sub>5</sub> (0.12%) and MnO (0.05%).

The EFs (enrichment factors) averages of the major elements relative to the average shale (AS), K, Ca, Mg, and Na in the Kaista shale and are more enriched than those of the Ora shale, while Fe, A, and Na are more enriched in the Ora shale (Fig. 5A).

## 4.2. 2. Trace elements

The concentrations of the trace elements are presented in table-2. On average, the elemental content of shale from Kaista, is phosphorus (P: 596), barium (Ba: 552 ppm), and sulfur (S: 1439. ppm. In contrast, their corresponding average values in Ora shale are 493 ppm, 509 ppm, and 6959 ppm respectively. The concentrations of these elements are significantly higher than Mo, Co, and Zn, whose average concentration values from the Kaista and Ora shale are 21, 7, 128 ppm, and 7, ~3, 51 ppm, respectively.

Based on the enrichment factor averages, the Ora shales are enriched in Pb, Ga, V, Cr, and Ni, compared with Kaista shales, which are relatively enriched in U, Th Mo, Zr, Ba, Rb, Sr, Zn, Cu, and Co (Fig. 5B).



**Figure 3.** Representative X-ray diffractograms of the main clay and non-clay minerals components in the studied shales. K=Kaolinite; I/S= Illite/Smectite; I=Illite; I/M=Illite/Mica; Ch=Chlorite, Qz= Quartz; C= Calcite; F= Feldspar; R=Rutile; G=Goethite.

Pyrite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.7	0.0	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.7	1.0	0.7	0.7	0.9	0.0	0.5	1.0	0.8	1.2	1.1	0.6	0.8	0.0	0.7	0.8	0.5	0.8	0.5	0.7	1.0
Goethite	5.7	5.1	2.9	6.7	2.0	0.0	5.9	8.2	7.5	3.0	3.9	2.5	3.3	1.4	0.9	0.6	0.0	4.6	1.3	6.7	6.5
Dolomite	1.7	0.8	0.0	0.0	9.0	0.0	0.5	0.0	9.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.5	1.3	1.2	0.9	0.0
Calcite	2.4	1.8	15.3	11.4	9.4	28.9	26.4	0.6	0.6	2.1	0.0	0.0	0.0	0.0	1.5	1.5	15.2	1.8	0.9	0.0	0.7
Feldspars	7.6	2.6	3.1	8.2	8.1	0.7	5.1	1.8	3.3	4.1	9.8	6.2	1.6	3.1	5.8	6.7	2.5	4.1	3.1	0.0	0.2
Quartz	28.2	24.6	15.8	12.8	27.9	29.1	24.4	24.4	33.0	8.9	28.6	57.7	20.9	72.7	25.3	19.6	44.2	33.3	42.2	36.6	65.4
Chlorite	1.7	1.3	5.8	5.6	2.1	5.7	4.8	2.9	0.0	0.0	4.9	2.4	0.0	0.0	0.0	0.0	2.3	2.5	0.0	0.0	3.5
Kaolinite	0.0	02	1.1	0.9	1.0	0.0	0.0	2.9	2.1	10.1	8.5	1.7	13.0	0.0	7.9	8.0	0.0	0.0	0.0	5.8	2.5
Pyrophyllite	2.4	0.4	1.6	0.5	2.0	5.1	0.0	1.7	3.0	12.4	9.6	3.8	13.0	5.0	12.2	12.1	0.0	0.0	0.0	0.0	0.0
Illite/Mica	22.5	31.1	21.1	12.6	4.2	18.1	12.3	16.0	24.4	23.3	26.2	18.4	14.7	8.8	13.7	17.6	19.3	25.8	27.1	25.2	9.6
Mixed I/S	28.9	28.6	30.0	34.6	34.3	34.0	33.7	10.0	33.3	22.6	23.7	24.5	17.8	28.7	4.9	32.0	32.9	25.7	23.4	22.1	5.0
Sample No.	Ora 21	Ora 20	Ora 19	Ora 18	Ora 17	Ora 16	Ora 15	Ora 14	Ora 13	Ora 12	Ora 11	Ora 10	Ora 9	Ora 8	Ora 7	Ora 6	Kaista 5	Kaista 4	Kaista 3	Kaista 2	Kaista 1

Table 1. Mineralogical composition (percent) of the studied selected samples from the Kaista and Ora formations.

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Sample No.	TOC	$SiO_2$	$AI_2O_3$	$TiO_2$	${\rm Fe}_2{\rm O}_3$	MnO	MgO	CaO	$K_2O$	$Na_2O$	$P_2O_5$	Sum	CIA	PIA	ICV	K/AL	CaCO <sub>3</sub>
Ora 21	5.00	61.12	28.59	2.56	1.78	0.03	0.50	0.11	3.40	0.49	0.15	98.73	98.30	98.07		0.19	5.80
Ora 20	3.86	60.66	24.31	2.21	3.69	0.03	0.64	0.28	2.58	0.78	0.10	95.28	96.84	96.47		0.17	6.62
0ra 19	0.52	64.53	10.92	0.57	5.08	0.01	0.21	0.61	1.01	0.80	0.20	83.49	93.07	92.41	0.70	0.15	11.15
Ora 18	3.95	52.50	23.33	1.51	8.55	0.05	1.15	0.50	2.29	1.08	0.11	91.07	95.51	95.05	0.63	0.15	10.63
Ora 17	1	44.80	8.22	0.62	12.04	0.02	0.77	1.27	0.61	0.61	0.38	69.43	92.97	92.45	1.79	0.12	15.23
Ora 16	1.62	49.19	19.84	1.48	10.39	0.07	1.54	1.72	2.39	1.06	0.02	87.07	94.79	94.12	0.86	0.19	16.88
Ora 15	1.7	54.27	30.29	2.23	6.16	0.05	0.95	0.47	4.00	0.93	0.10	99.45	96.97	96.52	0.47	0.21	10.28
Ora 14	0.9	52.16	19.53	1.11	9.30	0.05	1.85	1.06	2.81	0.93	0.10	88.90	95.43	94.70	0.82	0.23	14.48
Ora13	0.39	48.72	20.59	1.47	10.98	0.07	2.34	0.63	2.52	1.30	0.10	88.72	93.97	93.19	0.91	0.19	11.08
Ora 12	0.58	52.78	16.59	0.98	9.39	0.07	2.04	0.79	2.85	0.46	0.10	86.05	97.23	96.67	0.95	0.27	13.06
Ora 11	1.19	43.31	20.77	1.14	10.83	0.07	2.54	6.70	2.99	06.0	0.02	89.27	95.31	94.56	0.89	0.23	34.8
Ora 10	0.93	46.71	20.91	1.19	11.32	0.07	1.83	1.55	3.43	0.77	0.10	87.88	96.35	95.66	0.89	0.26	15.30
Ora 9	0.71	46.76	20.72	1.18	11.29	0.07	1.98	1.53	3.43	1.06	0.10	88.12	95.03	94.11	0.92	0.26	15.01
Ora 8	1.16	48.65	20.89	1.36	9.52	0.05	1.86	2.36	4.05	0.47	0.01	89.22	97.59	97.03	0.83	0.30	22.3
Ora 7	0.93	53.22	21.17	1.41	7.37	0.05	2.49	0.77	4.86	0.29	0.10	91.73	98.60	98.20	0.78	0.36	12.0
Ora 6	0.63	52.83	19.15	1.27	7.53	0.05	2.65	1.94	4.37	0.45	0.01	90.25	97.51	96.80	0.85	0.36	21.94
Average	1.57	52.01	20.36	1.39	8.45	0.05	1.58	1.39	2.98	0.77	0.11	89.94	95.97	95.38	0.88	0.23	14.78
.Max	5.00	64.53	30.29	2.56	12.04	0.07	2.65	6.70	4.86	1.30	0.38	99.20	98.60	98.20	1.79	0.36	34.8
.Min	0.39	43.31	8.22	0.57	1.78	0.01	0.21	0.11	0.61	0.29	0.01	80.76	92.97	92.41	0.47	0.12	5.8
Kaista 5	0.19	51.73	13.60	1.02	9.93	0.06	2.63	2.29	1.68	0.42	0.17	82.95	96.74	96.29	1.16	0.19	8.36
Kaista 4	0.29	47.46	20.92	1.00	11.25	0.06	1.49	0.91	3.80	0.18	0.10	86.27	99.07	98.86	0.85	0.28	3.36
Kaista 3		60.83	21.16	1.61	3.01	0.02	2.33	0.10	6.19	0.10	0.00	95.17	99.52	99.32	0.63	0.46	1.49
Kaista 2	5.00	54.18	18.73	1.71	6.82	0.04	2.79	0.70	5.26	0.10	0.10	89.87	98.89	98.46	0.90	0.44	2.06
Kaista 1	3.86	50.90	16.50	0.71	4.26	0.04	1.98	9.43	4.15	0.07	0.24	88.22	98.62	98.16	0.69	0.39	16.78
Average	2.3	53.02	18.18	1.21	7.05	0.05	2.25	2.69	4.22	0.17	0.12	88.50	98.57	98.22	0.85	0.35	6.42
max	5.0	60.83	21.16	1.71	11.25	0.06	2.79	9.43	6.19	0.42	0.24	95.17	99.52	99.32	1.16	0.46	16.78
Min	0.19	47.46	13.60	0.71	3.01	0.02	1.49	0.10	1.68	0.07	0.00	82.95	96.74	96.29	0.63	0.19	1.49

Table 2. Major-element oxides (in wt%) and the chemical index of alteration (CIA), plagioclase index of alteration (PIA), and index of chemical variability (ICV) from the Kaista and Ora formations.

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Ba/ Sr	0.00	0.00	23.44	30.88	35.01	4.41	0.00	7.78	1.90	13.92	2.59	7.41	6.55	2.47			11.17	35.01	1.90	1.79	6.61	27.11		3.54	9.76	27.11	1.79
Rb/K	0.003	0.005	0.000	0.006	0.005	0.005	0.005	0.006	0.006	0.006	0.006	0.005	0.005	0.005	0.005	0.006	0.005	0.006	0.000	0.004	0.005	0.005	0.004	0.005	0.004	0.005	0.003
Sr/ Ba			0.04	0.03	0.03	0.23		0.13	0.53	0.07	0.39	0.13	0.15	0.40	0.53		0.22	0.53	0.03	0.56	0.15	0.04		0.28	0.26	0.56	0.04
Ti/ Al	0.10	0.10	0.06	0.07	0.09	0.08	0.08	0.06	0.08	0.07	0.06	0.06	0.06	0.07	0.08	0.08	0.08	0.10	0.06	0.08	0.05	0.09	0.10	0.05	0.08	0.10	0.05
Zr/Al	16.56	24.00	42.01	14.37	49.36	17.57	8.84	13.52	20.25	15.88	14.56	18.81	18.68	19.76	22.54	25.42	21.38	49.36	8.84	76.91	46.17	48.31	36.61	60.59	53.72	76.91	36.61
IV/AI	4.63	4.09	2.40	9.69	3.04	0.30					3.77			.80		.08	5.64	3.04	80.	0.98		.66		06.03	4.18	06.03	.66
Ti H	.04 4	.03 3	26 15	.05 3	.45 38	.01 1	00.	00.	00.	00.	10.	00.	00.	.01	00.	.00	.10 7.	.45 38	.00	.12 10		00.		.25 12	.12 7	.25 12	00.
U) II	75 0	78 0	83 0	71 0	0 00	68 0	72 0	54 0	81 0	28 0	48 0	54 0	58 0	57 0	17 0	37 0	61 0	0 00	17 0	89 0	67	64 0	57	49 0	65 0	89 0	49 0
 	4 1.	7 1.	8	0 1.	2.	7 1.	8	8 1.	1	9 1.	6 1.	9 1.	0 1.	3 1.	3 1.	7 1.	4	3 2.	8 1.	7 1.	0 1.	6 1.	3 1.	2 1.	6 1.	2 1.	
Th	9 0.4	3 0.3	8 0.2	9 0.5		4 0.5	6 0.4	3 0.8	8 0.3	9 1.6	4 1.0	3 0.8	4 0.8	0 0.8	7 2.1	3 1.3	7 0.8	8 2.1	7 0.2	2 0.1	7 0.6	2 0.6	0 0.8	8 1.0	4 0.6	2 1.0	8 0.1
	2 2.2	1 2.7	3 3.5	4 1.9		4 1.7	2 2.0	1.1	3.18	1 0.5	8.0.9	6 1.1	0 1.2	8 1.2	0.4	0.7.	3 1.6	2 3.5	0.4	0 5.8	4 1.6	3 1.5	1.2	8 0.9	1 2.2	4 5.8	3 0.9
/ Sr	7 18.9	5 5.9	4 2.2	7 1.6	5 1.0′	·6·0 (	4 5.3	4 2.4	3 0.70	0 2.5	5 3.3	2 4.6	3 4.5	2.2	5	5	5 4.0	5 18.9	5 0.70	9 5.2	2 11.4	2 4.7	0	2 6.2	5 6.9	9 11.4	2 4.7
Ga	0.27	0.35	0.5	0.3	9.55	7 0.3(	0.2	1 0.2	0.33	0.20	5 0.25	0.22	7 0.23	7 0.21	5 0.16	7 0.16	0.8	9.55	0.16	0.59	5 0.32	0.12	0.12	0.12	0.2	0.59	0.12
Cr			1.78	0.65	3.15	1.07	0.0(	1.64	1.4(	1.96	2.35	1.8(	1.97	1.57	.0.9	1.37	1.67	3.15	0.65	1.5(	2.46		0.47	1.77	1.55	2.4(	1 0.47
Ni/ Co	7.3	5.2	10.0				8.6								19.0		T.T	19.0	5.2			5.15		2.64	3.89	5.15	2.64
V/ (V+NÌ)			0.84	0.80	0.86	0.77		0.84	0.81	0.86	0.87	0.84	0.85	0.87	0.79	0.84	0.84	0.90	0.78	0.84	0.84		0.65	0.91	0.81	0.91	0.65
Ba	0	0	513	585	1038	181	0	509	82	613	273	890	921	158	354	0	510	1038	82	183	781	639		608	552.73	781.10	183.06
>	0	0	155	112	240	154	0	219	202	224	312	235	251	245	148	197	207	312	112	187	285		73	250	199	285	73
Mn	205	223	115	354	189	566	372	421	558	506	578	545	546	422	365	377	396	578	115	457	482	192	341	304	355	482	192
Cr	283	232	87	173	76	144	224	133	138	114	133	130	128	156	156	144	153	283	76	124	116	189	156	142	145	189	116
'n	18	17	~	12	∞	13	23	6	20	5	6	12	13	12	9	6	12	23	5	Ξ	10	21	18	10	14	21	10
Mo	17	25	16	9	12	2	-	3	5		4	5	S	9	~	10	~	25	-	26	23	19	14	23	21	26	14
· Nb	1 21	9 24	3 20	7 16	5 17	4 16	2 13	) 13	1 18	9 13	) 14	8 17	5 17	8 18	2 20	8 20	8 17	9 24	9 13	4 37	1 36	1 38	3 27	9 35	9 35	4 38	3 27
Zr	) 25	306	1 240	177	3 215	2 182	142	14(	5 22	3 139	16(	208	1 20:	218	252	7 258	208	1 30	130	) 554	1 511	1 54	365	520	496	) 554	1 36
	7 4(	3 51	12	) 52	10	42	1 25	5 22	46	4 23	6 33	0 33	1 37	4 35	32	23	45	1 12	9 22	2 55	8 54	4 24	52	2 26	4 38	2 55	5
p S	9 6	6 5.	3	4	<u></u>	1 4	9 13	.4 6:	11	35 4.	5 10	8 12	57 14	6 6	9	0 10	27 6	l6 14	=	5 10	00 11	31 22	4	5 17	33 10	34 17	5 2
Lh R	8	6 9	5	6 9	0	7 1	1 L	8 12	6 1(	8	9 12	1;	=	0 10	4 2	2 19	9	[4 2]		3	6 1(	4 2	5 23	0 10	9 1:	15 23	3
	0	5	4	0	0	0	0	0	0	0	0	0	0	0	0	0	80	.25	92	4	-	6	5	5	4	6	-
Pb	15	16	15	18	20	16	16	12	10	15	13	14	4	13	13	16	15 3	20 4	10	15	6	6	24	13	14	24	6
As	12	15	12	19	21	16	14	6	9	13	Ξ	12	13	11	6	14	13	21	9	17	3	2	27	~	12	27	7
Ga	33	33	12	34	17	35	44	29	33	28	36	34	36	34	35	30	32	44	12	20	32	27	27	20	25	32	20
Zn	9	17	33	22	54	78	12	96	74	97	103	53	52	57	40	28	51	103	9	478	09	28	51	23	128	478	23
Cu	4	6	10	12	28	4	25	27	61	18	31	26	31	28	16	21	24	61	4	20	10	5	121	27	37	121	5
N	22	26	30	29	39	45	26	43	48	37	48	45	46	38	38	38	37	48	22	36	53	29	39	25	37	53	25
ů ·	3	5	3	0	0	0	3	0	0	0	0	0	0	0	2	0	3	5	2	0	0	9	0	10	~	10	9
Sample No	Ora 21	Ora20	Ora 19	Ora18	Ora 17	Ora 16	Ora15	Ora 14	Ora13	Ora12	0ra 11	Ora10	Ora9	Ora8	0ra7	Ora 6	Avg	Max	Min	Kaista5	Kaista 4	Kaista3	Kaista2	Kaistal	Avg	Max	Min



**Figure 4.** Scanning electron microscopic (SEM) images of the Kaista and Ora shales illustrate; (A and B) Degraded kaolinite plates (K), the fine illite fibers growing up from kaolinite (illitization of kaolinite "white arrows"), common pores (p) and fracture (f) in between kaolinite plates. Note the authigenic illite fibers (dashed white arrows) attached to the surface of detrital mica flake and scattered carbonate grains and/or lumps in the upper right side of image A. A- image is from the Ora shale (sample Ora 6) and B image from the Kaista shale (sample Kaista 3). C- Mixed layers I/S interlocked fibers (arrows) are present in between kaolinite plates (K) and mica flakes (M), note also fine carbonate grains distributed throughout the image. This image is from the Kaista shale (sample Kaista 4). D- Degraded kaolinite plates (K) and common carbonate grains distributed throughout the image. This image is from the Kaista shale (sample Kaista 3). E- Cabonate grains, quartz and plagioclase fill the pore space of clayey matrix. F- Enlarged view of area outline in E showing quartz overgrowths (Q-o) associated with plagioclase-feldspar (Pf). E image is from the Kaista shale (sample Kaista 5).



**Figure 5.** EFs diagram of the selected major (A) and trace (B) elements in the Kaista and Ora formations. A horizontal line (EF = 1) denotes an element enrichment or depletion.

#### 4.3. TOC content

The TOC values in the studied shale samples of the Kaista and Ora formations ranged from 0.10 to 0.57 (avg. = 0.320) and 0.39 to 5.00 (avg. = 1.57), respectively (Table 2).

It's worth noting that the Ora shale has a higher TOC concentration than the Kaista shale.

#### 5. Discussion

## 5.1. Paleoenvironmental condition

#### 5.1.1. Paleoclimate and paleosalinity

The chemical index of alteration (CIA=  $[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$ ) proposed by Nesbitt and Young (1982) is widely used as a proxy for paleoclimate change as well as to assess the degree of weathering of the parent rock (Wang et al., 2020).

Generally, CIA ranges from 50 to 100, reflecting different climatic conditions: cold and dry climate (CIA = 50–60), warm and humid climate (CIA = 60–80), and hot and humid climate (CIA = 80–100) (Nesbitt and Young, 1982, 1989). The CIA values of the Ora and Kaista formations range from 92.9 to 99.5, and from 96.74 to 99.5, respectively (Table 2), indicating a hot and humid climate during their deposition. The CIA values of the present study are higher than the average NASC (North American Shale Composite) value of 57 (Gromet et al., 1984) and typical shale values (PAAS: 70 – 75; Taylor and McLennan, 1985), indicating intense chemical weathering at the source rocks.

The degree of chemical weathering of sediments and sedimentary rocks can also be estimated using the Plagioclase Index of Alteration [PIA: Fedo et al., 1995; PIA =  $[(Al_2O_3 - K_2O)/(Al_2O_3+Na_2O+CaO*-K_2O)] \times 100$  (molecular proportions)]. The PIA values of Ora and Kaista shale (PIA: 92.4 – 99.3 and 96.2 -99.3 respectively) are consistent with CIA values, which further supports that these shales have undergone intense weathering at the source area.

In the A-CN-K diagram (Fedo et al., 1996; Fig. 6), all the studied samples fall above the K-feldspar-plagioclase line, and most of them are parallel to the A–K join and close to the muscovite point. This weathering trend indicates a high loss of Ca, Na, and K in the shale samples, as they tend to plot close to the A apex, suggesting that most feldspars have converted to clay minerals. This could be reflected by the type of clay minerals, whereas intense chemical weathering under humid conditions results in a kaolinite-rich composition of sediments (Chamley, 1989). Thus, the high content of degraded kaolinite (Fig. 4) and the predominance of kaolinite over illite in the studied shale samples are likely a result of intense chemical weathering and may correlate with the Hangenberg climatic event at the Devonian/Tournaisian boundary (Misch et al., 2018).



**Figure 6.** A-CN-K  $[Al_2O_3 - (CaO^*+Na_2O) - K_2O;$  all in molar proportions] ternary plot for the Kaista and Ora shales (After Nesbitt and Young, 1982; Fedo et al., 1996)

The paleosalinity levels during the deposition of sediments were measured by ratios of Rb/K (Campbell and Williams, 1965) and Sr/Ba (Zhen et al., 2020, Li et al., 2020). Ratios of Rb/K  $\leq$  0.004 infer freshwater column, 0.004  $\leq$ 0.006 designates a fresh to the brackish water environment, and >0.006 values suggest fully marine water conditions. According to (Li et al. 2020, and Zhen et al., 2020), ratios of Sr/ Ba more than 1 show saline water conditions, from 1.0 to 0.6 represent brackish environments, and less than 0.6 indicates freshwater conditions. In addition, the Sr/Ba ratio can be used to distinguish between marine and lake environments, in lake deposits less than 0.6, and ranging from 0.8 to 1.0 in marine sediment conditions. The Rb/K ratios of the Kaista and Ora formations shale (0.003 to 0.005; average: 0.004) and (0.000 to 0.006; average: 0.005), respectively are characteristic of freshwater to brackish water conditions, while the Sr/Ba ratios of the samples from the Kaista and Ora formations vary from (0.04 to 0.56), with an average of 0.26 and from (0.03 to 0.53) with an average of 0.22 respectively, indicating a freshwater environment during deposition. The relatively moderate TOC content of the Ora shale may be attributed to water stratification, resulting from the freshwater influx, which diminishes oxygen exchange with the atmosphere and further intensifies reducing conditions favorable for organic matter preservation (Li et al., 2017).

## 5.1.2. Paleoredox Conditions

Redox-sensitive trace elements such as V, Ni, U, and Mo in the sediments have been used extensively to infer paleo-redox conditions of water because these elements are insoluble in reducing environments and are enriched under anoxic conditions more than oxic conditions (Hatch and Leventhal, 1992; Jones and Manning, 1994; Algeo and Maynard, 2004; Tribovillard et al., 2006). The V/(V+Ni) ratio is also widely used for paleo-redox reconstruction and tends to indicate consistently lower oxygen regimes than other paleoredox indicators (Rimmer, 2004). Hatch and Leventhal (1992) suggested that V/(V+Ni) ratios are between 0.46-0.60 for dysoxic environments, 0.54-0.82 for anoxic environments, and up to 0.84 for euxinic environments. In this study, the V/ (V+Ni) ratios of Kaista and Ora shale vary from 0.64-0.91 (avg. = 0.80), and 0.77-0.90 (avg. = 0.83) respectively (Table 3). These values coherently indicate deposition under anoxic conditions.

Another elemental value such as the Th/U ratio is also used to evaluate paleo-redox conditions. The geochemical properties of Th and U are quite different in oxidizing environments but are similar in reducing environments (Wignall and Twitchett, 1996). These researchers recommended that Th/U ratios between 0 and 2 indicate a reducing environment, from 2 to 7 in the oxic environment and > 8 implies a strongly oxidizing environment. Th/U ratios of Kaista and Ora shale are 0.17-1.02 (avg. = 0.66) and 0.00 - 2.13 (avg. = 0.84), (Table 3), respectively also suggesting anoxic conditions. Similarly, some researchers used the U index [ $\delta U = U/-0.5 \times (Th/3 + U)/-0.5 \times (Th/3 + U)/-0.$ U)] to reconstruct the depositional condition, where its value is more than 1 refers to a reducing environment and less than 1 indicates an oxidizing environment (Steiner et al2001 .). The  $\delta U$  values of the Kaista and Ora shale range from 1.49 to 1.89 (avg. = 1.65) and from 1.17 to 2 (avg. = 1.61) respectively also suggesting an anoxic condition.

#### 5.1.3. Transgressive system tracts

The transgressive and highstand system tracts are defined by different characteristics and can be related to many variables, such as anoxic conditions, low detrital input index, strong paleo-productivity, and condensed sections. Generally, it should be noted that the top of the section of a transgressive system tract is due to the existence of a condensed section (Hou et al., 2022).

Transgressive systems tracts (TST) are characterized by relatively higher levels of organic richness as compared to other tracts, so the higher amount of organic matter in shales might be due to paleosalinity, dilution, paleoproductivity, and redox conditions (Katz, 1995). During the transgressive period, the organic matter may increase due to the contribution of terrigenous organic matter supplies from the neighboring continent and highly productive marine sources by active circulation (Hyun et al., 2006).

The transgressive system tracts can be reflected by the variations in the concentrations of major and minor elements and their ratios. In the present study, it was observed that there is an increase in the Rb,  $K_2O$ , Th, K/Al, and TOC values of the major and trace elements and the elemental ratios from the Kaista upward to the Ora Formation. Conversely, there is a

decrease in the same trend of Zr/Al, Ti/Al, Mo, P, Zn, and Zr (Fig. 2). This variation of elemental ratios at the transitional area from the Kiasta to Ora shale could be related to TST, which has been confirmed by Al-Juboury et al. (2012). Furthermore, Sharland et al. (2001) considered the Ora shale in Northern Iraq to have the maximum flooding surface of D30, deposited in a sub-tidal shelf environment.

#### 5.1.4. Paleo-productivity proxies

The organic matter accumulation of the marine shale has been influenced by several factors, such as primary productivity, redox condition, palaeoclimate, palaeosalinity, and paleogeography (Fu et al., 2009; Wang et al, 2010; Zeng et al., 2015).

Fu et al. (2007) proposed that the organic carbon preservation in the shale may be influenced dominantly by anoxic conditions rather than high primary productivity, and such a factor cannot be ruled out.

Phosphorus (P) is an important nutritional element, which can greatly control the paleo-productivity of marine and lacustrine shales (Tyrrell, 1999). Therefore,  $P_2O_5$  concentrations are widely used to analyze variations in paleo-productivity (Latimer and Filippelli, 2002). To decrease the influence of authigenic minerals and organic matter on the P dilution effect from terrigenous detritus, other indicators, including P/Ti and P/Al, are more effective for assessing paleo-productivity conditions (Latimer and Filippelli, 2002; Algeo et al., 2011).  $P_2O_5$  content, P/Ti, and P/Al ratios determined are shown in Tables (2 and 3). Similar change curves are found for each of these indicators, and the maximum values of  $P_2O_5$ , P/Ti, and P/Al ratios are found in samples 17, 19, and 21 for Ora shale (Table 3)

The average values of  $P_2O_5$  content, P/Ti, and P/Al ratios of the Ora shale are 0.11%, 0.1 and 75.64, and those of the Kaista shales are 0.12%, 0.12, and 74.18, respectively. However, the average value of P/Ti is less than 0.34, which indicates lower productivity, whereas values greater than 0.79 refer to higher productivity, and values between 0.34 and 0.79 indicate a moderate level of primary productivity (Algeo et al., 2011). The P/Ti values are low in Ora shales (<0.34; Table 3). In addition, the correlations of P/Ti versus TOC in the Ora Formation (r = -0.098) and P/Al versus TOC (r = -0.064) exhibit a very weak negative correlation, respectively (Table 3), suggesting low primary productivity and that the paleoredox conditions in Ora shales play a significant role in the preservation of organic matter.

## 5.1.5. Hydrothermal activity

Large amounts of organic material and various types of metals were transported from the deep oceanic basin and accumulated in the sedimentary environments along the continental shelf, resulting in the enrichment of these metals in the black shales (Wu et al., 2017). Trace elements and rare earth elements are important in the study of ancient hydrothermal systems (Choi and Hariya., 1992; Hatch and Leventhal, 1992). Submarine hydrothermal activities can be identified by using several geochemical indices such as Co– Zn–Ni, U/Th, and Ba/Sr ratios.

The ternary diagram of Co-Zn-Ni can be used to

discriminate between hydrogenous and hydrothermal deposits (Choi and Hariya, 1992). In this diagram, the studied samples of Kaista and Ora shale generally fall into the hydrothermal field (Fig. 7). The U/Th ratio can also be used to estimate the influence of hydrothermal fluids (Dickson. and Scott, 1997). Uranium–thorium ratios larger than 1 indicate that hydrothermal activity was present during the depositional period, whereas U/Th <1 indicates normal seawater depositional conditions. In the studied samples of the Kaista and Ora formations shale, U/Th values range from 0.98 to 5.82 (avg.= 2.24) and 0.47 to 3.58 (avg.= 1.67) respectively, suggesting input from deep hydrothermal sources.



**Figure 7.** Ni-Zn-Co ternary plot for the Kaista and Ora shales, distinguishing hydrothermal and hydrogenic sediments (Chen et al., 2019).

The Ba/Sr ratios are also used by many researchers to indicate hydrothermal activity (Smith and Cronan, 1983; Peter and Scott, 1988). Where its ratios range from 5.0 to 20, with an average of 11, indicating the influence of submarine hydrothermal fluids (Liu et al., 2021). Ba/Sr ratios of the Kaista and Ora formations shale range from 1.79 to 27.11 (avg.= 9.76) and from 1.89 to 35.01 (avg.= 12.4) (Table 3) respectively, depicting that depositional area was affected by hydrothermal activity. In addition, the petrographic study indicates the presence of quartz overgrowth associated with plagioclase (Fig. 4 E-F), which suggests that solutions rich in silica were probably derived from hydrothermal activity (Zaghloul et al., 2010). Additionally, the presence of pyrophyllite in the Ora shales (Table 1) may suggest the effect of hydrothermal origin (Swindale and Hughes, 1968). All the data sets above might suggest that there was hydrothermal activity in the basin during the deposition.

The Late Devonian-Early Carboniferous was interpreted as a period of extension and compression with Hercynian back-arc rifting, inversion, and uplift formed by subduction of the southern margin of Paleo-Tethys (Sharland et al., 2001). This is supported by the presence of Devonian-Carboniferous volcanic and metamorphics in the Kuh-Sefid area of the Sanandaj-Sirjan Zone (Davoudzadeh and Weber-Diefenbach, 1987). The study area was not so far distance from the Sanandaj-Sirjan Zone which suggests that the hydrothermal activity in the study area was probably affected by this subduction.

## 6. Conclusion

The Late Devonian-Early Carboniferous succession of the Kaista and Ora formations from northern Iraq is composed mainly of calcareous shales intercalated with sandstones, siltstones, and limestone (dominantly dolomitic). Geochemical and mineralogical investigations of the shale units were carried out to constrain paleoclimate, paleosalinity, paleo redox conditions, transgressive system tract, paleoproductivity, and hydrothermal activity. In addition to the kaolinite-rich composition of the studied shale samples, chemical indices such as the chemical index of alteration (CIA), the plagioclase index of alteration (PIA), and the A-CN-K plot indicate intense chemical weathering in the source area under humid climate conditions. The Rb/K and Ba/Sr ratios suggest that the depositional area experiences freshwater to brackish water conditions. Paleo redox trace elements proxies such as V/(V+Ni), Th/U ratios, and U index indicates deposition under anoxic conditions. The variation of some major and trace elements and their elemental ratios (Rb, K<sub>2</sub>O, Th, Mo, P, Zn, Zr, Zr/Al, Ti/Al, and K/Al) in the transitional area from Kiasta to Ora shale could be related to transgressive systems tracts (TST). The reduced primary productivity and paleoredox conditions are responsible for the preservation of organic matter in the Ora Formation. The ternary plot of Co-Zn-Ni, U/Th, and Ba/Sr ratios indicate that the depositional setting was affected by hydrothermal activity probably due to the subduction of the southern margin of Paleo-Tethys.

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