Investigation of the Geochemical Properties and Origin of the Crude Oils Accumulated in the Mishrif Reservoirs in the Zubair, Halfaya, and Buzurgan Oilfields, Southern Iraq

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Abstract
The Mishrif Formation is among southern Iraq’s most important reservoirs, which contains a third of the oil in the Cretaceous reservoirs, which is a broad carbonaceous succession in Iraq and the surrounding area. For detecting differences in the geochemical characteristics of crude oil, three crude oil samples were obtained from the Mishrif carbonate reservoir intervals in the Cretaceous at the Zubair, Halfaya and Buzurgan oilfields in southern Iraq. Analyses utilize API gravity, sulfur concentration, Gc, Gc/Ms, and bulk carbon isotope compositions. The low API (23 to 28) and high sulfur content (4.45 to 5.36 wt%) of the oils studied can be linked to the deposition of a marine carbonate environment under sulfate-reducing environments. The anoxic, non-biodegradation, organic matter type II-S, marine carbonate depositional was indicated by the pristane/nC17 (0.16 to 0.26), phytane/nC18 (0.29 to 0.31), narrow Pr/Ph ratio range from 0.76 to 0.78, high C29/C30 hopane ratios of 1.01–1.71, and low C26/C25 tricyclic terpene ratios in the related source-rock. TAS3 (CR) ratios of 0.33 to 0.36, C27 Ts of 0.18 to 0.22, and 29 sterane 20S/20R sterane ratios all refer to early maturity. Biomarker parameters and bulk carbon isotope values in the oil analysis match those found in the Sulaiy and Yamama sources of the Late Jurassic-Early Cretaceous.

Keywords: Mishrif Formation; Geochemical properties; Zubair Oilfield; Buzurgan Oilfield; Halfaya Oilfield

1. Introduction
The Cenomanian-Turonian Mishrif reservoir (Chatton and Hart, 1991) is composed of carbonate deposits from rudist-bearing units and extends throughout southern and central Iraq within the Mesopotamian foredeep and Zagros fold belt (Aqrawi et al., 2010). With its excellent reservoir and petrophysical characteristics, it is regarded as one of Iraqi most important reservoirs (Al-Mimar et al., 2018). It contains oil in various oilfields, including Amara, Gharraf, Majnoon, Buzurgan, Jabal Fauqi, Halfaya, East Baghdad, Ahdab, North and South Rumaila, West Qurna, Noor, Tuba, Ratawi and Nasiriyah (Fig. 1) (Aqrawi et al., 2010), and its oil reserves account for almost 40% of Iraqi total oil reserves (Al-Sakini, 1992). The Mishrif Formation is a widespread carbonate succession including regions throughout the Arabian Gulf. It is stratigraphically believed to be part of the Wasia Group (Mahdi and Aqrawi, 2014, Al-Mimar and Awadh, 2019). The Yamama, Zubair, Mauddud, Rumaila,
and Mishrif formations are all part of Megasequence Arabin Plate 8 (AP8). These carbonate formations that the oilfield's major oil-bearing strata, represent more than half of the oilfield's reserves and production in the Arabian Plate (Sharland et al., 2001).

Fig. 1. Locations map of the oilfields in Central and Southern Iraq, including studied oilfields

Although a multitude of deep-water basins occurred inside the shelf during the Cretaceous Period, these successions were deposited on the passive margin, which was later covered by shallow water (Murris, 1980) Porous Cenomanian and early Turonian shelfal shelf-margin limestones are found across Iraq (Fig. 2). For the first time in the Zubair Oilfield, Rabanit (1952) reported the Mishrif Formation type section at well Zb-3. Numerous researchers and petroleum companies have studied the Mishrif Formation in many Iraqi oilfields over the past decades (Al-Khersan, 1973; Buday and Jassim, 1987; Aqrawi et al., 1998; Aqrawi et al., 2010 and Mahdi and Aqrawi, 2014). In comparison, there have been limited organic geochemical studies of the oil reserves in the Mishrif Formation. The first geochemical study published was (Al-Ameri et al., 2009), which was followed by subsequent studies such as: Al-Khafaji (2015); Al-Ameri and Al-Zaide (2014); Awadh et al. (2018); Al-Khafaji et al. (2018; 2019a; 2020 and 2021a); Al-Mimar et al., 2018; Abdula, (2020); Boschetti et al., 2020; and Alsultan et al. (2021).

The most of the oil and gas discovered in Iraq's Middle and South originated from organic-rich, oil-prone carbonates in the Middle Jurassic Sargelu and Naokelakan formations. These source rocks are widely scattered and mature for oil and gas generation over the Zagros fold-belt and Mesopotamian foredeep. The Upper Jurassic-Lower Cretaceous Sulaiy and Lower Cretaceous Yamama oil-prone source rocks also had a key role in the generation of considerable amounts of hydrocarbons (Al-Ameri et al., 2009; Pitman et al., 2004; Al-Ameri et al., 2014; Abeed et al., 2011; Chafeet et al., 2020; Al-Khafaji et al., 2019b, and 2021b).

The study's goal is to detect any differences in the geochemical characteristics of crude oil in the Mishrif Formation, in three oilfields in Maysan and Basra, as well as to infer sedimentary environment of the corresponding source rocks.
Fig. 2. Generalized stratigraphic column of southern Iraq, and the major tectonic events, modified from (Al-Khafaji et al. 2021)

2. Geologic Setting

The Zubair Oilfield is located in the Mesopotamian Basin's Zubair Subzone in Basra, while the Halfaya and Buzurgan oilfields are located in the Mesopotamian Basin's Euphrates Subzone in Maysan, southern Iraq (Fig. 3). Over 3000 m of sediments of the Cretaceous Period were accumulated in this basin and throughout most of the Cretaceous because the Mesopotamian basin of southern Iraq was part of the wider carbonate platform on the Arabian Plate's NE passive border due to tectonic, eustatic, and climatic conditions. The warm shallow waters of Neo-Tethys encountered this margin. A deep carbonate accumulation is deposited results of the transition environment from pelagic facies to foraminiferal-rich lagoonal and reefal. The limestones of the Mishrif Formation are significant oil reserves as mentioned in Sadooni (2005). The porosity of the Mishrif reservoir is mostly developed in the hightstand parts of sequences, which are separated by argillaceous limestones deposited as transgression strata above sequence borders (Sadooni, 2005). According to Sadooni and Aqrawi (2000), the Mishrif Formation was deposited during the Late Cenomanian, during the period of generally high sea levels (Murris,
The Mishrif Formation, which is overlain by a sharp contact of Khasib Formation that corresponds to an early-middle Turonian unconformity. The Mishrif Formation, however, penetrates gradationally into the Rumaila Formation (Fig. 2) near its lower limit, and the two formations are difficult to be distinguished from each other in many wells. According to Buday and Jassim (1987), the Buzurgan Oilfield is located in the Folded Zone, the Halfaya Oilfield is located in the Mesopotamian Basin’s Euphrates Subzone, and the Zubair Oilfield is located in the Mesopotamian Basin’s Zubair Subzone (Fig. 4).

![Tectonic Map of Iraq](image)

**Fig. 3.** The tectonic map of Iraq (after Buday and Jassim, 1987)

### 3. Methods and Materials

Three crude oil samples were obtained from the Mishrif carbonate reservoir intervals in Zubair Oilfield in Basra, Halfaya, and Buzurgan oilfields in the Maysan (Table A and B) and applied to detailed analytical investigations, including, sulfur content, API gravity and carbon isotope analyses, as well as saturated hydrocarbon fraction. The GeoMark Research Institute in Houston, Texas, USA, analyzed the studied samples.

The crude oil gravity analysis (API) was carried out on 1–2 ml of the studied oil samples and evaluated at 60 °C using the Anton Par DMA of the 500-density m. The sulfur content (weight percent) in the crude oil samples was determined using various isotope selective elemental instruments. The asphaltene concentration in the oil samples was caused by using the pentane solvents, and the residual maltenes were fractionated into polar fractions, saturated, aromatic, and in alumina high-performance
liquid chromatography using hexane, methylene chloride, and 50:50 mix of methylene chloride and methanol, respectively.

An Agilent mass spectrometer was used to analyze the saturated fraction utilizing gas chromatography-mass spectrometry (GC-MS). For the GC experimental analysis, a flame ionization detector (FID) that used in a length of 50 m of an HP-column, a diameter of 0.2 mm, and a film thickness of 0.11 m.

Fig.4. The Cretaceous Supersequence IV and its equivalent Megasequence AP8 global chronostratigraphic frame (Sharland et al., 2001 and Aqrawi et al., 2010 modified by Mahdi and Aqrawi, 2014)

Table 1. The bulk composition property (A) geochemical analyses results (B) of crude oils taken from Mishrif carbonate reservoir of the studied oilfields, in southern Iraq

<table>
<thead>
<tr>
<th>Field</th>
<th>Zubair</th>
<th>Halfaya</th>
<th>Buzurgan</th>
<th>Field</th>
<th>Zubair</th>
<th>Halfaya</th>
<th>Buzurgan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well</td>
<td>Zb-179</td>
<td>HF-5</td>
<td>Bu-3</td>
<td>Well</td>
<td>Zb-179</td>
<td>HF-5</td>
<td>Bu-3</td>
</tr>
<tr>
<td>Upper Depth (ft)</td>
<td>24866</td>
<td>31785</td>
<td>33530</td>
<td>Upper Depth (ft)</td>
<td>24866</td>
<td>31785</td>
<td>33530</td>
</tr>
<tr>
<td>API</td>
<td>26.55</td>
<td>28.92</td>
<td>23.31</td>
<td>C_{18}/C_{23}</td>
<td>0.12</td>
<td>0.14</td>
<td>0.12</td>
</tr>
<tr>
<td>S%</td>
<td>5.36</td>
<td>4.45</td>
<td>5.14</td>
<td>C_{22}/C_{21}</td>
<td>1.08</td>
<td>1.01</td>
<td>1.05</td>
</tr>
<tr>
<td>Sat %</td>
<td>33.51</td>
<td>34.37</td>
<td>28.05</td>
<td>C_{23}/C_{23}</td>
<td>0.27</td>
<td>0.29</td>
<td>0.26</td>
</tr>
<tr>
<td>Aro %</td>
<td>43.03</td>
<td>37.48</td>
<td>43.90</td>
<td>C_{30}/C_{25}</td>
<td>0.72</td>
<td>0.73</td>
<td>0.76</td>
</tr>
<tr>
<td>NSO %</td>
<td>16.76</td>
<td>12.86</td>
<td>13.57</td>
<td>Tet/C_{23}</td>
<td>1.24</td>
<td>1.37</td>
<td>1.23</td>
</tr>
<tr>
<td>Asph %</td>
<td>6.70</td>
<td>15.29</td>
<td>14.48</td>
<td>C_{29}/H</td>
<td>1.65</td>
<td>1.62</td>
<td>1.74</td>
</tr>
<tr>
<td>Sat/Aro</td>
<td>0.78</td>
<td>0.92</td>
<td>0.64</td>
<td>C_{31}/R/H</td>
<td>0.33</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>δ^{13}C_{sat}</td>
<td>-27.52</td>
<td>-27.66</td>
<td>-27.42</td>
<td>GA/C_{31}R</td>
<td>0.23</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>δ^{13}C_{aro}</td>
<td>-27.78</td>
<td>-27.66</td>
<td>-27.49</td>
<td>C_{35}S/C_{34}S</td>
<td>1.11</td>
<td>1.06</td>
<td>1.07</td>
</tr>
<tr>
<td>CV</td>
<td>-3.70</td>
<td>-3.08</td>
<td>-3.31</td>
<td>%C_{27}</td>
<td>34.00</td>
<td>33.50</td>
<td>33.90</td>
</tr>
<tr>
<td>Pr/Ph</td>
<td>0.76</td>
<td>0.78</td>
<td>1.07</td>
<td>%C_{28}</td>
<td>24.80</td>
<td>25.20</td>
<td>24.50</td>
</tr>
<tr>
<td>Pr/nC_{17}</td>
<td>0.19</td>
<td>0.19</td>
<td>0.26</td>
<td>%C_{29}</td>
<td>41.20</td>
<td>41.30</td>
<td>41.70</td>
</tr>
<tr>
<td>Ph/nC_{18}</td>
<td>0.29</td>
<td>0.29</td>
<td>0.31</td>
<td>C_{29}20S/R</td>
<td>0.64</td>
<td>0.64</td>
<td>0.57</td>
</tr>
<tr>
<td>CPI</td>
<td>0.91</td>
<td>0.94</td>
<td>0.96</td>
<td>C_{27}Ts/Tm</td>
<td>0.18</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C_{29}Ts/Tm</td>
<td>0.07</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TAS3(CR)</td>
<td>0.33</td>
<td>0.33</td>
<td>0.36</td>
</tr>
</tbody>
</table>
The stable carbon isotope concentration (δ\(^{13}\)C) of the saturate and aromatic fractions was determined using Isoprimevario's Vision isotope and isotope ratio mass spectrometers (IRMS). The values are expressed regarding Pee Dee Belemnite using the traditional delta-notation (PDB). The detected carbon isotope levels were used to identify the cured oils and determine where the likely source rocks came from.

4. Results and Discussions

4.1. Carbon Isotope and Physical Characteristics

The examined oils had greater API gravities ranging from 23.31 to 28.92 than the average of the other Mishrif samples from the southern Iraq oilfields (Table 1A), but they also have a high sulfur (S) concentration of up to 5.36 wt%. The low API and maturity of the crude oil samples is usually attributed to sulfur-rich oils or biodegradation (Fig. 5) (Peters et al., 2005).

![Fig.5. The average API gravity value and sulfur content of the studied samples](image)

Also, observe that the sample from Buzurgan well-3 had the lowest value of sulfur content and the highest API gravity. The high sulfur content (4.45 to 5.36 wt percent) of the oils investigated can be attributed to the deposition of a marine carbonate environment during sulfate-reducing settings. The saturated (-27.42 to -27.66) and aromatic (-27.49 to -27.78) hydrocarbon fractions (δ\(^{13}\)C) of the analyzed Mishrif oil samples (Fig. 6) indicate Upper Jurassic to Lower Cretaceous marine source rock deposition (Andrusevich et al., 1984).

![Fig.6. The Sofer plot of the stable carbon isotope ratios indicates marine carbonate organic matter (Sofer, 1984). The age of source rocks mention in figure based on (Al-Khafaji et, al. 2019)](image)
4.2. Biomarker and Non-Biomarker Distributions

Fig. 7 depicts the distribution of C₄-C₃₅ normal alkanes and isoprenoids, which displays C₄-C₁₅ n-alkanes dominating over C₂₀-C₃₅ n-alkanes. As shown in Table 1B, the carbon preference index (CPI) values were low, ranging from 0.91 to 0.96, and the phytane (Ph) greater than pristane (Pr), resulting in a rather narrow Pr/Ph ratio range of 0.76 to 0.78. The Pr/Ph ratio easily differentiates crude oils from various source rocks. Pr/Ph < 1 in Zubair and Halfaya crude oil implies anoxic source-rock deposition, especially when substantial porphyrin and sulfur concentrations are present, but Pr/Ph > 1 in the Buzurgan sample indicates more oxic deposition (Peters et al., 2005).

Fig. 7. Saturated hydrocarbon fraction gas chromatograms of the examined Mishrif oil samples from southern Iraq. Non-biodegradation oils were identified by the presence of a full suite of alkanes and acyclic isoprenoids.

In the related source-rock depositional environment, the pristane/nC₁₇ (0.16 to 0.26) and phytane/nC₁₈ (0.29 to 0.31) ratios indicated an anoxic, non-biodegradation, organic matter type II-S, as illustrated in Fig. 8. Even though the Pr/Ph of petroleum reflects the composition of the organic matter that contributes to it, it normally rises with thermal maturation (Peters et al., 2005). As a result of its higher maturity than other samples, the Buzurgan sample has a high Pr/Ph. All the tested samples are within the range of biologic non-biodegraded oil at the beginning of its thermal maturation and are...
derived from the II-S kerogen type, as shown in Fig. 8. Low concentrations of tricyclic and tetracyclic terpenes, as well as pentacyclic terpenes, appear in the m/z 191 ions of mass fragmentograms (Fig. 9). As illustrated in Fig. 9, abundant C_{29}-norhopane leads to high C_{29}/C_{30} ratios of 1.62-1.74 (Table 1A), which is common in crude oils derived from marine carbonate sources (Fig. 10) (Peters et al., 2005). The homohopane distributions were controlled by C_{31}, which rapidly declined in content as carbon levels increased in all samples.

The C_{31}/C_{30}-hopane ratio of the oil samples studied ranges from 0.33 to 0.35, indicating that they are derived from marine carbonate sources (Petres et al., 2005). Marine oils typically have C_{26}/C_{25} tricyclic terpene ratios of 0.72-0.76 confirmed the previous finding. The C_{35} homohopane index (C_{35}S/C_{34}S hopenes) of the tested oil samples was found to be in the range of 1.06–1.11, while the gammacerane index (Ga/C_{31}R hopane) was found to be in the range of 0.20–0.23 (Fig. 11; Table 1B), indicating higher salinity and marine carbonate source rocks.

**Fig. 8.** Non-biodegraded, early thermal maturity, kerogen type II-S, and anoxic depositional environment are indicated by a plot of Pr/n-C_{17} against Ph/n-C_{18} for the studied Mishrif oil samples.

**Fig. 9.** The terpane and sterane distribution that are found in ion fragmentograms of m/z 191 and m/z 217, for the three oil samples.
Fig. 10. Plots of C$_{22}$/C$_{21}$, C$_{24}$/C$_{23}$, C$_{26}$/C$_{25}$ tricyclic terpene and C$_{31}$/C$_{30}$-hopane ratio, indicated carbonate source rocks of oil samples (modified from Peters et al. (2005)).

Fig. 11. Plots of the C$_{35}$/C$_{34}$S homohopane, C$_{29}$/C$_{30}$, and Ga/C$_{31}$R hopane, for the studied oil samples, indicated anoxic environments (modified from Peters et al. (2005)).

Gammacerane can be used to differentiate between the various petroleum families. The presence of gammacerane biomarkers in the oil samples, as well as relatively high C$_{35}$/C$_{34}$S homohopane
indicators, imply anoxic marine carbonate source rock deposition (Peters et al., 2005). According to prior biomarker findings, the oils originated from sulfur-rich kerogen Type II-S and marine carbonate source rocks were deposited in an anoxic environment.

4.3. Thermal Maturity

Many particular maturity biomarker ratios are determined using m/z 191 and m/z 217 mass analysis results of the saturated hydrocarbon fraction as maturity indicators. TAS3 (CR) ratio is considered a more fundamental indicator of maturity parameter than Ts/(Ts+Tm) since it is less reliant on source organofacies (Fig. 12A). The samples showed a ratio of 0.33 to 0.36, indicating that the oil had been early maturation. Because of its so resistance to biodegradation, the C27 Ts/Tm is indeed a thermally sensitive terpane parameter (Fig. 12B). The ratio in the investigated samples range from 0.18 to 0.22, reflecting early maturation. The C29 sterane 20S/(20S+20R) sterane ratios, which increase with maturation, are also used to determine the maturity level of oils (Fig. 12C). The studied oil samples exhibit low ratio of the C29 sterane 20S/(20S+20R) in the range of 0.38–0.41 and 0.43–0.45, showing that they are usually consistent early-mature source rock origin (Zumberge et al., 2005) (Fig. 12D).

4.4. Age of Source Rocks

In the Mesopotamian Basin, the Sulaiy and Yamama formations from the Late Jurassic to Early Cretaceous as well as Middle Jurassic Sargelue are the most well-known likely source rocks, which formed in an anoxic marine carbonate environment (Abeed et al., 2011; Al-Khafaji et al., 2021a and 2021b).

Fig.12. Many thermal maturity biomarker parameters indicate early thermal maturity of oil samples

The biomarkers distribution of the Yamama and Sulaiy source rock in e.g. Al-Khafaji et al. (2019a) is similar to those of the oils investigated in this study. The calculated C28/C29 ratio of 0.8 indicates that the Mishrif-reservoired oil was originated from carbonate source rocks from Upper Jurassic to Lower Cretaceous, confirmed by e.g. Al-Ameri et al. (2009) (Fig. 13).
Fig. 3. The average C\textsubscript{28}/C\textsubscript{29} sterane ratio (0.8) of the examined Mishrif oils from southern Iraq corresponds to an Upper Jurassic to Lower Cretaceous source rock.

Furthermore, biomarker parameter ratios and carbon isotope values from both probable source rocks and crude oils were used to set similarity. As a result, the Sulaiy and Yamama formations of the L. Jurassic to E. Cretaceous are potential sources for the oils studied in this work. This result is supported by previous studies such as Al-Khafaji et al. (2019a and 2019b).

5. Conclusion

The geochemical properties of crude oils in the southern Iraqi oilfields of Buzurgan, Halfaya, and Zubair have been investigated. The oils studied have a high sulfur content, aromatic hydrocarbon components, and low API gravity. The oils are derived from a source rock which has a high-S kerogen content (Type II-S). Low Pr/Ph ratios, Ga/C\textsubscript{31}R hopane, and C\textsubscript{35} homohopane index, all indicate sulphate-reducing conditions during source rock deposition. The maturity biomarkers ratio such as TAS3 (CR), C\textsubscript{27} Ts, C\textsubscript{29} sterane 20S/ (20S+ 20R) sterane, API gravity in the oils all point to early maturation. The biomarker ratios and bulk carbon isotope values of the oils match those of the L. Jurassic to E. Cretaceous source rocks.

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