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Clay Minerals and Organic Matter from Deeply Buried Ordovician-Silurian Shale in Western Iraq: Implications for Maturity and Hydrocarbon Generation

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Abstract

The present work is conducted on the Paleozoic (Ordovician) Khabour and the (Silurian) Akkas shales in the Akkas-1 well of western Iraq. The study is aiming to determine the implications of clay mineral transformation, organic mineral distribution and maturity of hydrocarbon generation, using X-ray diffraction (XRD), scanning electron microscopy (SEM) in addition to organic matter concentrations. In the shale of the Khabour Formation, amorphous organic matter is common and includes various Tasmanite-type organic matter, vitrinite, inertinite, and bituminite. The main clay minerals observed include illite, chlorite, kaolinite, in addition to mixed-layer illite-smectite and rare smectite. In Silurian shale, high content of organic matter is recorded in addition to abundant vitrinite and low content of grainy organic matter (Tasmanites) and pyrite. Illite and kaolinite are commonly found in addition to chlorite and illite-smectite clay minerals. Conversion of smectite to mixed-layer illite-smectite (I-S) and an increase in vitrinite reflectance are commonly observed below 2500 m depth in the studied formations, which coincides with oil and gas generation. These results could be used as an indication of higher maturity and hydrocarbon generation in the deeply buried shale of the Khabour and Akkas formations in western Iraq.

Keywords: Organic matter; illite-smectite; maturity; Ordovician -Silurian shale; Iraq

الخلاصه

اجري العمل الحالي على صخور السجيل لتكوين الخابور (الأوردوفيشي) وتكوين عكاس (السليوري) في البئر عكاس (1) في غرب العراق بهدف ايجاد اثر دراسة المعادن الطينية وتوزيع ونضوج المواد العضوية على تكوين الهايدروكاربونات باستخدام تقنيات الأشعه السينية الحائده و المجهر الألكتروني الماسح فضلا عن

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دراسة نوعية المواد العضوية. في سجيل الخابور تكون المواد العضوية غير المتبلورة هي الاكثر شيوعا والتي تتضمن مواد عضوية من نوع (تسمنايت)و الفترينايت، الانيرتنايت والبتيومينايت، بينما تتمثل مجموعة المعادن الطينية بالانواع، الالايت والكلورايت والكاؤولينيايت فضلا عن الصفائح المزدوجة من الالايت-سمكتايت وندرة من السمكتايت. أما في سجيل تكوين عكاس، فان كمية اكبر من المواد العضوية قد تم تشخيصها والتي تتضمن الفيترنايت وبعض المواد من اصل (تسمنايت) مع البايرايت مع شيوع معادن الالايت والكاؤولينايت كمعادن طينية بالاضافة الى الكلورايت ومعدن الالايت-سمكتايت. تحول السمكتايت الى الصفائح المزدوجة من الاليات-سمكتايت مع زيادة بنسبة الانعكاس الفيرنايتي تلاحظ بوضوح في السجيل المطمور تحت العمق من الاليات-سمكتايت مع زيادة بنسبة الانعكاس الفيرنايتي تلاحظ بوضوح في السجيل المطمور تحت العمق المرادي ويتمون النفط والغاز في هذه الطبقات. هذه النتائج يمكن استخدامها كدليل النضوج العالي وتكون الهايروكابرونات في السجيل المطمور عميقا في تكويني المنور وعكاس من غربي العراق.

Introduction

Clay minerals and organic matter usually coexist in clastic rocks and are used as a tool to identify potential hydrocarbon generation and expulsion due to their high susceptibility to temperature changes that control related mineral conversions and organic maturity [1-5]. Clay minerals and organic matter also have significant influences on the origin, preservation, and production of shale gas due to the substantial role of their nanoscale pores in the generation, storage, and seepage of shale gas [6].

To assess the thermal maturity of sedimentary rocks, several paleothermometers are used as thermal maturity indicators to reconstruct palaeotemperature histories; a technique that is widely applied in petroleum exploration [3, 7, 8]. Frequently used parameters include vitrinite reflectance (%Ro), maximum pyrolytic temperature (Tmax), fluid inclusion data, conodont alteration index, level of thermal maturity of organic matter (OM), and clay mineral transformation ratios [3, 9-11]. Coexisting clay minerals and organic matter in the reservoir sandstones and shale source rocks are sensitive to temperature changes that accompany hydrocarbon generation and expulsion processes [4-5].

After deposition of the source rocks in a sedimentary basin, oil and gas are generated and the rock is termed mature at a temperature of about 60°C and depth of 1.5 km [12]. The type, richness, and thermal maturity of these source rocks can be evaluated using the mineralogical and geochemical parameters as mentioned above. For example, the degree of ordering of illite-smectite (I-S) clay minerals is useful for studying hydrocarbon generation. A coincidence is commonly observed between the temperature for the conversion from random to ordered I-S and the temperature for the onset of peak oil generation [4, 13-17].

The Akkas-1 well in western Iraq (Figure-1) contains the most complete Ordovician and Silurian succession in Iraq and was designated as the subsurface reference section for the Ordovician Khabour and Silurian Akkas Formations, comprising an interbedded succession of sandstones and shale between 1463 m and the total depth of 4238 m [18-19]. Based on their economic and depositional significance, the shales in the Khabour and Akkas Formations were described in numerous papers, theses and reports [18-25]. Most of these works focus on the stratigraphy, depositional evolution, palynostratigraphy, organic geochemistry, hydrocarbon potential and exploration of Paleozoic prospects in western Iraq. Nevertheless, the relationship between clay mineral transformation and organic matter in hydrocarbon generation was not previously investigated.

Concerning source rock potential of the Paleozoic source rocks in Iraq, Aqrawi *et al.* (2010) [26] revealed that the lower Ordovician shales (assigned to Member 7 of the Khabour Formation, according to Al-Hadidy, 2007, [18]) and the lower Silurian ("hot" shale of the Akkas Formation) could be regarded as principal hydrocarbon source rocks in the Paleozoic sequence of western Iraq, similar to their role across the region in Jordan Syria, Libya, and Saudi Arabia [27, 23, 25]. The lower "hot" shale unit of the Silurian Akkas Formation, western Iraq, has an average-good source rocks (TOC 1.2-5.25 wt%, mean 2.2 wt%; S2 1.2-8.7 kg/tonne, mean 4.2 kg/tonne) [28]. Whereas, TOC values are 0.17-1.42wt% for the 2750-3000m interval and 0.5-1wt% for the 3570-3650m interval in the Khabour Shale of Akkas-1 well, as suggested by Al-Ameri (2010) [23]. Shales in the Khabour Formation were also identified as the source rocks for the gas found in sandstone reservoirs in the K1 to K4 members [23].

The present work correlates the transformation of clay minerals and changes in organic matter maturity in the shales of the Ordovician Khabour and Silurian Akkas Formations in western Iraq, aiming to determine their implications for organic matter maturity and hydrocarbon generation.



Figure 1-A The structural provinces of Iraq after Buday and Jassim (1987) [35] showing the location of the Akkas-1 and Khleisia-1 wells. (B) Inset map showing countries neighboring Iraq.

Stratigraphy and Paleogeography

During the Palaeozoic, the Arabian Plate formed a part of the long and wide northern passive margin of Gondwana, bordering the Paleo-Tethys Ocean [29-31]. Iraq occupies the northeastern part of the Arabian Plate, which lies in higher southern latitudes with dominant clastic sedimentation [32-34],

The stratigraphy of Iraq has been strongly affected by the structural position of the country within the main geostructural units of the Middle East region, since Iraq lies on the border between the Arabianpart of the African (Nubian-Arabian) shield and the Asian branches of the Alpine tectonic belt.

Western Iraq formed a part of the stable shelf of the Nubio-Arabian shield. Clastic deposition of alternating sandstones and shales was dominant in Iraq during the Early Paleozoic (Ordovician and Silurian [36]). These clastic units were deposited in shallow-marine epeiric seas over large areas of the Arabian Platform [37-40, 19]. The areal extent of the seas changed in response to eustatic controls as the Paleozoic era advanced [30, 41]. These epicontinental shallow epeiric seas regressed and transgressed over vast areas throughout the Paleozoic, resulting in variable bed thicknesses and lithotype associations [42-43]. In western Iraq, the thickness of the Paleozoic successions ranges between 3-4 km. North-south trending graben structures prevailed in some areas during the Infracambrian and Paleozoic, which resulted in thicker deposition in these grabens. These grabens indicate an extensional tectonic regime, but they were all aborted and never developed into full-fledged rifts [42].

In the Akkas-1 well Figures-(1 and 2), the alternating marine shales and sandstones in the Ordovician Khabour and the Silurian Akkas Formations are more than 2775 m thick [22-23]. There is large petroleum potential in these Paleozoic strata, where a series of shale source rocks have been identified [44, 18-19]. The oldest shale in the lower part of the Ordovician Khabour Formation comprises about 600 m of black fissile shale, while other shale units interbedded with sandstones are present higher in the Ordovician succession. All these shales are highly mature and organic matter-rich and are considered to be suitable source rocks for hydrocarbons.

The overlying Silurian Akkas Formation contains two important high gamma-radiation (hot) shales (Figure-2). The basal hot shale is 39 m thick while the second unit (19 m) occurs about 60 m above it in the Akkas-1 well [20, 22, 45]. Silurian hot shales are believed to be the main Palaeozoic source rocks in the western and southwestern deserts of Iraq [27]. These hot shales



Figure 2-Lithologic section of the Ordovician Khabour Formation and the Silurian Akkas Formation in the well Akkas-1, west Iraq, illustrating the stratigraphic variation in clay minerals in the studied formations. Note that Ordovician Khabour Formation is divided into seven members (K1-K7) based on biostratigraphic data, whereas Akkas Formation is divided into two member namely (Hoseiba and Qaim) based on the gamma-ray log and organic matter content [18].

are black, fissile, calcareous, bituminous, pyrite-spotted throughout, and organic-rich with TOC values ranging between 0.96% and 16.6% in Akkas-1, and 0.94% and 9.94% in Khleisia-1 [27]. The Silurian hot shales could be over-maturing in the deeper areas of southwestern desert of Iraq, whereas in other

shallower western areas they might be immature. The difference in maturation distribution between the deeper and shallower Silurian hot shales was complicated by an intense 'Hercynian-age' horst-graben tectonic phase [22].

Materials and methods

Twenty one core samples of shale (Figure-2) were studied to identify the main mineralogical composition using X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) techniques accompanied by backscattered electron imaging. A randomly oriented X-ray powder diffractogram was obtained using Spellman DF3 diffractometer. Quantitative determination was performed using the SIROQUANT V3 program developed by the CSIRO (Commonwealth Scientific and Industrial Research Organization), Australia. A JEOL JSM 6460A scanning electron microscope equipped with a backscattered electron detector and energy-dispersive system was used in the morphological and geochemical analysis of selected minerals. For organic matter typing of polished blocks of shale samples, the procedures of Falcon and Snyman (1986) [46] were used. All these analyses were carried out in the laboratories at the University of Wollongong, Australia.

Results

Clay mineralogy

Illite, mixed-layer illite-smectite, kaolinite, and chlorite are the main clay minerals indicated by XRD analysis in the studied Ordovician shale (Table-1, Figure-2). The non-clay fraction includes quartz, feldspars, mica and dolomite (Figure- 3 A, C and E). Whereas in the Silurian shales, the main clay minerals observed are illite, kaolinite, few chlorite, and traces of illite-smectite mixed layer clays, in addition to non-clay minerals represented by quartz, dolomite, mica, calcite and feldspar (Figures-2 and 4A).

Variation in clay components with depth in the Akkas-1 is illustrated in Figure-2. It is interesting to note that an increase in illite and chlorite and a decrease in kaolinite clay minerals is observed in the upper hot shale units of the Silurian Akkas Formation (samples 6-7 at depth 2200-2225m, see Figure-2). Below this depth, where the Ordovician Khabouir Formation existed, a common increase in illite, chlorite and mixed-layers illite with an increase in illite crystallinity are well observed (Figure-2).

Scanning electron microscopic study of the Khabour shale in Akkas-1 revealed the presence of randomly interstratified illite-smectite and neoformed iron-rich chlorite (Figures- 3 and 5). Incipient development of illite fibers in a honeycomb illite-smectite (Figure- 3 B, D and F) is an indication of random interstratification of illite-smectite at a depth of 2,400 m in the Khabour shale. Commonly in shale buried below this depth, the randomly interstratified illite-smectite changed to a regular or well-developed orderly interstratified (OI) form [47].

In deeper buried shales in the well, mica is commonly observed and these shales become more fissile with common irregular pyrite patches [19]. The enrichment with mica and the common presence of illite plates and thick hexagonal platy kaolinite (dickite) in these deeper shales is clearly observed (Figures-3 F and 5), while disc-shaped chlorite together with hexagonal kaolinite (Figure-5 B) is also present as pore fillings. This gradual conversion of smectite into mixed-layer I-S and mica with increasing burial depth and increasing temperature is common in shales deposited in subsiding basins [48]. This reaction starts with randomly distributed I-S layers that become gradually ordered and accompanied with chlorite, dickite, and the dissolution of potassium feldspars as depth increases [49, 13]. This conversion was clearly seen within the studied Khabour shale.

In the overlying Silurian Akkas Formation shale, kaolinite is commonly present as hexagonal plates, some of which are degraded (Figure- 4B-C). Illite is commonly present as fibres and fine white flakes. There is good evidence that the fibrous illite grew from precursor kaolinite (illitization of kaolinite, see Figure- 4B); this characteristically occurs during burial diagenesis. Quartz overgrowth and carbonates are also present.

Sample number	Illite	Kaolinite	Chlorite	Mixed layers illite	Illite Crystallinity
1	29.4	40	3.1	0	0.35
2	49.3	28	3.1	0	0.45
3	46.7	27.6	3	0	0.46
4	44.5	26.9	0.9	0	0.21
5	43.6	27.2	1.2	0	0.43
6	19.7	2.4	0.9	0	0.41
7	53.3	0.1	0	0	0.45
8	23.1	1	0	0	0.5
9	19.6	19.6	9.6	0	0.25
10	21.1	18.8	8.9	0	0.11
11	59.2	0.6	3.3	0.3	0.18
12	63.8	0.4	0	0.1	0.25
13	54.9	0.9	3.3	0	0.82
14	46.6	0.3	4.2	1	0.77
15	41.2	0.6	5.3	1.9	0.52
16	52	0.7	7.4	6.3	0.14
17	32.3	0.5	4.3	3.1	0.66
18	57.5	0.8	4.6	6.5	1
19	19	0.4	2.1	0.1	0.33
20	66.5	0.6	1	0.2	1.3
21	68.1	0.6	3.6	5.4	0.7

Table 1-Quantitative percentages of various clay minerals in the studied bulk shale samples based on XRD results



Figure 3-X-ray diffraction scans (A, C, E) for the bulk shale samples and scanning electron micrographs (B, D, F) of selected shale samples of the Khabour Formation in Akkas-1 well. (A) X-ray diffractograms from shale at a depth of 2350 m, showing the common clay and non-clay minerals present. (B) SEM image of the same sample illustrating the occurrence of illite-smectite mixed layers (I-S) with development of illite fibers; carbonate cement (d = dolomite) fills a fracture in shale. (C) XRD of shale at a depth of 2500 m. (D) SEM image of the same sample showing the hexagonal plates of kaolinite (K), some are replaced by authigenic illite fibers. (E) XRD for shale at a depth of 4170 m. (F) SEM image of the same sample showing the common illitization (I) in this deeply buried shale sample and the presence of mica (M) and quartz (Qz). See Figure-2 for sample locations.



Figure 4 A- X-ray diffractogram of bulk shale sample from the Silurian Akkas Formation, Akkas-1 well, western Iraq (depth 2222 m). B- Degraded kaolinite (k) and illitization of kaolinite (arrow). C-Quartz overgrowth (Qz), degraded kaolinite (partly rounded) plates (arrows), illite flakes (I), and carbonates (C) in the Silurian upper hot shale member at a depth of 2222 m. See Figure-2 for sample locations.



Figure 5-Scanning electron micrographs of shale samples illustrating the main clay minerals observed with their variation with burial depth of the studied Khabour shales. (A) Illite smectite mixed layers (I-S) with incipient fibers of illite and mica (M) in shale of the near shore inner shelf facies (depth 2350 m). (B) Disc-shape chlorite (arrows) and hexagonal kaolinite plates (K) of the transition zone between the shelf and shore-face areas (depth 3108 m). (C) Illite-smectite and illite fibers filling part of pores and cavities in basinal shale (depth 4025 m). (D) Complete fill of illite (I) plates and fibers in Khabour basinal shale, same sample as before. (E) Dominant mica (arrows) in deeply buried shale (depth 4170 m). (F) Illite (I) plates in shale and kaolinite (dickite, K), same sample as before. See Figure- 2 for samples location.

Organic matter

According to the Maturation Range Chart (Cook 1982) [50], the color and type of the preserved organic matter in the studied shales may be referred to as mature-type organic matter in the deeply buried Ordovician Khabour shale. Amorphous organic matter is common, in addition to the various types of vitrinite, inertinite, and the algal *Tasmanites* that were commonly recorded. These organic matter constituents show no fluorescence. In the basal shale of the Khabour Formation at a depth of more than 3500 m, bituminite, amorphous bituminite and many other types of organic matter are recorded. Pyrite and other mineralized matter are also observed. The groundmass is commonly brown-black Figures-(6 and 7).

In Silurian shale, many types of amorphous organic matter are recorded in addition to abundant vitrinite and pyrite as well as large fragments of vitrinite and some very grainy organic matter (*Tasmanites*) (Figure-7 F). According to the Maturation Range Chart of Cook (1982) [50], the color and type of the preserved organic matter in these shales may also be referred to as mature-type organic matter, similar to those of the more deeply buried Khabour shale.



Figure 6 A- Replaced organic matter (arrow) in shale at a depth of 2350 m, x50. B- Laminated mineral matter (white arrow) and amorphous organic matter (black arrow), at a depth of 2400 m, x32. C- Bituminite (yellow fluorescence) in shale at a depth of 2460 m, x32. D- Big lithotype organic matter (white arrow), laminated, uniform and amorphous organic matter, depth 2468 m, x50. E-Abundant organic matter in black groundmass, at depth of 2500m, x32. F- Algal type Tasmanites (white arrow) and large fragment of vitrinite like shape (black arrow) at depth of 3560 m, x50.



Figure 7 A- Framboidal pyrite grains in shale at a depth of 3765 m, x32. B- Brown color Tasmanite at a depth of 3700 m, x50. C- Typical Tasmanite in shale at a depth of 3688 m, x50. D- Shell fragment (arrow) and mineral matter in deeply buried shale (depth 4000 m) in the Khabour Formation, x32. E. Mineral matter and pyrite in shale at a depth of 3800 m, x50.-F- Common vitrinite (arrow) and organic matter in Silurian shale (depth 2290 m), x50.

Discussion

The Khabour Formation shales (Ordovician) are highly-mature, marine, organic-rich rocks with total organic carbon content (TOC) values of 0.9–5% by weight in the Akkas-1 well in western Iraq [20]. Whereas shales in the Silurian Akkas Formation are black, fissile, calcareous, bituminous, pyrite-spotted, and organic-rich with TOC values ranging between 1.0 - 16.6% in the Akkas-1 well [20]. The "hot" shale units (Figure- 2) are likely to form the principal hydrocarbon source rock in the Palaeozoic sequence of western Iraq and were deposited mostly under anoxic conditions [22, 23, 25, 28].

Al-Haba *et al.* (1994) [20] suggested that hydrocarbons generated in Akkas field were derived from the Khabour shale source rocks while overlying shales in the formation could act as cap rocks for the older Khabour sandstone reservoirs. These uppermost Khabour sandstones are composed of silty quartz, as well as mica, pyrite, and glauconite [20].

The Paleozoic Khabour and Akkas Formations were continuously deposited over a wide geographic area in shallow subsiding epicontinental or epeiric seas in a homoclinal ramp setting [19].

In the present study, the clay mineral illite-smectite transformation in addition to organic matter content reveal that shale units in the Ordovician Khabour and Silurian Akkas Formations can be recognized as an organically mature oil shale, especially in the more deeply buried basinal areas. According to vitrinite reflectance data, the paleogeothermal gradient at the time of maximum burial in the study area was 55 °C/km, giving an estimated maximum burial temperature of approximately 80-120 °C in the Khabour Formation [47].

Majidee (1999) [45] used a quantitative technique to calculate the anomalous temperature gradient and heat generation across the "hot" shale at 2,208–2,327 m of Akkas-1 well. He attributed the higher temperature gradient ($6.1^{\circ}C/100$ m) to two factors: (1) the high uranium content in the "hot" shale of up to 33.8 ppm [28] which increases the rate of radiogenic heat generation to about 5.0 microWatt per cubic meter; and (2) the dominance of shale in the Akkas Formation which reduces the conductivity and increases the thermal gradient.

Commonly, temperature increases after deposition in subsiding basins coincide with the onset of the transformation of smectite to illite [51]. The gradual conversion of smectite into mixed-layer illite-smectite (I-S) with increasing burial depth and increasing temperature is common in shales deposited in subsiding basins [48]. This conversion is coincident with the generation of oil in sedimentary basins, as seen in the topmost oil bearing horizons in the US Gulf Coast Tertiary succession [48].

Fine-grained smectite layers may initially protect organic matter from oxidation and then catalyze its transformation into petroleum. Water released by the fixation of interlayer potassium may aid in flushing hydrocarbons out of source rocks and into reservoirs, and pore space resulting from the collapse of smectite layers could provide pathways through source rocks for petroleum migration [4, 48, 52].

This reaction first produces random distributions of I-S layers that gradually become ordered and accompanied by the authigenic development of chlorite and dickite, along with the dissolution of potassium feldspar [49, 13]. This conversion and its mineral associations are seen in the Khabour Formation Figures-(3-5) and were also noted from intercalated sandstones in the Silurian Akkas Formation [53].

Source rocks with organic matter from higher plants have a hydrocarbon compound known as the vitrinite maceral. Various types of vitrinite, inertinite and bituminite, in addition to algae of *Tasmanite*-type, are recognized in the Khabour Formation Figures-(6 and 7). Vitrinite reflectance has been widely used to determine the maturity of hydrocarbon source rocks. Vitrinite reflectance percentages (%Ro) in the Khabour and lower Akkas Formations (Figure-8) commonly exceed the value of 1, which indicates a high level of organic maturity in the rocks [12, 54].

According to the hydrocarbon generation potential scheme proposed by Al-Ameri (2010) [23] (Figure-8), it is evident that some levels within the Khabour Formation in Akkas-1 well generated condensates and wet and dry gas with kerogen type B. In the Akkas Formation, mixed kerogen types A and B and oil generation were shown by Al-Ameri (2010) [23]. The degradation of the organic matter down to a depth of 3000 m may result in abundant amorphous organic matter, including 70-75% amorphogen.

In the present study, algal-type *Tasmanites* and traces of vitrinite are common at depths below 3000 m in Akkas-1 Figures-(6 and 7). The marine algal phytoplankton *Tasmanites* is an important type of organic matter in the Ordovician to Devonian black shales in the Appalachian basin. They correspond

to type I kerogens that appear to be derived from extensive bacterial reworking of lipid-rich algal debris [55]. The common amorphous and laminated organic matter at shallower depths may be the type II kerogen of Peters and Moldowan (1993) [55] which corresponds to the wet gas and condensates recorded by Thompson and Dembicki (1986) [56].

Clay mineral distribution (Figure-8) shows that the studied shales include illite, chlorite, kaoloinite, and illite-smectite mixed layers. The main change in clay mineralogy with depth is an increase of illite, dickite (kaolinite), and mica downwards.

Al-Juboury (1999) [47] showed that the change from random to regular mixed-layered illitesmectite due to burial diagenesis occurs at a depth of about 2400 m, at which vitrinite reflectance is about 0.6%. A specific relationship of vitrinite reflectance to I-S expandability and illite crystallinity is observed and is probably controlled by thermal history. This relationship is in accordance with the depletion in kaolinite content and disappearance of K-feldspar leading to an overall increase in amounts of illite and illite-smecite. It gives an indication of the exhaustion of K-feldspar as a source for the formation of I-S mixed-layer clays.

The depth of 2400 m also represents the contact between the shallower Silurian inner neritic environment and the deeper outer neritic Ordovician sequences [19, 23]. These Paleozoic formations were rapidly deposited in grabens with elevated geothermal gradients, so that the diagenetic processes were controlled by thermal history (tempreture+time of residence) in these tectonic-environmental-sedimentologic settings.

The conversion of smectite into mixed-layer illite-smectite (I-S), and subsequently from random to ordered I-S, associated with increasing vitrinite reflectance, is commonly observed below 2500 m depth in Khabour Formation in Akkas-1 well (Figure-8).

From a regional perspective, the current study deals with the relation between clay minerals distribution and diagenesis with organic matter typing in two promising formations including shale-gas units [57]. This study can contribute to the regionally trending studies on unconventional shale gas around the world in North America, Latin America, Middle East, North Africa, Central Asia, Russia, and China [4, 58, 59], with the fact that clay-organic fabric controls the clay mineral effects on hydrocarbon generation.





Conclusions

The Ordovician Khabour and Silurian Akkas shales are important potential source rocks in western Iraq. The recorded conversion of smectite into mixed-layer I-S and, subsequently, from random to ordered I-S with changes in illite-smectite crystallinity, associated with increasing vitrinite reflectance in the Akkas-1 well, are commonly associated with oil and gas generation (kerogen and dry gas). In the studied shales, these changes are associated with algal-type *Tasmanites*, various vitrinite/vitrinite-like macerals, and kerogen. Hence, the results from this study could be used as an indication of higher maturity and hydrocarbon generation in the deeply buried rocks of the Khabour and Akkas Formations in western Iraq. These results could also have a regional perspective, since they deal with the relation between clay minerals distribution and diagenesis with organic matter typing and can contribute to the regionally trending studies on unconventional shale gas around the world.

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References

- 1. Scotchman, I.C. 1987. Clay diagenesis in the Kimmeridge Clay Formation, onshore UK, and its relation to organic maturation, *Mineralogical Magazine*, 51: 535-551.
- 2. Velde, B. and Lanson, B. **1993**. Comparison of I/S transformation and maturity of organic matter at elevated temperatures, *Clays and Clay Minerals*, **41** (2): 178-183.
- 3. Littke, R., Bayer, U., Gajewski, D. and Nelskamp, S. 2008. Dynamics of Complex Intracontinental Basins: Three Example of the Central European Basin System, pp. 1-519, Springer-Verlag, Berlin-Heidelberg.
- **4.** Shu, J. **2012**. Clay Minerals from the Perspective of Oil and Gas Exploration, in: Valaskova, M. and Martynkova, S.R. (Eds.) Clay Minerals in Nature-Their Characterization, Modification and Application. InTech Croatia.
- 5. Piane, C. D., Bourdet, J. M., Clennell, M. B., Rickard, W.D.A. and Saunders, M. et al. 2018. Organic matter network in post-mature Marcellus Shale: Effects on petrophysical properties. *AAPG Bulletin*, 102(11): 2305-2332.
- Gu, Y., Wan, Q., Yu, W., Li, X. Yu, Z., 2018. The effects of clay minerals and organic matter on nanoscale pores in Lower Paleozoic shale gas reservoirs, Guizhou, China. *Acta Geochimica*, 37 (6): 791–804.
- 7. Allen, P.A. and Allen, J.R. 2005. *Basin Analysis Principles and Applications*, 2nd edition. Blackwell Publishing, Oxford.
- **8.** Hartkopf-Fröder, CH., Königshof, P., Littke, R. and Schwarzbauer, J. **2015**. Optical thermal maturity parameters and organic geochemical alteration at low grade diagenesis to anchimetamorphism: A review, *International Journal of Coal Geology*, **150–151**: 74–119.
- 9. Peters, K.E. and Casa, M.R. 1994. Applied source rock geochemistry, in: The petroleum system-from source to trap, L. B. Magoon and W. G. Dow, Eds. *AAPG Bulletin.*, 60: 93-120.
- **10.** Velde, B. **1995**. Origin and Mineralogy of Clays: Clays and the Environment, pp. 1-334. Springer Verlag, Heidelberg.
- **11.** Suggate, R.P. **1998**. Relations between depth of burial, vitrinite reflectance and geothermal gradient. *Journal of Petroleum Geology*, **21** (1): 5-32.
- 12. Tissot, B. and Welte, D. 1984. Petroleum Formation and Occurrence, pp. 1-699, Springer-Verla
- **13.** Hower, J., Eslinger, E.V., Hower, M.E. and Perry, E.A. **1976**. Mechanism of burial metamorphism of argillaceous sediments. I. Mineralogical and chemical evidence. *Bull. Geol. Soc. America*, **87**: 725-737.
- 14. Weaver, C.E. 1979. Geothermal alteration of clay minerals and shale: Diagenesis: Tech. Rept. ONWI-21, Georgia Inst. Tech., Battelle Off. Nucl. Waste Isolation.
- **15.** Foscolos, A.E. and Powell, T.G. **1980**. Mineralogical and geochemical transformation of clays during catagenesis and their relation to oil generation: *Canadian Society of Petroleum Geologists*. Memoir **6**: 153-172.
- **16.** Bruce, C.H. **1984**. Smectite dehydration- its relation to structural development and hydrocarbon accumulation in northern Gulf of Mexico basin. *AAPG Bulletin*. **68**: 673-683.
- **17.** Pollastro, R.M. **1993**. Considerations and applications of the illite/smectite geothermometer in a hydrocarbon-bearing rocks of Miocene in Mississippian age, *Clays and Clay Minerals*, **41**: 119-133.
- **18.** Al-Hadidy, A.H. **2007**. Paleozoic stratigraphic lexicon and hydrocarbon habitat of Iraq. *GeoArabia*, **12**(1): 63-130.
- **19.** Al-Juboury, A.I. and Al-Hadidy, A.H. **2009**. Petrology and depositional evolution of the Paleozoic rocks of Iraq. *Marine and Petroleum Geology*, **26** (2): 208-231.
- **20.** Al-Haba, Y., Al-Samarrai, A., Al-Jubori, F., Georgis, N.N. and Ahmed, I.M. **1994**. Exploration for the Paleozoic Prospects in Western Iraq, Part 1, Exploration of the Paleozoic system in Western Iraq. In: Proceedings of the Second Seminar on Hydrocarbon Potential of Deep Formations in the Arab Countries (OAPEC), Cairo.
- **21.** Baban, D.H.M. **1996**. Palynostratigraphy and organic maturation of the lower part of Paleozoic in the western desert of Iraq. Ph.D. thesis, Baghdad University, Iraq.

- 22. Aqrawi, A.A.M. 1998. Paleozoic stratigraphy and petroleum systems of the western and southwestern deserts of Iraq. *GeoArabia*, 3(2): 229-248.
- 23. Al-Ameri, Th. K. 2010. Palynostratigraphy and the assessment of gas and oil generation and accumulations in the Lower Paleozoic, western Iraq. *Arabian Journal of Geosciences*, Springer, 3 (2): 155-179.
- 24. AlKhafaji, M.W., AlJubouri, Z.A. and AlDobouni, I.A. 2015a. Depositional environment of the lower Silurian Akkas hot shales in the western desert of Iraq. Results from an organic geochemical study. *Marine and Petroleum Geology*, 64: 294-303.
- **25.** AlKhafaji, M.W., AlJubouri, Z.A. and AlDobouni, I.A. and Littke, R. **2015**b. Hydrocarbon potential of Ordovician–Silurian successions in Akkas field, western desert of Iraq. *AAPG Bulletin*, **99**(4): 617–637.
- 26. Aqrawi, A. A., Goff, J.C., Horbury, A.D. and Sadooni, F. N. 2010. *The Petroleum Geology of Iraq*, pp. 1-424, Scientific Press, UK.
- 27. Lüning, S., Craig, J., Loydell, D.K., Storch, P. and Fitches, B. 2000. Lower Silurian "hot shales" in North Africa and Arabia: regional distribution and depositional model. *Earth-Science Reviews*, 49: 121–200.
- **28.** Al-Juboury, A.I., Howard, J., Qader, F.M., Vincent, S.J., Al-Hadidy, A.H., Thusu, B., Kaye, M.N.D. and Vautravers, B. **2019**a. Whole rock geochemistry, mineralogy and source potential of the shale of the Silurian Akkas Formation, western Iraq, resubmitted to AAPG Bulletin.
- **29.** Sengör, A.M.C. **1990**. A new model for the Late Palaeozoic-Mesozoic tectonic evolution of Iran and implications for Oman. In: Robertson, A.H.F., Seale, M.P., Ries, A.C., (Eds.) The Geology and Tectonics of the Oman Region. *Geological Society of London, Special Publication*, **49**:797-831.
- **30.** Beydoun, Z.R. **1991**. Arabian plate hydrocarbon, geology and potential: A plate tectonic approach, AAPG Studies in Geology, No. 33, 77pp.
- **31.** Loosveld, R.J.H., Bell, A. and Terken, J.J.M. **1996**. The tectonic evolution of interior Oman, *GeoArabia*, **1**: 28-51.
- **32.** Husseini, M.I. **1992.** Upper Paleozoic tectono-sedimentary evolution of the Arabian and adjoining plates. *Journal of the Geological Society*, London, **149**: 419-429.
- **33.** Beydoun, Z.R. **1997**. Arabian plate oil and gas: Why so rich and so prolific. *Episodes*, **21**(2): 74-81.
- **34.** Al-Fares, A.A., Bouman, M. and Jeans, P. **1998**. A new look at the Middle to Lower Cretaceous stratigraphy, offshore Kuwait. *GeoArabia*, **3** (4): 543-560.
- **35.** Buday, T. and Jassim, S.Z. **1987**. The Regional Geology of Iraq. Tectonism, Magmatism and Metamorphism, Publication of the Geological Society of Iraq.
- 36. Al-Omari, F.S. and Sadiq, A. 1977. Geology of Northern Iraq, Dar Al-Kutib press, Mosul University, Iraq.
- **37.** Husseini, M.I. **1990**. The Cambro-Ordovician Arabian and adjoining plates: a glacioeustatic model. *Journal of Petroleum Geology*, **13**: 267-288.
- **38.** McGillivary, J.G. and Husseini, M.I. **1992**. The Paleozoic petroleum geology of central Arabia. *AAPG Bulletin*, **76**: 1473-1490.
- **39.** Beydoun, Z.R. **1993**. Evolution of the northeastern Arabian Plate margin and shelf: Hydrocarbon habitat and conceptual future potential. *Revue de l'Institut Français du Pétrole*, **48**: 311-345.
- **40.** Al-Sharhan, A.S. and Nairn, A.E.M. **1997**. Sedimentary Basins and Petroleum Geology of the *Middle East*. pp. 1-843, Elsevier, Amsterdam.
- **41.** Numan, N. M. S. **1997**. A plate tectonic scenario for the Phanerozoic succession in Iraq. *Iraqi Geological Journal*, **30**: 85-110.
- 42. Sharland, P. R., Archer, R., Casey, D. M., Davies, R. B., Hall, S., Heward, A. P., Horbury, A. D. and Simmons, M. D. 2001. Arabian Plate Sequence Stratigraphy, Manama, Bahrain, Gulf Petrolink, pp. 1-371,
- **43.** Konert, G., Al-Afifi, A.M., Al-Hajri, S.A. and Droste, H.J. **2001**. Paleozoic stratigraphy and hydrocarbon habitat of the Arabian Plate. *GeoArabia*, **6**(3): 407-442.
- 44. Jassim, S.Z. and Al-gailani, M. 2006. *Hydrocarbons. In S.Z. Jassim and J.C. Goff (Eds.). Geology* of *Iraq.* Chapter 18, pp. 232-250, Dolin and Moravian Museum, Czech Republic.

- **45.** Majidee, F.M.Q. **1999**. The reasons of high temperature in well Akkas-1 and its effects on maturation's time of source rocks. M.Sc. thesis, University of Baghdad.
- **46.** Falcon, R.M.S. and Snyman, C.P. **1986**. An introduction to coal petrography: Atlas of petrographic constituents in the bituminous coals of southern Africa, pp/1-27, The Geological Society of South Africa.
- **47.** Al-Juboury, A.I. **1999**. Clay diagenesis in the buried Ordovician-Carboniferous shales, western Iraq. In: 4th International Conference on Geochemistry, 223-235, Alexandaria University, Egypt.
- **48.** Eberl, D.D. **1984**. Clay mineral formation and transformation in rocks and soil. *Phil. Trans. R. Soc. London*, **A31**:241-257.
- **49.** Perry, E.D., and Hower, J. **1970**. Burial diagenesis in the Gulf Coast pelitic sediments. *Clays and Clay Minerals*, **16**:165-177.
- **50.** Cook, A.C. **1982**. The origin and petrology of organic matter in coals, oil shales and petroleum source rocks, pp. 1-106, University of Wollongong Printery, Wollongong.
- **51.** Akande, S., Viczian, I. and Erdtmann, B. **2005**. Prediction of petroleum generation intervals in Southern Nigeria Rift basins by means of clay transformations, vitrinite reflectance and fluid inclusion studies. *NAPE Bulletin*, **16**: 38-51.
- **52.** Zhao, J., Jin, Z., Jin, Z., Hu, Q., Hu, Z., Du, W., Yan, C. and Geng, Y. **2017**. Mineral types and organic matters of the Ordovician-Silurian Wufeng and Longmaxi Shale in the Sichuan Basin, China: Implications for pore systems, diagenetic pathways, and reservoir quality in fine-grained sedimentary rocks. *Marine and Petroleum Geology*, **86**: 655-674.
- **53.** Al-Juboury, A.I., Howard, J., Nichols, G., Vincent, S., Manning, CH. and Vautravers, B.P. **2019**b. Sedimentology and geochemistry of potential sandstone reservoirs of the Akkas Formation, western Iraq. *Journal of Petroleum Geology*, **42**(3):261-280.
- **54.** McCarthy, K., Niemann, M., Palmowski, D., Peters, K. and Stankiewicz, A. **2011**. *Basic petroleum geochemistry for source rock evaluation*. Oilfield Review 32-43. Schlumberger, Paris.
- **55.** Peters, K.E. and Moldowan, J.M. **1993**. The Biomaker Guide, pp. 1-363, Prentice Hall, Englewood Cliffs, New Jersey.
- **56.** Thompson, C. and Dembicki, H. **1986**. Optical characteristics of amorphous kerogen and the hydrocarbon-generating potential of source rocks. *International Journal of Coal Geology*, **6**(3): 229-249.
- **57.** Al-Juboury, A.I. and Thani, M.A. **2018**. Silurian gas-rich "Hot Shale" from Akkas gas field, Western Iraq: Geological importance and updated hydrocarbon potential and reservoir development estimations of the field. In Al-Juboury A.I. (Ed.) Shale Gas- New Aspects and Technologies, InTech Open (London), 41-66.
- **58.** Zhang, Y., Jin, S., Jiang, H., Wang, Y. and Jia, P. **2015**. Review of Well Logs and Petrophysical approaches for shale gas in Sichuan Basin, China. *The Open Petroleum Engineering Journal*, **8**: 316-324.
- **59.** Rahman, H.M., Kennedy, M., Löhr, S.C. and Dewhurst, D.N. **2017**. Clay-organic association as a control on hydrocarbon generation in shale. *Organic Geochemistry*, **105**: 42-55.
- **60.** Bujak, J.P., Barss, M.S. and Williams, G.L. **1977**. Offshore East Canada's organic type and color and hydrocarbon potential, *The Oil and Gas Journal*, **75**:198-201.