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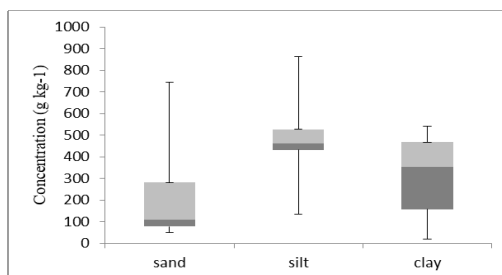
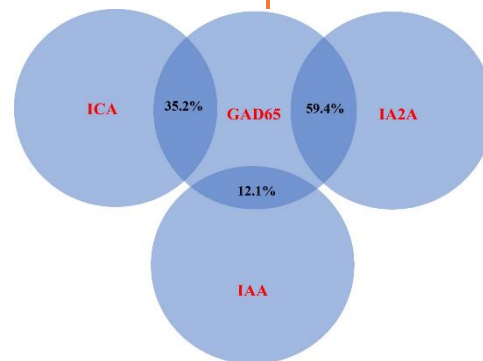
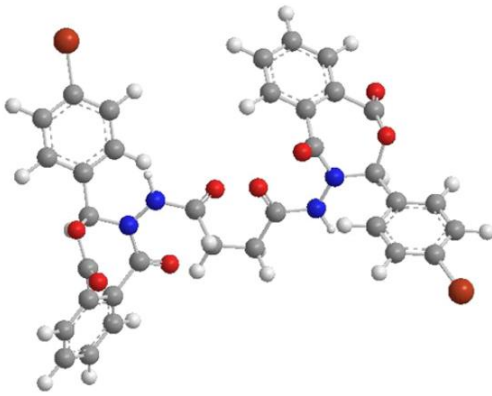
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Hydrocarbon generation potential and thermal maturity of the outcropped Palaeozoic formations from Khabour Valley, Kurdistan Region, Northern Iraq

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Article info	Abstract
Original: 20/06/2023 Revised: 15/08/2023 Accepted: 20/08/2023 Published online: 20/12/2023	In this study, 12 outcropped rock samples from the Khabour, Kaista, Ora, and Harur formations (Paleozoic) in the Khabour Valley were studied. The location is in northern Iraq, in the Imbricated Thrust Zone, northeast of Duhok City. Rock-Eval Pyrolysis was utilized to assess the thermal maturity, organic matter composition, hydrocarbon potential, and organic richness of the Khabour, Kaista, Ora, and Harur formations situated within the Khabour Valley. The content of Total Organic Carbon ranges from 0.19 to 0.37 wt.%, with an average of 0.29 wt.% for the Khabour formation, 2.07 to 3.09 wt.% for the Kaista formation, 0.58 wt.% for the Ora formation, and 0.31 to 1.55 wt.% for the Harur formation. The source rock was rated poor based on the TOC wt.% content. According to the results, the Khabour Valley formations have low amounts of S ₂ (average 0.12 mg HC/g Rock, range 0.01-0.29 mg HC/g Rock) and Hydrogen Index (HI) (average 15.2 mg HC/g TOC, range 2-41 mg HC/g TOC). Drawing insights from the analysis of Rock-Eval data, the formations exhibit kerogen types classified as type IV kerogen. According to the cross plot of S ₂ versus TOC%, all the samples show a poor potentiality to create hydrocarbons. The graph of HI vs Tmax demonstrates that Tmax ranges from immature to postmature.

Key Words:

Khabour, Kaista, Ora, Harur, Palaeozoic, Hydrocarbon potentiality, Thermal Maturity, Kurdistan, Iraq

Introduction

Evaluation of the source rock is seen to be an important effort in oil exploration. Additionally, it could be applied to source rock assessment, which includes defining paleoenvironmental conditions and figuring out a rock's types of organic matter content and maturation levels [1]. This allows for the definition of a formation's potential. When conducting initial research for oil and gas exploration, the evaluation of source rock in conjunction with other geological characteristics, such as sedimentology, petroleum geology, stratigraphy, geophysics, etc., will be a vital approach [2]. The Khabour Quartzite-Shale formation is the oldest formation in Iraq's geological column that has been formally described and recorded. The type section of the formation is positioned roughly 2 kilometers west of Kaista Village and extends downward to the stream directly north of Chalki Nasara Village in Iraqi Kurdistan. Wetzel first described the formation in 1950 in an unpublished paper [3].

Literature Review

In the Northern Thrust Zone, just across the Turkish-Iraqi border, the Kaista and Ora formations are both exposed. The Kaista formation was first described as being of Late Devonian (Famennian) age by Wetzel and Morton [4] in Bellen et al. [5] from the Northern Thrust Zone region of Iraq, whereas the Ora formation was first described by Wetzel [4] in Bellen et al. [5] from the same region as being of Early Carboniferous or Late Devonian - Early Carboniferous. The Khabour Formation was originally documented by Wetzel [3], marking a pivotal discovery in the geological understanding of the region. This formation is characterized by a well-exposed section spanning approximately 800 meters within the Khabour Valley. This notable section has provided valuable insights into the stratigraphy, sedimentary dynamics, and geological history encapsulated within the Khabour formation [3].

There are other studies on this region's Paleozoic sequence such as the scholarly work by Omer, M. F. [6] has extensively explored the Sedimentology and Geochemistry of the Khabour Formation. Furthermore, Baban and Lawa [7] have provided valuable Palynological and Stratigraphical evidence pertaining to the age assessment of the exposed Khabour Formation. Notably, the comprehensive study undertaken by Al-Ameri [8] concerning Palynostratigraphy, coupled with the meticulous assessment of Gas and Oil generation and accumulations within the lower Paleozoic, has notably enriched the field's body of knowledge. Hasson [9] which studied the Palynostratigraphy of Upper Devonian–Lower Carboniferous strata by using the borehole data; Al-Lami [10] studied Palynology of part of the lower Carboniferous in the well Akkas-1; and Baban [11] which studied Palynostratigraphy and maturation of lower Paleozoic strata in western Iraqi desert are the three significant studies that have been done in Paleozoic period. Numerous additional research endeavors have been undertaken to advance our understanding of various aspects, such as weathering processes and paleogeography, carried out by scholars like Absar et al. [12], Zimmermann and Spalletti [13], Akkoca and Karatas [14], Tobia and Mustafa [15]. Further contributions have been made in exploring the paleoenvironmental conditions and provenance history of these rocks by Armstrong-Altrin et al. [16], Jafarzadeh and Hosseini-Barzi [17], Dostal and Keppie [18], as well as Armstrong-Altrin [19] and Armstrong-Altrin et al. [20]. The primary focus of many of these studies has been directed towards the middle Paleozoic sequence, encompassing sequence stratigraphy as demonstrated by Al-Juboury et al. [21], depositional environments and facies analysis as highlighted by Al-Juboury and Al-Hadidy [22], and palynostratigraphy investigations carried out by Sherwani et al. [23] and Al-Hasson [9]. Notably, research endeavors have also delved into subjects like palynology, oil and gas generation, as evident in works such as Abdula et al. [24] and Al-Lami [10], while Al-Juboury et al. [9] have examined the conditions of anoxic marine environments. The efficiency of oil and gas generation has been scrutinized by Abdula et al. [24]. Wetzel and Morton [4] within Bellen et al. [5] were the pioneers in identifying and describing the Harur formation from the Ora fold situated in the Amadia district of the Northern Thrust Zone of Iraq. In its type section, the Harur formation has a total thickness of around (62) meters [5]. This study has examined a total of 12 outcropped rock samples from the Khabour, Kaista, Ora, and Harur formations in the Khabour Valley, to determine what is the thermal maturity level, types of organic matter, hydrocarbon potentiality, and organic richness of the different formations represented by the collected samples.

Geological Setting

The research area falls within the geographical scope of the Northern Thrust Zone, a geological domain outlined by Buday [30], which aligns with the Imbrications Zone encompassing the foreland basin of Numan [31]. The arrangement of rocks in this region's Thrust Zone is instrumental in revealing the presence of the oldest Paleozoic rock formations. Visualized in Figure 1, the structural configuration depicts a notably elongated anticlinorium characterized by its east-west orientation, hosting three distinctive dome-shaped culminations. It is worth noting that the southern slopes of this anticlinorium exhibit a steeper incline, while the northern flanks exhibit a lesser degree of faulting indications. These geological attributes find their

origins in the pronounced Caledonian-Hercynian movement, a significant geological event that prevailed during the specified historical era [5].

Turning our focus to the Kaista formation, the original researcher attributed it to the Late Devonian epoch, specifically the Famennian stage. However, alternative perspectives have been proposed by researchers such as Gaddo & Parker [32] and Ditmar [33]. They suggest considering both the Early Carboniferous and Late Devonian epochs as plausible periods for the formation of the Kaista formation.

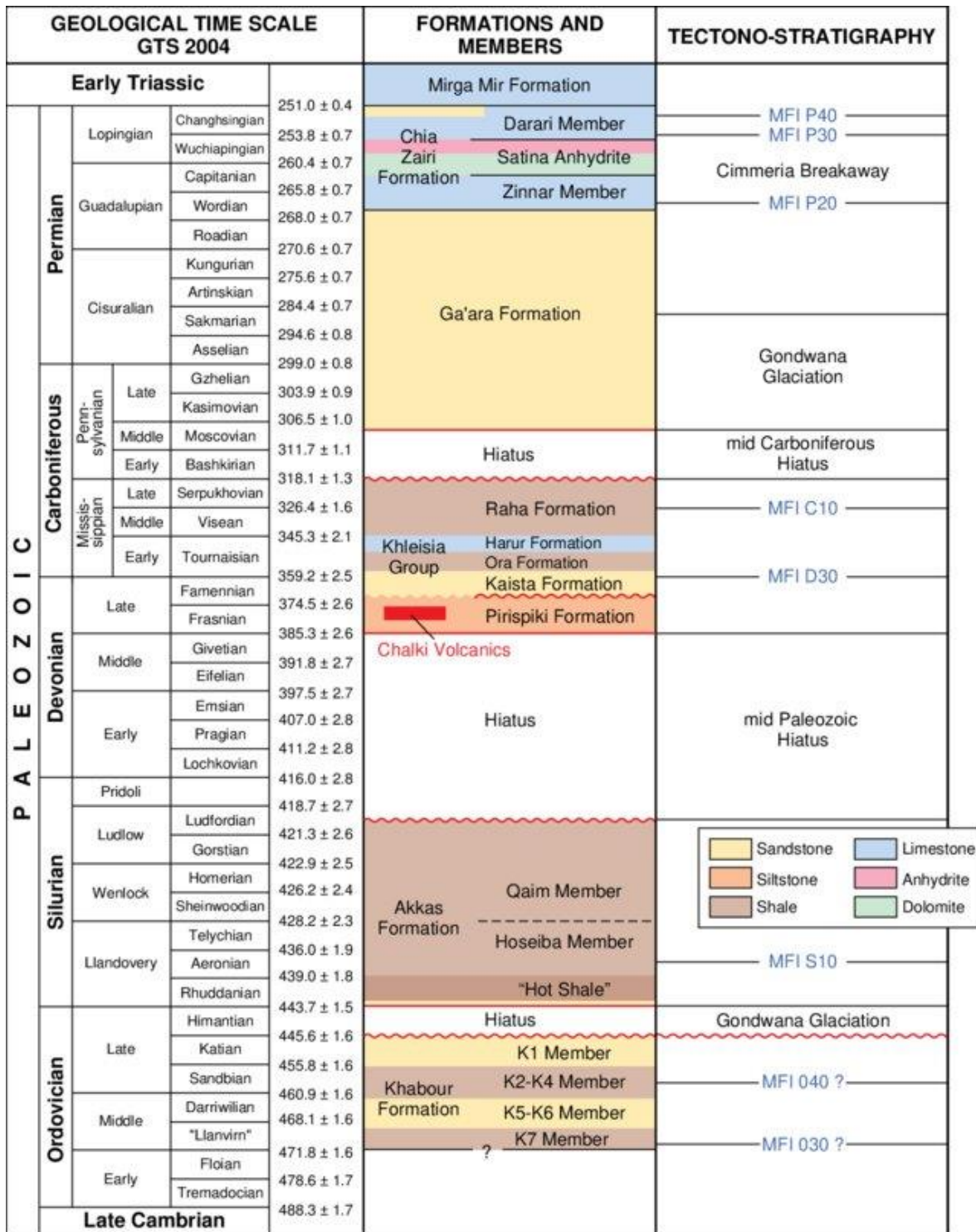


Figure 1: Stratigraphic column of rock layers from the Paleozoic era in Iraq (revised from the Stratigraphic Lexicon of Iraq, as presented by van Bellen et al. [5]). Additionally, the diagram presents the alignment with the Geological Time Scale GTS 2004 (adapted from Gradstein et al. [32], with modifications to the names of Ordovician stages).

Materials and Methods

Study Area

The research endeavours take place within the distinctive geological setting of the Imbricated Zone, a region renowned for its intricate tectonic complexities. Situated to the northeast of Duhok City in the Kurdistan Region of Iraq, this area is characterized by a mosaic of geological structures that have shaped its unique landscape. Central to this study is an exploration of the outcropped geological formations found within the Khabour Valley. This valley, nestled within the Imbricated Zone, holds particular significance due to its rich geological heritage. The formations of interest namely the Khabour, Kaista, Ora, and Harur formations serve as focal points for unravelling the geological history and dynamics of the region.

The Khabour Valley, with its diverse rock exposures and stratigraphic sequences, provides an unparalleled canvas for understanding the intricate interplay of geological processes over time. As researchers delve into the details of these formations, a deeper understanding emerges of the sedimentary environments, tectonic influences, and potential hydrocarbon prospects that have shaped this geological enclave.

In summary, this investigation situates itself within the Imbricated Zone near Duhok City, centering on the geologically significant Khabour Valley. Through an intricate analysis of the Khabour, Kaista, Ora, and Harur formations, this research in this area focuses on the evaluation of Hydrocarbon generation potential and thermal maturity (Figure 2).

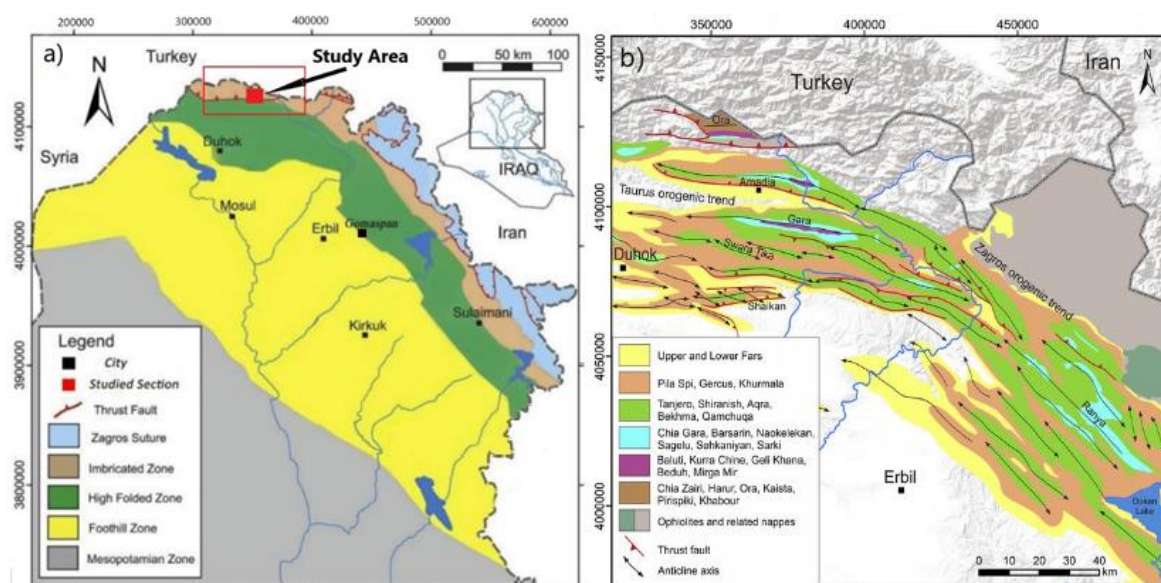


Figure 2: (a) A tectonic map illustrating the geographic configuration of Iraqi Kurdistan. The specific study area is demarcated by a red rectangular enclosure (Adapted from Jassim and Goff, 2006 [26]); (b) A simplified geological map of Kurdistan, accentuating the anticlinal axes and the associated thrust faults present in the formations being studied (Adapted from Sissakian and Hagopian [27]; Sissakian [28]; Csontos et al. [29]).

Samples and general data

A total of 12 outcropped rock samples from the Khabour, Kaista, Ora, and Harur formations have been collected (Table 1). Rock-Eval pyrolysis has been systematically utilized to appraise each sample analyzed by Robertson Research, all the selected samples are subjected to this test. After being homogenized, pulverized, and crushed, the samples were examined using a Rock-Eval 6 apparatus. A tiny amount of powdered rock (70–100 mg) is heated continuously during the process at a controlled temperature between 100–850 °C in an inert atmosphere (helium or nitrogen gas). The sample was heated starting at 100 °C and kept there for several minutes before being heated automatically at a rate of 25 °C per minute to a maximum temperature of about 850 °C. The following publications can be used to learn more about this method and its

parameters: Tissote and Welte [2], Espitalie et al. [34], Peters [35], Peters and Cassa [36], Lafargue et al. [37], and Behar et al [38].

Table 1: General data for the selected samples of Khabour, Kaista, Ora and Harur formations in Khabour Valley, Kurdistan Region, Northern Iraq.

General Data					
Sample Depth (Metres)	Sample Type	Formation	Analysed Lithology / Description	Thickness (Metres)	Remarks
K5079	Outcrop	Khabour	SH, dk gy, hd	800	The sample was procured from the upper part of the Khabour formation.
K5098B	Outcrop	Khabour	SH, dk gy, hd		
K5097	Outcrop	Khabour	SH, dk gy, hd		
K5082	Outcrop	Kaista	SH, dk gy, hd	65	The sample was procured from the lower part of the Kaista formation.
K5083A	Outcrop	Kaista	SH, dk gy, hd		The sample was procured from the transitional zone proximate to the Ora formation.
K5084A	Outcrop	Ora	SH, dk gy, hd		The sample was procured from the transitional zone proximate to the Harur formation.
K5101	Outcrop	Ora	SH, dk gy, hd	226	The samples were procured from the middle and upper part of the Ora formation.
R2012-108A	Outcrop	Ora	SH, brn-gy, calc		
R2012-108 B	Outcrop	Ora	SH, ol-gy		
R2012-108B (A)	Outcrop	Ora	SH, dk gy		
R2012-109A	Outcrop	Ora	SH, ol-gy, calc		
R2012-110B	Outcrop	Harur	LST, ol-gy, arg	62	The sample was procured from the middle part of the Harur formation.

This method has provided the four main parameters:

- I. S1; represents thermo-vaporized free and adsorbed hydrocarbons released at about 300 °C.
- II. S2; corresponds to the thermal degradation of kerogen at a temperature between 300-650 °C.
- III. S3; provides CO and/or CO₂ that is released from organic compounds containing Oxygen element.
- IV. Tmax, which represents the Rock-Eval pyrolysis temperature (°C) at maximum S2 peak generation.

The parameters such as S1, S2 and S3 are used to calculate the following parameters:

- Quantity of Total Organic Carbon (TOC, wt. %).
- Hydrogen Index (HI), calculated as S2 divided by TOC multiplied by 100 (expressed in mg hydrocarbons per gram of TOC).
- Oxygen Index (OI), determined by dividing S3 by TOC and then multiplying by 100 (measured in mg CO₂ per gram of TOC).
- Genetic Potential (GP), calculated as the sum of S1 and S2 values.
- Production Index (PI), obtained by dividing S1 by the sum of S1 and S2.

Results and discussion

Chemical Analysis

The content of Total Organic Carbon (TOC wt. %) for the Khabour formation ranged from 0.19-0.37 wt. %, average 0.29 wt. %, Kaista formation ranged from 2.07-3.09 wt. %, average 2.58 wt. %, Ora formation ranged from 0.31-1.55 wt. %, average 0.83 wt. % and Harur formation is 0.98 wt. % (Table 2). They are considered as a poor source rock based on TOC wt. % content [39]. The presence of low Total Organic Carbon (TOC) content in Paleozoic rocks within the Khabour Valley in Iraq can be attributed to a combination of geological and environmental factors that influenced organic matter accumulation and preservation during the Paleozoic Era. The Khabour Valley may have predominantly experienced shallow marine or terrestrial depositional environments that were not conducive to the accumulation of significant amounts of organic matter. High TOC is often associated with environments like swamps, lagoons, and anoxic basins where organic material can accumulate and be preserved.

The data reveals that these formations in Khabour Valley have low amounts of Hydrogen Index (HI) (average 15.2 and range from 2-41 mg HC/g TOC), low amounts of S2 (average 0.12, and range 0.01-0.29 mg HC/g Rock). The presence of low hydrogen index (HI) values in Paleozoic rocks within the Khabour Valley in Iraq can be influenced by a combination of geological, environmental, and diagenetic factors. The hydrogen index is a measure of the potential for hydrocarbon generation and is often indicative of the quality of organic material present in rocks. The maturity of organic matter can impact its hydrogen index. If the organic material has already undergone significant thermal maturation (such as during burial), its HI value may decrease [40]. Results are tabulated in Table 2.

Table 2: Rock-Eval Pyrolysis measurement data for the selected samples of Khabour, Kaista, Ora and Harur formations in Khabour Valley, Kurdistan Region, Northern Iraq (Unpublished data).

General Data				Chemical Analysis Data								
Sample Depth (Metres)	Sample Type	formation	Analysed Lithology / Description	TOC (% of rock)	Rock-Eval Pyrolysis							
					S1 (mg/g)	S2 / POT. YLD. (mg/g)	S3 (mg/g)	Tmax (°C)	HI	OI	PI	GP (S1+S2) (mg/g)
K5079	Outcrop	Khabour	SH, dk gy, hd	0.37	0.24	0.06	0.24	287	16	65	0.80	0.3
K5098B	Outcrop	Khabour	SH, dk gy, hd	0.32	0.81	0.13	0.38	289	41	119	0.86	0.94
K5097	Outcrop	Khabour	SH, dk gy, hd	0.19	0.01	0.04	50	500	21	26	0.20	0.05
K5082	Outcrop	Kaista	SH, dk gy, hd	3.09	0.55	0.24	0.1	606	8	3	0.70	0.79
K5083A	Outcrop	Kaista	SH, dk gy, hd	2.07	0.41	0.22	0.38	605	11	18	0.65	0.63
K5084A	Outcrop	Ora	SH, dk gy, hd	0.82	0.84	0.29	0.48	292	35	59	0.74	1.13
K5101	Outcrop	Ora	SH, dk gy, hd	1.13	1.17	0.24	0.75	287	21	66	0.83	1.41
R2012-108A	Outcrop	Ora	SH, brn-gy, calc	0.34	0.01	0.01	0.43	471	3	126	0.50	0.02
R2012-108 B	Outcrop	Ora	SH, ol-gy	0.83	0.03	0.02	0.74	602	2	89	0.60	0.05
R2012-108B (A)	Outcrop	Ora	SH, dk gy	1.55	0.06	0.04	0.6	601	3	39	0.60	0.1
R2012-109A	Outcrop	Ora	SH, ol-gy, calc	0.31	0	0.02	0.76	475	6	245	-	0.02
R2012-110B	Outcrop	Harur	LST, ol-gy, arg	0.98	0.04	0.15	0.61	430	15	62	0.21	0.19

SH: Shale.
 dk: Dark.
 hd: Hard.
 calc: Calcareous.

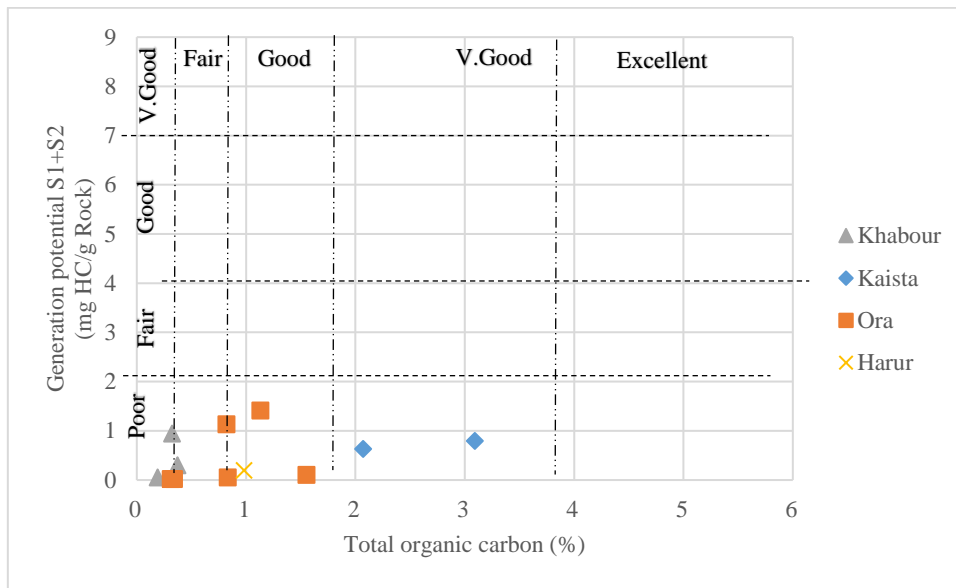
LST: Limestone.
 gy: Gray.
 ol: Olive.
 arg: Argillaceous.

Hydrocarbon Potentiality

The cross plot of GP versus TOC% content (Figure 3; A) revealed that the Khabour, Kaista, Ora and Harur formation in Khabour Valley showed a poor range of TOC% content to be a good source rock. Approximately, most of the samples have less than 1% of TOC content. While all of them showed poor genetic potential. Even though a good source rock should have relatively high TOC% contents, TOC% by itself is not a good indicator to determine how much hydrocarbon might be generated by the rock [41].

The cross plot of S2 versus TOC % (Figure 3; B) showed that all the samples have poor potentiality. Depending on this diagram, this rock unit showed poor potentiality to generate hydrocarbon.

A



B

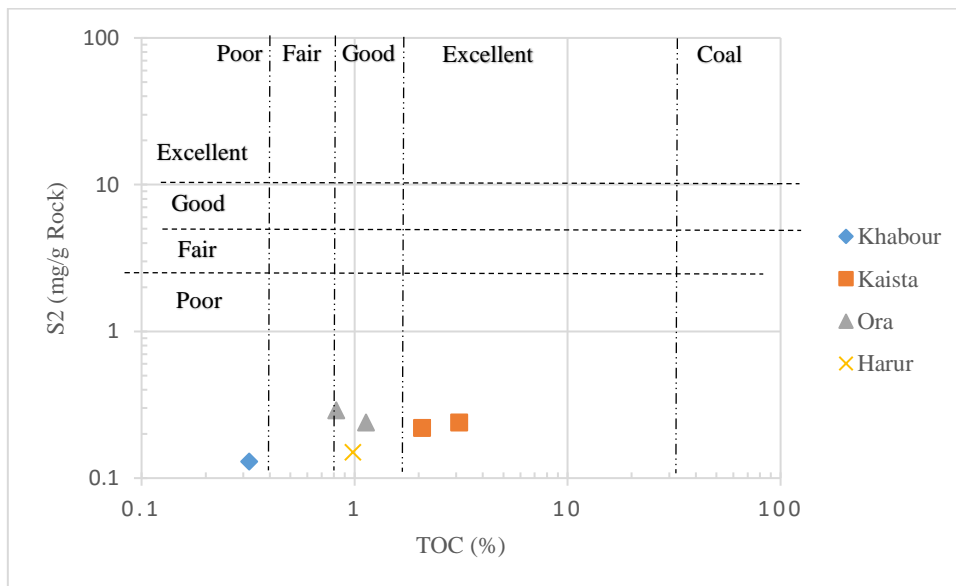


Figure 3: (A): A cross plot illustrating the comparison of TOC% content against Genetic Potential (according to Alaug et al.) [42]. (B): The cross plot showcasing the relationship between TOC% content and S2 (extracted from Dembicki) [41], observed in the studied samples sourced from the Khabour, Kaista, Ora, and Harur formations within the Khabour Valley.

Kerogen types

Finding the different types of kerogens in a source rock is essential since different kinds of organic materials have varied potentialities for producing hydrocarbons [2] and [43]. The relationship between OI and HI (Figure 4) shows the distribution of all the studied samples from the Khabour Valley, the primary kerogen type identified within the Khabour, Kaista, Ora, and Harur formations is kerogen type IV. This particular kerogen type, characterized by its relatively low hydrogen content and elevated oxygen content, has garnered the label "inert kerogen." This nomenclature stems from its limited propensity to facilitate the generation of hydrocarbons due to its distinct chemical composition and structural attributes [44].

The marked presence of kerogen type IV within these formations casts a significant influence on their hydrocarbon generation potential. As a result of its inherently low hydrogen-to-carbon ratio and the increased prevalence of oxygen in its molecular framework, this kerogen type inherently exhibits a diminished capacity to yield substantial amounts of hydrocarbons through thermal maturation processes.

Incorporating a comprehensive understanding of the specific kerogen types found in the Khabour, Kaista, Ora, and Harur formations, it becomes evident that these geological units possess a notably restrained capability to generate hydrocarbons. This conclusion aligns with the fundamental characteristics of kerogen type IV, underscoring its diminished potential to undergo the chemical transformations necessary for substantial hydrocarbon production. As such, the combination of kerogen type IV prevalence and low hydrocarbon generation potential collectively shapes the geological and geochemical backdrop of these formations in the Khabour Valley, offering valuable insights into their evolutionary history and their role within the broader geologic framework. The consistent vitrinite macerals, which are necessary precursors for kerogen type III, are absent from all the examined samples [2], [1], [45] and [35].

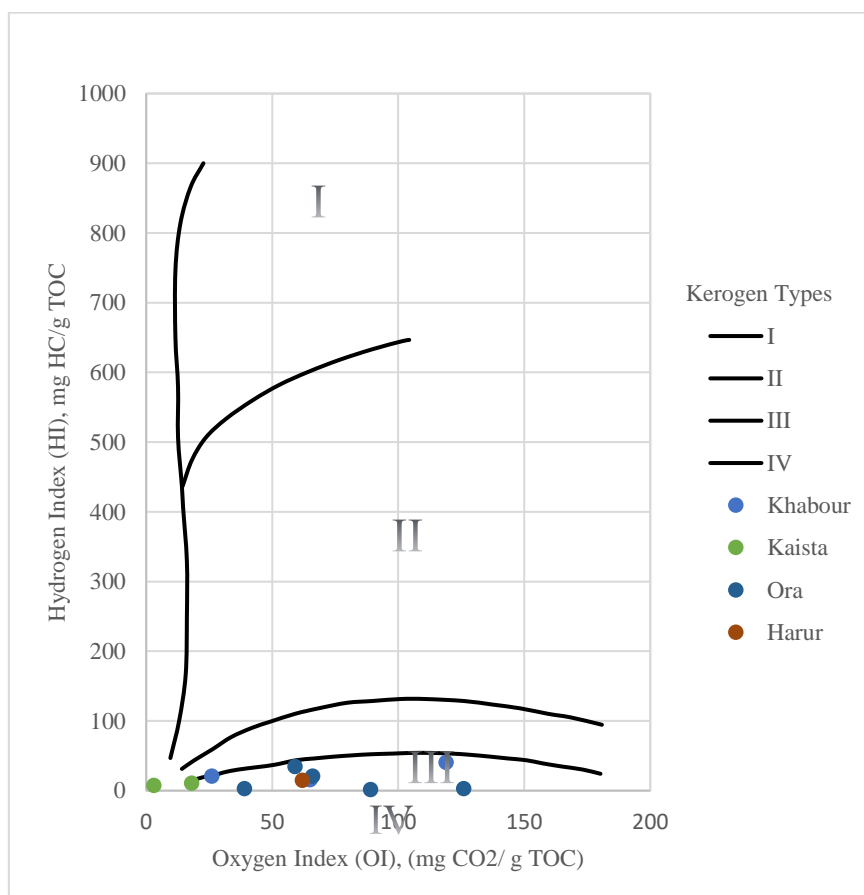


Figure 4: Analysed samples from the Khabour, Kaista, Ora, and Harur formations in the Khabour Valley have been plotted on the Oxygen Index (OI) versus Hydrogen Index (HI) diagram, using the diagram introduced by Hunt [1].

Thermal maturity

The cross plot of T_{max} versus HI is used for determining the kerogen quality and maturity assessment more than HI versus OI to eliminate the effects of OI value (Hunt). Graphical presentation of HI versus T_{max} (Figure 5) indicates a wide range of T_{max} from immature to postmature range. The distribution of the samples, based on T_{max} values, is nearly the same in Khabour and Ora formations. The samples are located either in the immature zone (circle group) or in the postmature zone (ellipsoid group). The low value of T_{max} is mostly related to the presence of recent organic matter (Texto-Uminie) as generally named mud additives. The high values of T_{max} are probably reflecting either residual contamination or possibly the presence of recycled organic matter, which is dominated by inertinite macerals [46].

The wide range of thermal maturity observed in pyrolyzed samples within the Khabour Valley can primarily be attributed to the diverse depositional history of the sediments. The valley's geological evolution involves a complex interplay of various environments, including marine, lacustrine, and terrestrial settings, where organic materials have been deposited over different time spans. These variations in depositional environments and durations have led to differences in burial depth, temperature history, and diagenetic processes, resulting in the observed range of thermal maturity levels.

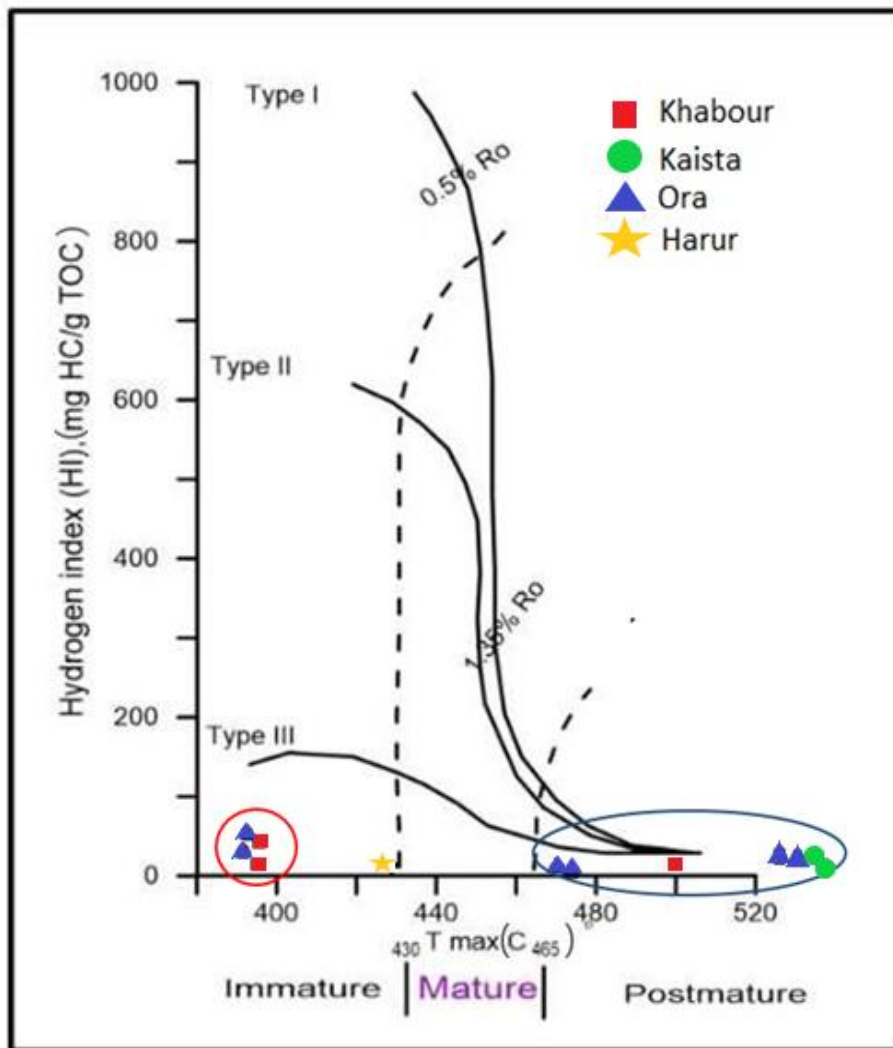


Figure 5: The HI versus T_{max} cross plot, originally devised by Hunt [1], portrays the analysed samples from the Khabour, Kaista, Ora, and Harur formations in the Khabour Valley. Immature samples are represented by circular group indicators, whereas postmature samples are depicted by ellipsoid-shaped group indicators.

Conclusions

The Khabour, Kaista, Ora, and Harur formations, as observed in the outcropped samples of the Khabour Valley, exhibit a limited organic matter content. These rock units are categorized as poor source rocks due to their low TOC% content, indicative of their reduced potential to generate hydrocarbons. The predominant kerogen type found within the Khabour, Kaista, Ora, and Harur formations in the Khabour Valley is kerogen type IV. This specific kerogen type exhibits a notably limited capacity for hydrocarbon generation within these formations. According to the Production Index (PI) parameter and cross plot of HI versus Tmax of Hunt [26], Most of the samples extracted from the Khabour, Kaista, and Ora formations within the Khabour Valley indicate that they have reached a thermally postmature condition. Furthermore, specific samples originating from the Khabour, Ora, and Harur formations display characteristics consistent with a thermally immature state.

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Conflict of interest

The authors confirm that they are not affiliated with or involved in any organization or entity with financial interests.

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