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The Impact of Hydrothermal Fluids on Porosity Enhancement and Hydrocarbon Migration in Qamchuqa Formation, Lower Cretaceous, Kirkuk Oil Company

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Abstract: The Lower Cretaceous reservoir core samples from the upper part of Qamchuqa Formation, Baba Dome, Kirkuk Oil Company, show evidence for multistage episodes of dolomitization and a complex diagenetic history. Optical microscope reveals muti-phase of diagenesis: an early stage of diagenesis and its alteration, later, by evaporated seawater under near-surface setting conditions, followed by different event of dolomitization. The stylolite microstructures postdate anhydrite and early matrix dolomite crystals (DI) and predated the coarse rhombohedral (DII) and saddle dolomite crystals (SD), which were formed under a deep burial realm. High-resolution data from stable isotopes integrated with intensive optical observation, ImageJ software, and litho-log are utilized to establish a qualified methods for mapping a better image of hydrothermal diagenesis under subsurface conditions. These methods revealed different types of dolomites, mostly focused on fractures and void spaces, and the paragenetic sequence shows the complex history of diagenetic carbonate rocks hosted in the limestone of Qamchuqa Formation. The sequence is started from older to younger as follow: Micritization, early anhydrite mineral formation, early dolomite, stylolization, rhombohedral dolomite, and saddle dolomite crystals. The early dolomite phase is usually corroded by hydrocarbon phase, and, geometrically, the hydrocarbon phase is overgrown by the early dolomite. Therefore, the dolomitizing fluids enhanced the porosity system and had positive impact on the hydrocarbon movement. This phase of dolomite and anhydrite formation were associated with the first groups of δ^{18}OVPDB and δ^{13}CVPDB data, a narrow range of oxygen values, and inverse Js of Lohmann curve fits towards the near-surface and shallow diagenetic settings. Detailed optical microscope and supportive data from oxygen-carbon isotopes of saddle dolomite confirm the presence of hot fluids under subsurface condition. The latter data were supported by light δ^{18}OVPDB and constant heavy δ^{13}CVPDB, which indicates a hot fluid possibly circulated in deep burial conditions, and this is channeled along the fracture and pore spaces, consistent with hydrocarbon migration. These pore spaces influenced by leaching were hydrocarbon migrations associated with hot fluids under deep sitting conditions. However, a remarkable part of pristine microfacies of host limestone was preserved. In summary, this study will add a new understanding and insight into the origin, genesis, and timing of these dolomites and their direct connection to hydrocarbon exploration and development in most reservoir oil rocks, which are exposed to hydrothermal fluids. Additionally, the study adds new data on hydrothermal fluids in subsurface conditions, whereas most of the previous reported work has mostly focused on exposed rock.

Keywords: hydrothermal fluids; hydrocarbon migration; subsurface deep diagenesis; lithology; stable isotopes; Kirkuk Oil Company

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1. Introduction

Most hot dolomite sources have been reported from different localities worldwide [1–3]. The sources of fluids revealed that they derived from high temperature and brine fluids, mostly evaporative rocks [4,5] or reflux of cold-meteoric fluid [6]. However, the source of dolomitizing fluids is still in debate. Many authors have followed the above-mentioned sources of fluids to achieve the paragenetic sequence of carbonate diagenesis [7,8]. The paragenesis is used as a key indicator tool to understand the complex diagenetic stages during the dolomitization process under subsurface conditions. Therefore, this work presents and focuses on the core samples, optical microscopy, and geochemistry of the diagenetic rocks to draw a paragenetic evolution of the Qamchuqa Formation as it is related to Kirkuk Oil Company, Northern Iraq. The goal in defining the depositional and diagenetic parts is to provide an overview of depositional controls exerted on initial porosity, as well as the contribution of diagenetic processes during fluid evolution. To understand the source and type of fluid flowed up after the deposition, the stable isotope signals are the direct indicator for tracking the fluid evolution in a post-depositional environment [9].

The Cretaceous carbonate reservoir is one of the major reservoirs in the Middle East. Qamchuqa Formation is a significant carbonate reservoir managed by Kirkuk Oil Company along Baba Dome. The common diagenetic processes in Qamchuqa Formation are fracturing, dissolution, dolomitization, etc. [10]. These diagenetic processes affected carbonates, which could contribute and add qualified characteristics of reservoir development, which make the foreland basin of Qamchuqa Formation one of the main targets for oil exploration in most of the oil fields in Iraq. The role of tectonics also in a foreland basin setting are linked to fracturing, fluid flow, and dolomitization, which have not been investigated in details in the region previously.

The fluids and petrogenesis of dolomites are developed as a result of consecutive events [8,11]. The sources of dolomitizing fluids are of two types: related to cold and high temperatures. Cold dolomitizing fluid mostly is associated with two major models: (i) near surface and (ii) marine–meteoric mixing [12–16]. Hot dolomitizing fluid is commonly the result of high temperature fluids, overprinting the host carbonates by a fluid temperature with more than 5 °C warmer than the surrounding carbonates [17].

Therefore, a few studies have been conducted on the diagenesis of host limestone from the exposed outcrops of Qamchuqa Formation samples, but this study is, for the first time, focused on the alternation of the subsurface core rocks using litho-log, thin sections, and stable isotopes in Baba dome to understand further the diagenetic processes and subsurface settings (Figures 1 and 2).

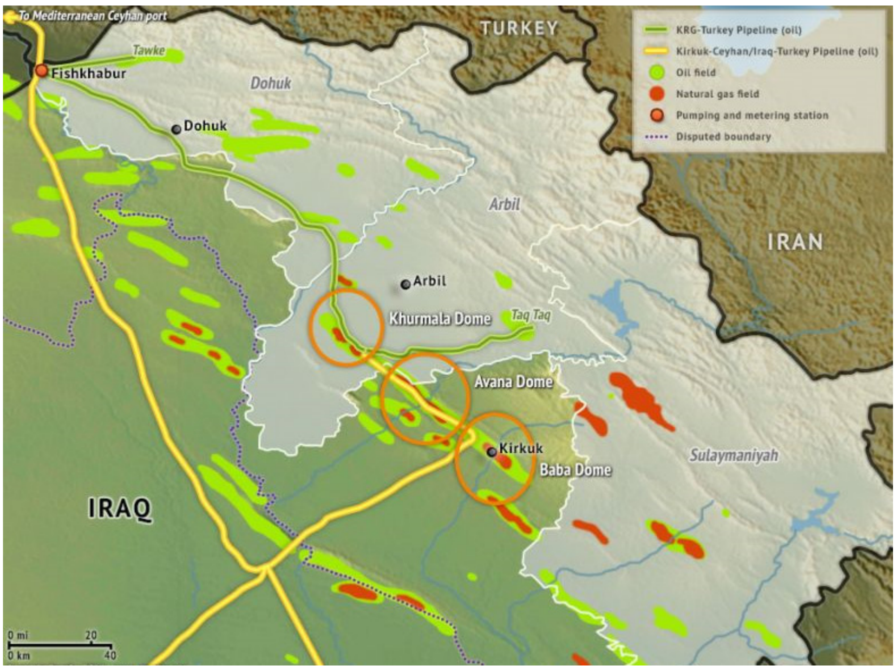

Figure 1. Illustration of the general location of oilfields in NE-Iraq. Close up the Baba Dome inside the lower circle shape.

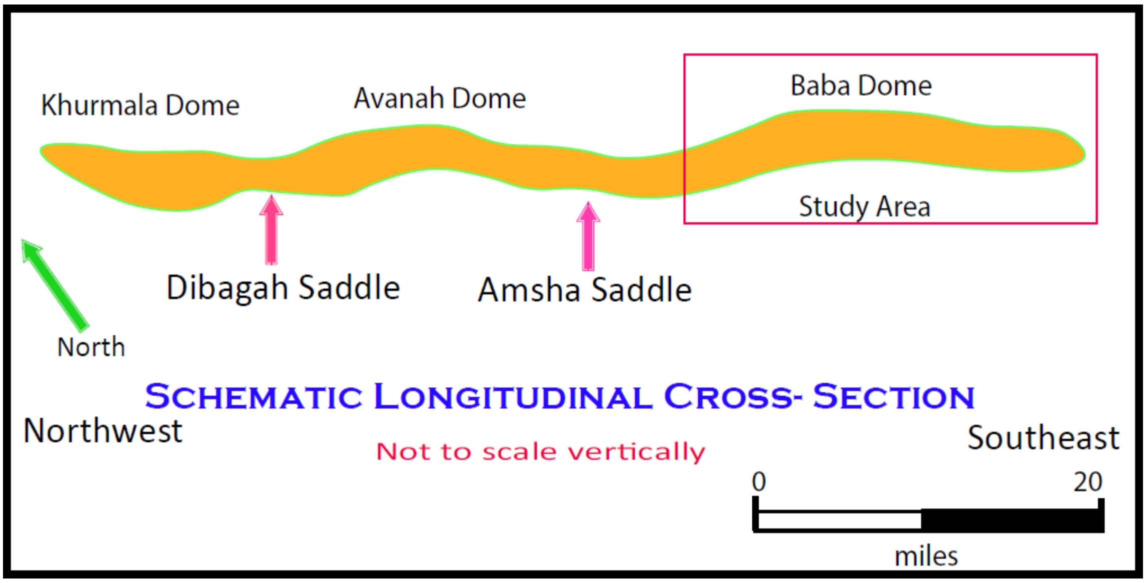

Figure 2. Schematic longitudinal cross-section of Kirkuk Structure, close up of the Baba Dome in the study area.

2. Geological and Structural Settings

The Early Cretaceous Arabian platform consists of a thick succession of dolomite and limestone. This succession covers most of Iraq (Kirkuk area) and some part of southwestern Iran, the Arabian Gulf, and Saudi Arabia. This basin is a portion of the subzone that contains the long anticlines of Hemrin, which form the SW border of the subzone, as well as the Bai Hassan anticline that forms the NE border. These anticlines are 130–200 km long, with several doubly-plunging domes [18]. The Kirkuk Oil Field is a sinuous anticline, some 100 km long and 4–5 km width towards SE-NW, divided by two prominent saddles (Amsha and debaka), forming three major structural culminations (Baba, Avanh, and Khormala). These structures are located in the Foothill Zone within the Unstable Shelf [19].

The Early Cretaceous Qamchuqa, Suaiba, and Mauddud formations are the main constructing units of this platform. These units are assumed to be important reservoirs for oil in the Middle East [18,20,21]. During the Late Tithonian-Early Turonian, they were associated with deposition of large intra-shelf basin with a new phase of ocean floor spreading in the Southern Neo-Tethys [18]. As a result of the opening of the Southern Neo-Tethys, a new passive margin formed along the northeast margin of the Arabian Plate [18]. During that period, the NE margin of the Arabian Plate was formed by a carbonate ridge along the north facing passive margin of the Southern Neo-Tethys [22]. The NE Arabian passive margin during the Albian-Cenomanian was covered by an extensive, continuously subsiding carbonate platform [18,23]. During the Albian, the Qamchuqa Formation was deposited and characterized by a relatively shallow-water platform extending over Dohuk, Mosul, Erbil, and Kirkuk [22].

3. Materials and Methods

Twenty-one core samples were obtained from the upper part of Qamchuqa Formation from core samples obtained at various subsurface depths from one of the production wells in Baba Dome, Kirkuk Oil Field. Forty-four thin sections were prepared in order to follow the direction of fluids that caused the dissolution and cementation, as well as to out-line any lithological variations in term of diagenesis.

ImageJ is a software that can be accessed in general. ImageJ software is developed by Wayne Rasband (Madison, WI, USA) and can run on various system supported by Java 1.1 or other versions of software. This software is used to measure the pore spaces between and within particle sizes within the total volume. Downloaded ImageJ is linked to the computer by running the program package. In this case, there are three versions of the 8-bit version, 32-bit version, and 64-bit version. This study used the 8-bit version, which contains sub-files that we can be dealt with. In this study, the last version of ImageJ is used (version 1.53t, 2022). The oxygen and carbon isotopic compositions of (23) samples were prepared from different facies changes, and the powder samples were obtained using a micro-drilling machine to avoid any mixing between recognized carbonate phases. However, the co-occurrence of fracture-filling calcite and dolomite crystals, and also evaporites in the host limestones, made it difficult to avoid 100% mixing between these phases. As a consequence, the dolomite and calcite are considered as one group, and host limestone and evaporite are considered as a second group. Carbonate powders were reacted with 100% phosphoric acid at 70 °C using a Gasbench II connected to a Thermo Fisher Delta V Plus mass spectrometer (Gaspench II, Erlangen, Germany). All values are reported in per mil relative to V-PDB. Reproducibility and accuracy were monitored by replicate analysis of laboratory standards calibrated to international standards NBS19, NBS18, and LSVEC. Laboratory standards were calibrated by assigning δ^{13}CVPDB values of +1.95‰ to NBS19 and −46.6‰ to LSVEC and by assigning δ^{18}OVPDBvalues of −2.20‰ to NBS19 and −23.2‰ to NBS18. The analyses (23 samples) were performed at the University of Erlangen (Erlangen, Germany, M. Joachimski).

4. Results

4.1. Field Observation

Based on the litho-log of the studied part of Qamchuqa Formation, the upper part of this formation is conformably blanketed by the Dokan Formation, and the lower part is underlain by the Dokan Formation (Figure 3). The subsurface litho-log divided the Qamchuqa Formation based on general litho-facies into two parts (Figure 3). The lower part is mostly composed of host limestone, and, in places, it is dolomitized with some marly deposits. The upper part is composed mostly of dolomitized rocks, and the host limestone part is extensively dolomitized. However, in a few places, the host limestone is poorly preserved. Our study is placed in the upper part where the formations are completely subjected to diagenesis.

4.2. Micro-Scale Observation

The project is mainly focused on the detailed study of digenesis and the associated processes through prepared thin sections under optical microscope and stable isotope data. Several diagenetic processes (micritization, cementation dissolution, replacement, stylolization, etc.) are observed from core samples that are obtained from the subsurface Qamchuqa Formation. The micritization process is the main and the earliest diagenetic stage that followed the deposition of the host carbonate rocks of the Qamchuqa Formation. (Figure 4A–D).

Furthermore, the recent study exhibits a vuggy and channel porosities caused by fabric-selective dissolution and non-fabric-selective dissolution (Figure 4D) through the cements and matrix containing carbonate crystals during diagenesis. Moldic porosity is observed inside the host limestone grains, such as inside the chambers of planktonic forams. Consequently, the pristine facies are dissolved and replaced by different facies and could be distinguished from surrounding rock (Figure 5A,B).

Fracturing and cementation are important processes in the diagenetic realm in this work. Cement is distinct from neomorphic spar. This is an in situ representation of calcium carbonate in the solid state. The cementation process was extensively affected by the subsurface samples, and it represents the commonest one between the other chemical diagenetic processes. Two types of cements were identified inside the fractures: (1) fracture-filling calcite crystals, with calcite crystals having a variety of sizes, precipitated as drusy and blocky cements; and (2) anhydrite, usually occupying the micro-scales of pore spaces (Figure 5A,B) and in places filling large macroscales of fracture. The anhydrite is characterized as colorless under PPL and as undulous extinction under XPL.

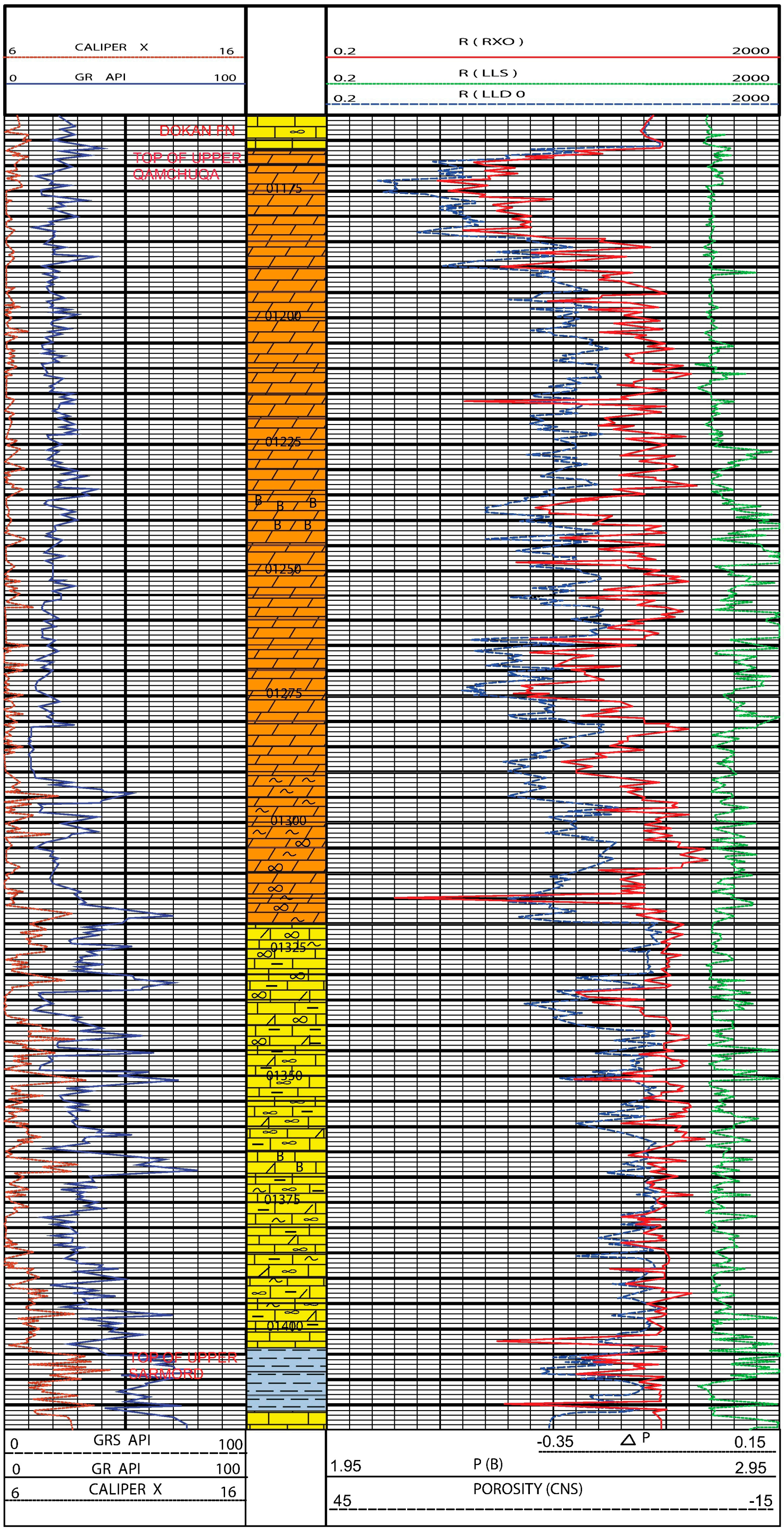

Figure 3. Lithological log for the Upper Qamchuqa Formation. Left-hand track shows gamma ray (GR) and API of the reservoir. The recent studied samples represented the depth interval from 1175 m to 1191 m.

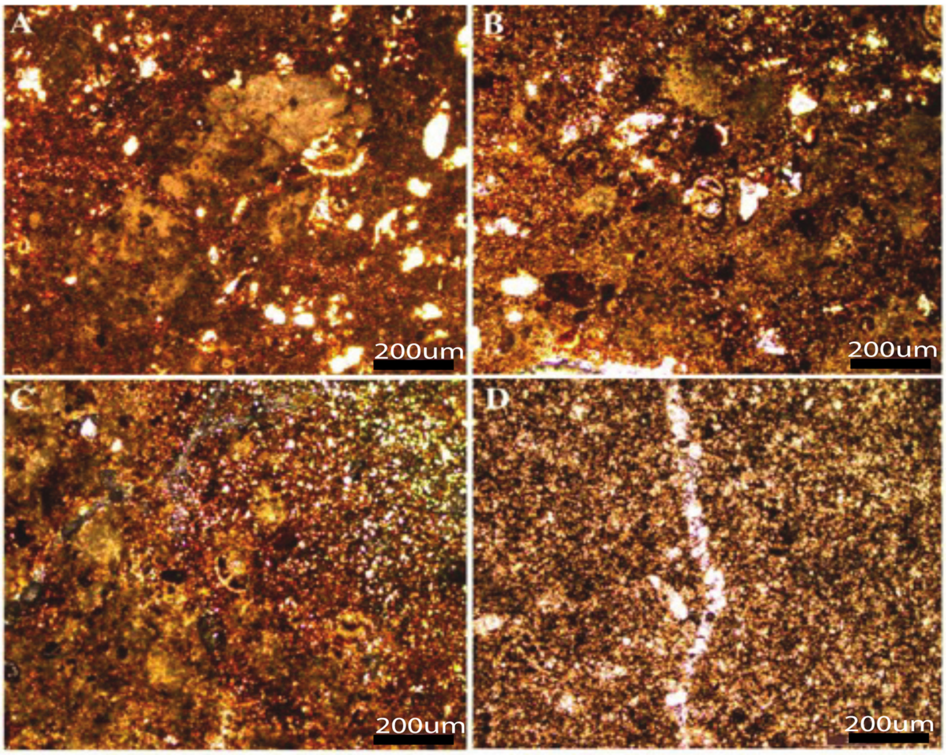

Figure 4. Photomicrographs showing: (**A**,**B**) precursor limestone with the micrite component giving a mudstone microfacies, close up the upper right part of (**A**) and the central part of photo (**B**) of planktonic foraminifera. (**C**) Mudstone microfacies are recognized in the lower part, while the upper right part illustrates the initiate of first replacement of micrite particles (early diagenesis). (**D**) The replacement process is commonly controlled in this micro-view, cross-cut by fracture-filling anhydrite minerals. This fracture still preserves the predated phase of fine dolomite.

Dolomitization is one of the main diagenetic processes in carbonate rocks that is influenced by deep burial fluids or fluxing of meteoric water. Three types of dolomitization are identified in this study: early coarse-crystalline dolomite and late dolomites. Early dolomite is characterized by fine size, rhombohedral shape, and displays a dark color (Figures 5C,D and 6A,B). Coarse-crystalline dolomite displays coarse sized-crystals up to 500 µm, and it usually filled the fractures and pore spaces. These crystals show planar characteristics, and they are rhombohedral in shape, besides having two sets of cleavages (Figure 5C,D). Late dolomite (saddle dolomite) displays a curved faced, dirty in color, and it is aggraded in its crystal sizes, filling the vuggy pores (Figure 6C,D). Under XPL, it shows a wavey extinction, while under PPL, it shows a clear rim and cloudy core. This dolomite considered as the last phase of diagenesis in the Upper Qamchuqa Formation.

4.3. ImageJ Software

The studied thin section is attached to the stage of optical microscope (Olympus type) equipped with different magnification lens using both PPL and XPL view. A digital camera (Nikon MODEL) is linked between the laptop (capturing images) and the microscope. Microscopic images for early and late diagenesis were converted to digital images to be analyzed to calculate the porosity percentage for both early and late phases of diagenesis.

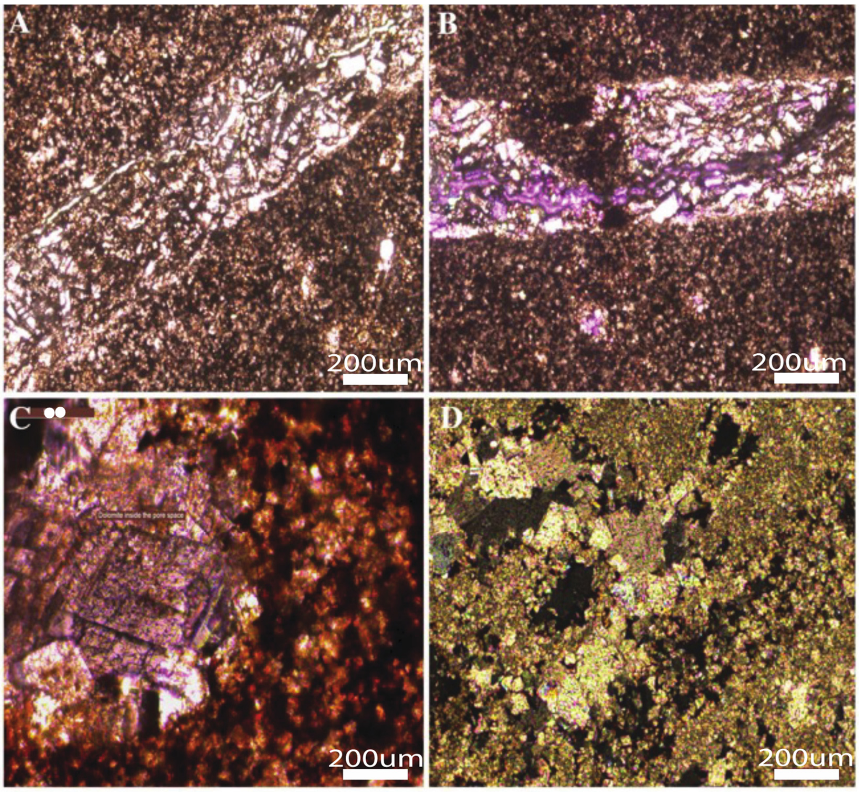

Figure 5. (**A**,**B**) photomicrographs showing the fine grain of dolomite crystals cross-cut by early dolomite crystals. (**C**,**D**) the aggrading increases of dolomite grains are obvious in the left part of ((**C**); see the rhomboheral shape) and sharp contact between fine grain dolomite in upper right part and rhombohedral crystals of dolomite in upper and lower left part of (**D**).

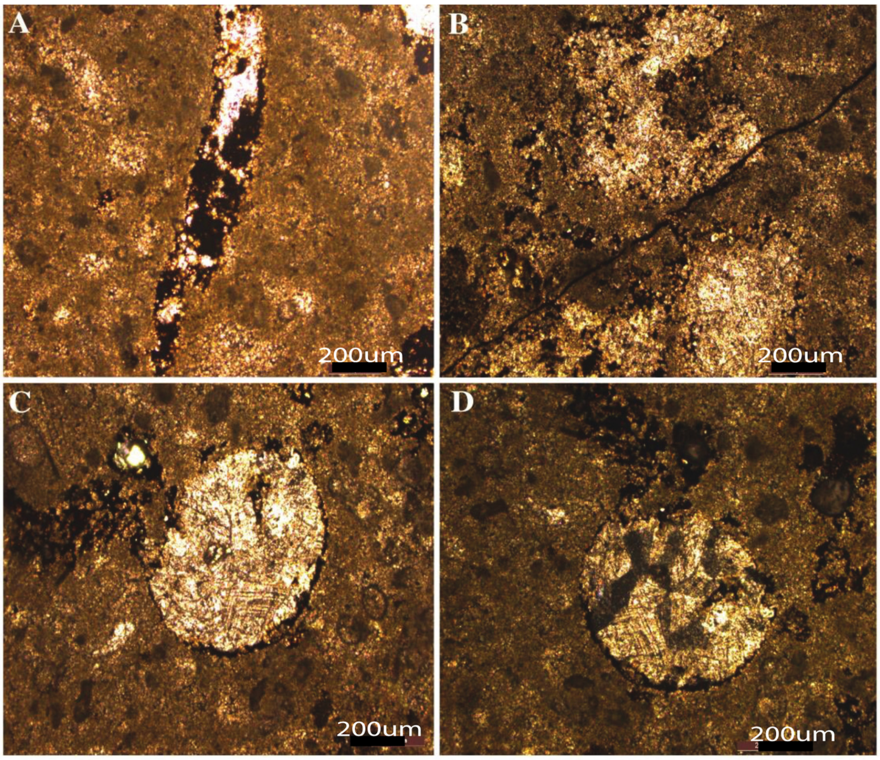

Figure 6. Photomicrographs (**A**,**B**) showing the dolomite crystals inside the fracture (**A**) and pore spaces filled by organic matter (**B**). (**C**,**D**) Voids filled by coarse crystalline saddle dolomite crystals

under PPL (**C**) and XPL (**D**). The dark spots and the outline of the voids are represented by the hydrocarbon accumulation. Geometrically, these photomicrographs (**A**–**D**) show that the hydrocarbon migration (see the black colored material) is always associated with dolomite formation, both early and late dolomite crystals.

4.4. Stable Isotopes

The stable isotopic composition of 23 samples shows a wide consideration signature of oxygen and carbon isotopic values. The δ^{18}OVPDB and δ^{13}CVPDB values vary between −9.9‰ to −4.6‰ (av. 8.1 ‰) and −2.0‰ to +2.3‰ (av. 1.2‰), respectively. The isotopic composition values are populated in two groups. The first group has a heavier isotopic composition than the second group. The values in the second group belong to cement-filled fractures and other pore spaces (Figure 7). All δ^{18}OVPDB values are depleted in comparison with the original isotopic compositions. Oxygen isotope records of tropical and temperate fossils and microfossils for the Mesozoic are updated from [24].

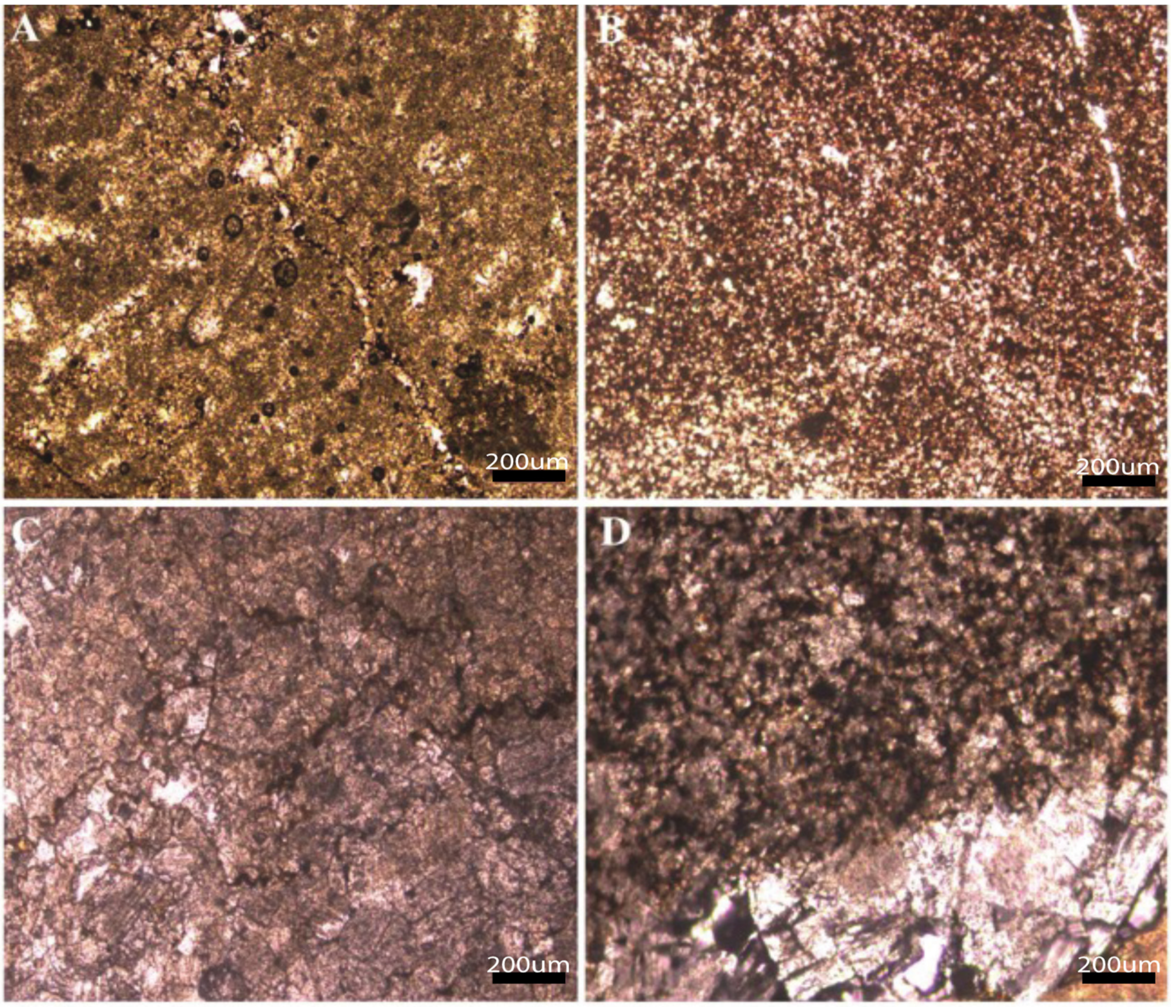

Figure 7. Photomicrographs of: (**A**) Host limestone of the Qamchuqa Formation, showing the dissolution-precipitation of moldic porosity, see the middle part of the photo which shows a low amplitude pressure solution structure. (**B**) preservation of precursor limestone even a slight diagenesis is observed, close up the lower right part of the photo (initiation od pressure solution structure). (**C**) High amplitude stylolite cross cut early dolomite crystals. (**D**) The boundary between host limestone and fracture filling coarse crystalline dolomite.

5. Discussion

Due to extensive diagenesis, only one sample shows original depositional facies. However, mudstone microfacies, including early anhydrite precipitation, mostly refer to recorded a shallow marine carbonate sedimentation during the Lower Cretaceous. They developed in facies unaffected by the mechanical compaction, as well as stylolitization within the depositional facies. This explains the early diagenesis, which was happed at near surface condition, including micritization, evaporation, and blocky/drusy calcite phase. The near-surface setting is characterized by the first generation of medium- to coarse -grained dominantly euhedral planar evaporite crystals (Figure 5A,B) and mudstone microfacies containing planktonic forams and echinoderms (Figure 4B).

Shallow burial diagenetic products include the first generation of wispy stylolites and various networks of fractures with development of the voids and remnants of earlier dolomite cements and thin fractures occluding much of the primary inter- and intra-particle porosities in the host limestone rocks. The early stylolites formed as a result of increasing pressure solution during this stage. They display amplitudes ranging from less than a millimeter (<0.5 mm) to a few centimeters in length. The shallow-burial diagenesis includes the first generation of wispy stylolite and various networks of fractures with development of the voids and fracture porosities, which were subsequently partly or totally cemented by the first generation of medium- to coarse-grained dominantly subhedral dolomite crystals (Figure 5). To evaluate the porosity percentage of early stage of diagenesis, imageJ converted the microscopic images to digital images, and the total porosity % for this early stage alteration is 1.7% under one view of the microscopic figure.

The last diagenetic phases are related to a huge quantity of hydrocarbon migration along the fracture and pore spaces, which is associated always with the saddle dolomite precipitation, as well as the formation of stylolites and fractures (Figure 7). The fractures and veins were subsequently cemented by the coarse-sized saddle dolomites (see Figure 6C,D). These saddles are pervasive and fabric destructive, and they lack the former host limestone. In places, there exist dissolution and/or corrosion of previous dolomite (early dolomite) by the latest dolomitizing fluid confirm the postdating of saddle dolomite. Because of the following observation, the late diagenesis of the Qamchuqa Formation underwent under deep burial setting (Figure 8):

(1) Geometrically, the saddle dolomite phase is postdated by all the previous diagenetic phases.
(2) The saddle dolomite formation postdated the stylolization process.
(3) The fractures and pore spaces cemented by small size of saddle dolomite compare to cm-sized saddle dolomite crystals on the exposed surface [25], and the tight arrangement of dolomite crystals in this study confirms that the growth mechanism of saddle dolomite formation takes a long term to form due to relatively constant temperature and pressure under surface conditions. This is in contrast to the large crystals of saddle dolomite, which formed in shallow diagenetic settings in the Bekhme Formation [25]. The influx of hydrothermal fluid, which precipitate the curved faces dolomites at shallow burial or near surface setting, always provides a huge dissolution and fracturing of previous carbonate rocks. This provokes a precipitation of very coarse-sized crystals of saddle dolomite [25] due to sudden change in hot fluid conditions, such as temperature and pressure, which move from deep burial conditions (high temperature and pressure) to shallow burial conditions (low temperature and pressure). For more details, see Figure 8, which explains each phase of diagenesis separately.

Therefore, the enhancement of porosities and fractures were dominantly provided by hydrothermal fluids. These hot fluids were associated with hydrocarbon migration and easily could be recognized under optical microscopy (Figures 6A–D and 7). These fluids percolate into the host limestone and other diagenetic rocks along the fracture and void spaces, resulting in dissolution of the reservoir and the development of significant secondary porosity.

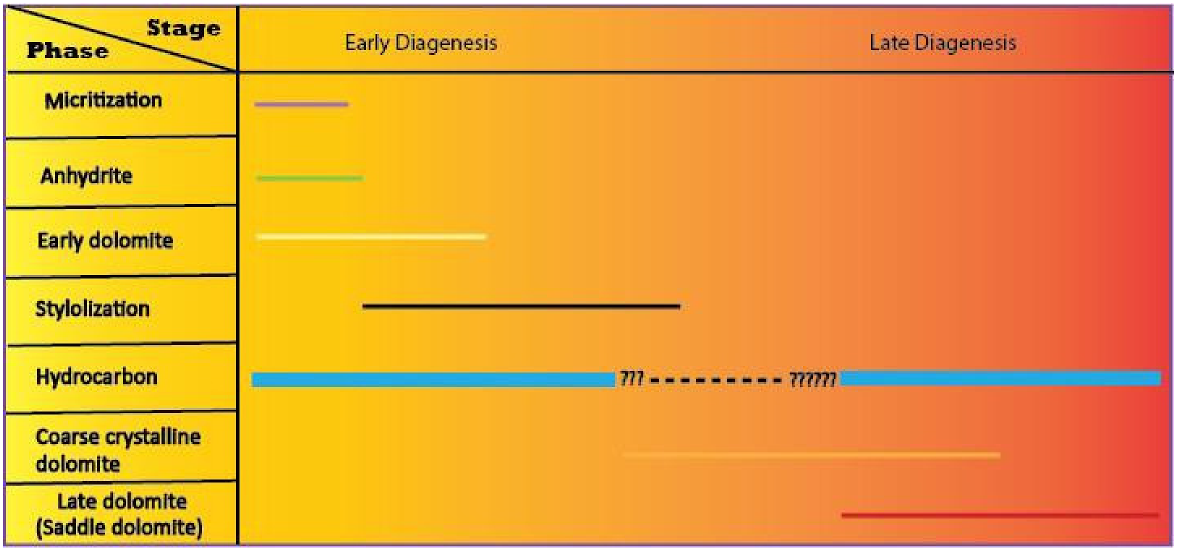

Figure 8. Paragenetic sequence of early and late diagenesis influenced the carbonates of the Qamchuqa Formation. Scale = 16 m.

The migration and accumulation of oil and gas in hydrocarbon reservoirs are due to one of the following mechanisms. (1) Thermal baking caused by the magmatic intrusion heats the surrounding rocks and results in mineral transformations. The thermal baking effect on hydrocarbon source rocks accelerates the generation of alkanes, organic acids, and carbon dioxide, reference [26] proposed that the concept of "contact diagenesis" the "abnormally high temperatures" from the magmatic intrusion result in changes in the authigenic mineral assemblage in the contact zone. (2) A series of water–rock reactions within the country rocks takes place as hydrothermal fluids move along migration pathways. This has a vital impact on reservoir performance. According to the recent findings in this study, the second mechanism could be applied to our model in the reservoir characteristics of the Qamchuqa Formation. However, more than one episode of hydrocarbon migration was observed in this study (Figure 8). Therefore, an episodic hydrocarbon migration associated with hydrothermal fluids is mostly indicated in our study. Subsequently, this stage of diagenesis significantly influences reservoir characteristics, and it increases the porosity from 1.7% to 2.6%. This calculation indicates enhancement of pore spaces after injection of host limestone by hot fluids (Figure 9).

To support the above data and the mechanism of saddle formation under subsurface conditions, using carbon and oxygen isotopes is a best and fit approach (Figures 10 and 11), and they are very sensitive to any compositional or environmental changes [10,27,28]. Near surface and shallow diagenetic features coincide with first group of oxygen–carbon isotope values (Figure 10), which have lighter δ^{18}OVPDB in comparison with the original marine signature of δ^{18}OVPDB ([29] see Figure 10) and heavier δ^{18}OVPDB compared to the second group (Figure 10). The distribution of the δ^{13}C values in the first group fits the inverse 'J' Lohmann curve ([9,30]; see Figures 10 and 11) pointing to a diagenetic alteration near surface conditions. Furthermore, the core samples from the upper part of the Qamchuqa Formation display evaporite minerals and fragments of echinoderms with drusy and blocky cements, beside the low range of first group of the O isotope (−5.2‰ to −4.6‰) and a wide range of carbon isotope (+1.5‰ to −2.0‰). These data point to near surface/shallow diagenetic settings (Figure 11).

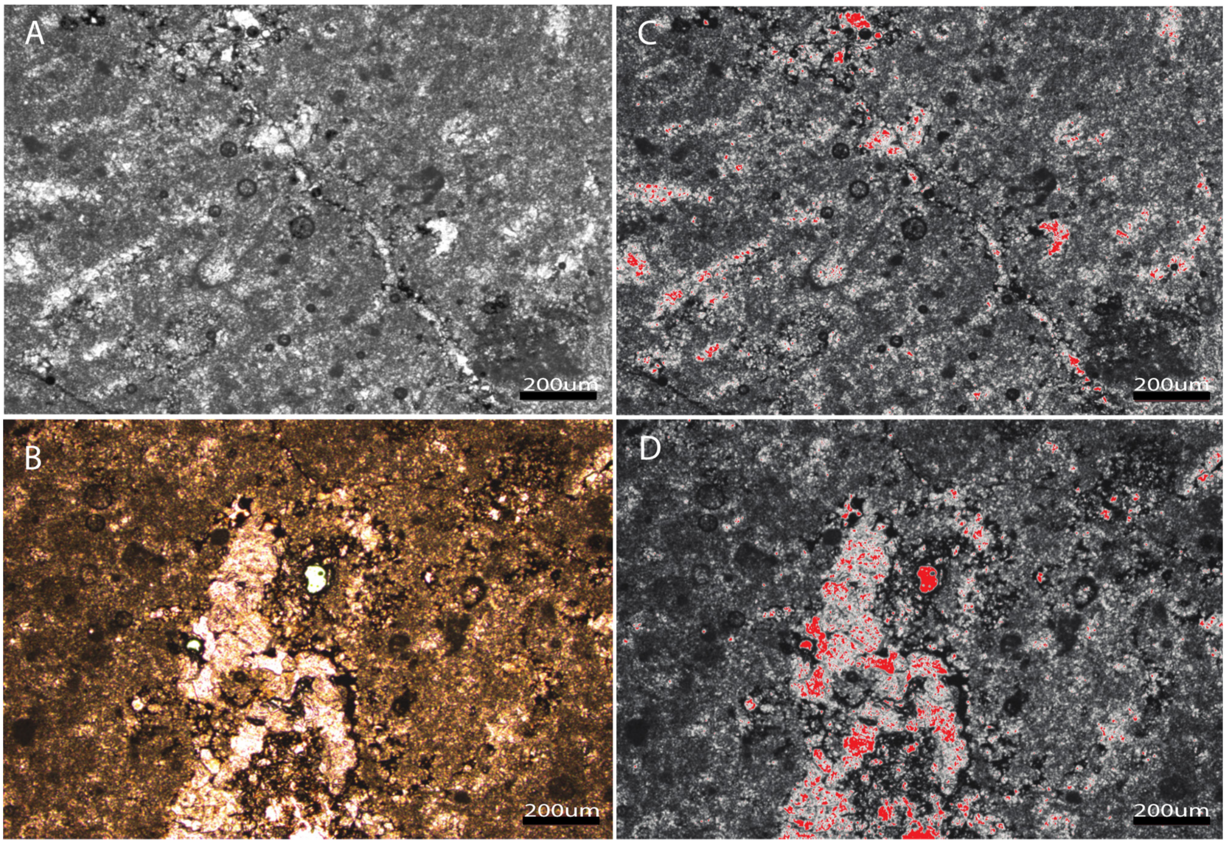

Figure 9. Microphotographs (**A**) of early diagenesis microfacies before analysis, (**B**) after analysis. (**C**) Late diagenesis microfa cies before analysis, (**D**) after analysis. The red contrast shows pore spaces.

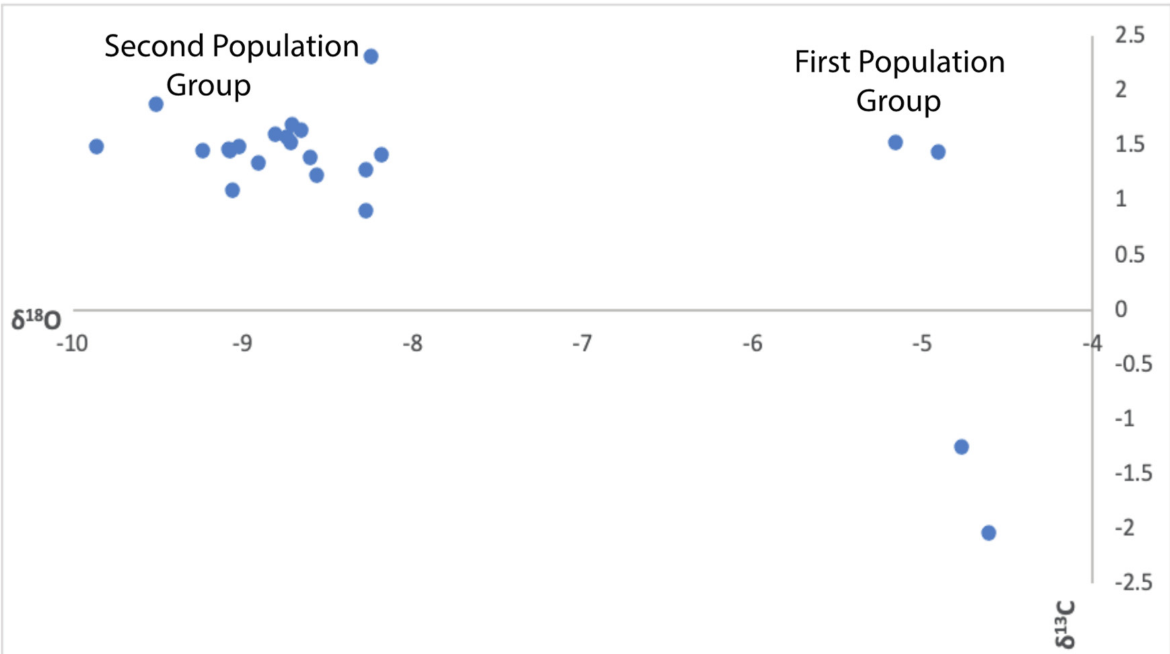

Figure 10. Oxygen and carbon isotopic compositions of carbonate rocks of the Bekhme Formation, close up two population groups of O-C isotope values.

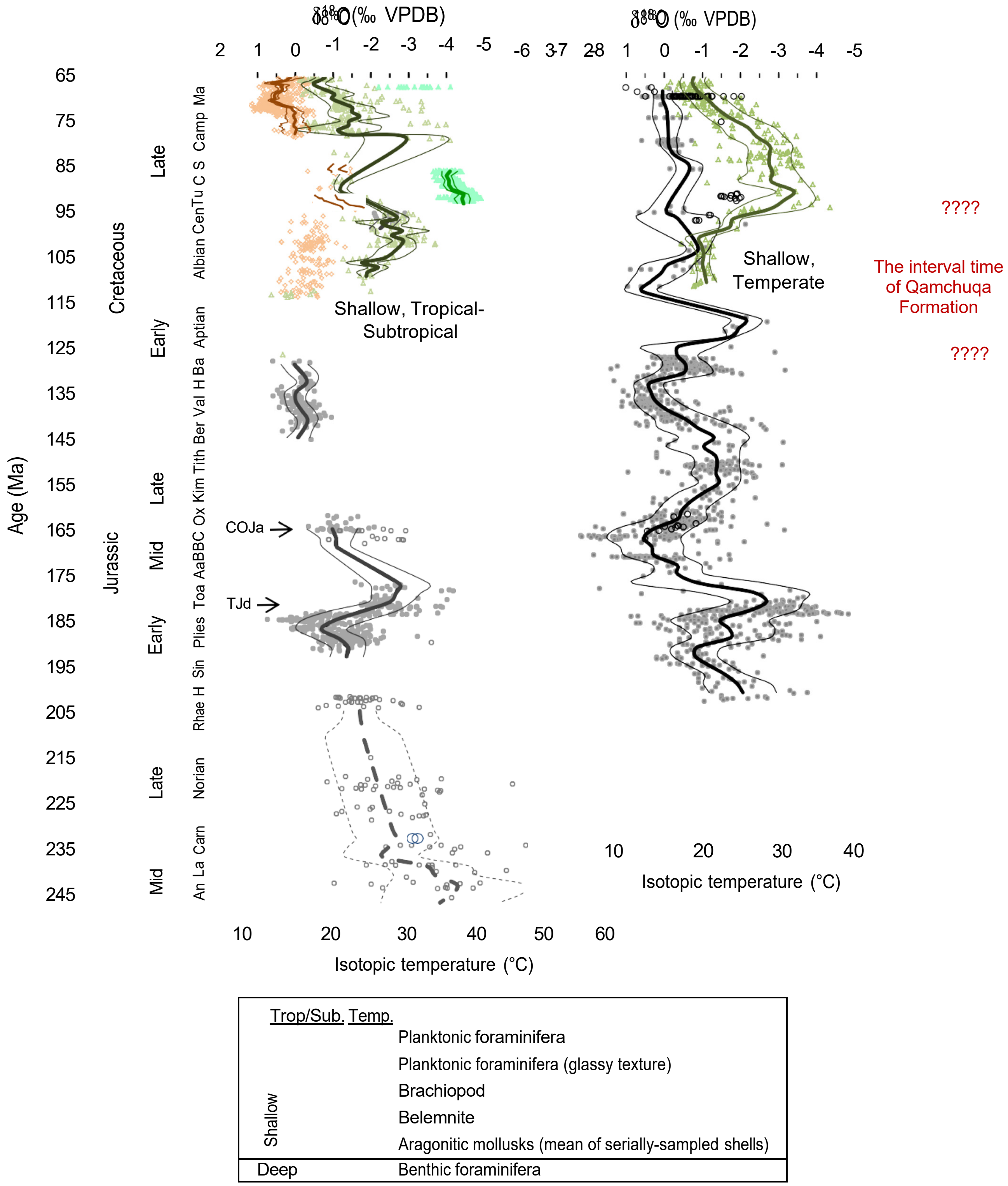

Figure 11. Oxygen isotope records for the Mesozoic, after [24]. The benthic foraminiferal data are obtained form [31].

The second populated group of O-C isotope values was associated with coarse crystalline dolomite. This dolomite is characterized by euhedral, curved faces, as well as wavey extinction, which is so-called saddle dolomite. Saddle dolomite postdates the stylolite micro-structures, since dolomite cross-cut the stylolite. Development of significant dolomite-filled pore spaces and fractures is probably linked to a post-depositional event.

These open spaces and stylolites are distinctly associated with an abundance of organic matter and hydrocarbon accumulation (Figure 6). This phase of post-depositional event is consistent with measurement of second group of stable isotope values. This group has a considerable range of oxygen values and constant carbon values compared to the first group. The δ^{18}OVPDB has very light values varied from (−9.9‰ to −8.2‰), as well as a heavier δ^{13}CVPDB (+1.0‰ to +2.3‰). Similar carbon and oxygen isotopic values were reported in the literature as the result of hydrothermal hot fluids under deep conditions (e.g., [32]). The δ^{18}OVPDB values from dolomite-filled pore spaces are lighter than those of the host rock. This distinct shift in δ^{18}O is toward light values associated with high temperature fluids and hydrocarbon accumulation in carbonates (Figures 6 and 10). The shift in δ^{18}O values is more consistent with the shift in δ^{13}C values toward enriched carbon isotopes than host limestone (first population group). These observations and measurement are in agreement with the evidence of hydrocarbon generation from the Western Canadian sedimentary basin [33].

6. Conclusions

The data from integrating litho-log, optical observation, ImageJ software, and stable isotopes can be used to draw the following conclusions from the current project:

(1) The Qamchuqa Formation underwent main three stages: early, middle, and late diagenesis stages. The micrite was considered as the first and early diagenetic product, and moldic pores are formed and predate the formation of anhydrite minerals. However, most of the samples were extensively dolomitized, and the host limestone still preserves the pristine facies.

(2) Multiple episodes of non-hydrothermal and hydrothermal fluids were accompanied by hydrocarbon migration, and the later fluids caused an activation for and formation of a new fracture system.

(3) The non-hydrothermal diagenesis started with anhydrite minerals and an early dolomitization process. Geometrically, the early dolomite cross-cut the anhydrite mineral.

(4) Different generations of dolomites formation are observed in this study: very fine, nonplanar early dolomite, planar rhombohedral dolomite crystals, curved faces, and nonplanar saddle dolomites. These two characteristics of saddle dolomites are applied to the mechanism of dolomite formation where the temperature of dolomitizing fluids is hot enough when fluxed to any stratigraphic unit.

(5) The distribution of hydrothermal dolomitizing fluids was found to be consistent with the direction of the fracture and open space system, which was indicated by the destructive dolomite fabric.

(6) The Qamchuqa reservoir formation shows an intensive dolomitization by two mechanisms: fracturing and dissolution by hot fluids, which caused porosity enhancement during early and late dolomitizing fluids.

(7) ImageJ software shows that hot fluids enhance the porous media and the migration of hydrocarbon processes.

(8) The tightly arranged dolomite crystals are along the fractures, pore spaces, and within the matrix; besides small-sized crystals of saddle dolomite compared with previous studies, these confirm that the growth mechanisms and the condition where these crystals formed are related to influxes of hot fluid under deep setting conditions.

(9) Stable isotopes reveal two population groups: the first group shows light δ^{18}OVPDB values, and a wide range of δ^{13}CVPDB fits the inverse 'J' Lohmann curve, and these values are linked to near surface/shallow diagenetic settings.

(10) The second group shows an overlapping of oxygen values with hot dolomitizing fluids under subsurface conditions. The shift of δ^{13}C values toward enrichment of δ^{13}C values is consistent with those of hydrocarbon generation.

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Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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