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Chemical and isotope composition of the oilfield brines from Mishrif Formation (southern Iraq): Diagenesis and geothermometry

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Keywords: Oilfield waters; chemical composition; geothermometry; oxygen and hydrogen stable isotope ratios; strontium isotopes.

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Abstract: This paper focuses on the geochemical composition and isotope geochemistry of brines in the Cenomanian-Turonian carbonate Mishrif reservoir of southern Iraq. Main dissolved constituents, trace elements, $\delta^2\text{H}$ and $\delta^{18}\text{O}$, $87\text{Sr}/86\text{Sr}$, mineral saturation indices and thermodynamic calculations were investigated in formation waters from the Mishrif Formation to obtain a better understanding of brine evolution and diagenetic effects over geological time. Previous published $\delta^{11}\text{B}$ data were also reinterpreted as a geothermometer tool. The results are compared with previous published data for local oilfields and coeval formations in the Arabian Gulf. The Mishrif brine has a marine origin and is diagenetically modified to Ca-excess and Na-deficit. Formation waters are quartz supersaturated and are in equilibrium with chalcedony and calcite-dolomite in the temperatures range of 50-75°C, which is also confirmed by calcite-water oxygen isotope fractionation and $\delta^{11}\text{B}$ geothermometer. The potential role of clays in conditioning brine chemistry during diagenetic processes was highlighted by activity diagrams; in particular, their adsorption/exchange effect on sodium could explain the lower temperature obtained by the Na/Li geothermometer (42 ± 6 °C). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values show that oxygen isotope composition of the brines was isotopically more affected by interaction with limestone during diagenesis than seawater evaporation. The main effect is an ^{18}O -enrichment on the brine starting from the SMOW value. Locally, dilution by present-day meteoric water was also detected (Rumaila South), which is shifted towards the local meteoric water line. The strontium isotope ratios range from 0.707713 to 0.707749 and correspond to a marine strontium of late Cenomanian-early Maastrichtian age, except for the Majnoon sample, which shows a more radiogenic value (0.708043). Radiogenic strontium and gypsum and anhydrite saturation indices of the Majnoon sample could indicate the contribution of calcium and sulphate from the strontium-rich sulphate minerals of the Cambrian salt domes occurring in the oilfields of southern Iraq. The higher manganese concentration (4 mg/l) and the slightly higher temperature inferred by geothermometers (up to 74 °C) in comparison with present-day could

indicate that the Majnoon brine is a hot fluid, probably related to a deeper structure such as the Zagros Foredeep Fault.

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There are no linked research data sets for this submission. The following reason is given:

The used data has been reported in the manuscript.

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Highlights

- Sr, O and H isotopic composition of formation brine from southern Iraq are presented
- Calcite-dolomite and chalcedony equilibria with water were achieved during diagenesis
- Chemically inferred and calcite-water oxygen isotope fractionation temperature agree
- Mineralogical composition is confirmed by plotting water samples on activity diagram

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1 **Chemical and isotope composition of the oilfield brines from Mishrif**

2 **Formation (southern Iraq): Diagenesis and geothermometry**

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26 **Abstract**

27 This paper focuses on the geochemical composition and isotope geochemistry of brines in the
28 Cenomanian–Turonian carbonate Mishrif reservoir of southern Iraq. Main dissolved
29 constituents, trace elements, $\delta^2\text{H}$ and $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, mineral saturation indices and
30 thermodynamic calculations were investigated in formation waters from the Mishrif
31 Formation to obtain a better understanding of brine evolution and diagenetic effects over
32 geological time. Previous published $\delta^{11}\text{B}$ data were also reinterpreted as a geothermometer
33 tool. The results are compared with previous published data for local oilfields and coeval
34 formations in the Arabian Gulf. The Mishrif brine has a marine origin and is diagenetically
35 modified to Ca-excess and Na-deficit. Formation waters are quartz supersaturated and are in
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37 which is also confirmed by calcite-water oxygen isotope fractionation and $\delta^{11}\text{B}$
38 geothermometer. The potential role of clays in conditioning brine chemistry during diagenetic
39 processes was highlighted by activity diagrams; in particular, their adsorption/exchange
40 effect on sodium could explain the lower temperature obtained by the Na/Li geothermometer
41 (42 ± 6 °C). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values show that oxygen isotope composition of the brines
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43 evaporation. The main effect is an ^{18}O -enrichment on the brine starting from the SMOW
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46 from 0.707713 to 0.707749 and correspond to a marine strontium of late Cenomanian–early
47 Maastrichtian age, except for the Majnoon sample, which shows a more radiogenic value
48 (0.708043). Radiogenic strontium and gypsum and anhydrite saturation indices of the
49 Majnoon sample could indicate the contribution of calcium and sulphate from the strontium-
50 rich sulphate minerals of the Cambrian salt domes occurring in the oilfields of southern Iraq.

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The higher manganese concentration (4 mg/l) and the slightly higher temperature inferred by geothermometers (up to 74 °C) in comparison with present-day could indicate that the Majnoon brine is a hot fluid, probably related to a deeper structure such as the Zagros Foredeep Fault.

Keywords: Oilfield waters; chemical composition; geothermometry; oxygen and hydrogen stable isotope ratios; strontium isotopes.

1. Introduction

In the Jurassic–Cretaceous petroleum system of southern Iraq, hydrocarbons are mainly trapped in Lower Cretaceous sandstone and carbonate reservoirs. Crude oil is generated from the organic-rich Upper Jurassic (Sargelu and Sulaiy formations) changing the Lower Cretaceous carbonates of the Yamama Formation and the Zubair Formation, a clastics reservoir (Abeed et al., 2012; Abeed et al., 2013). The chemical composition of formation waters from the Yamama reservoir in the Zubair and North/South Rumaila oilfields is mainly composed of chloride (up to 143,589 ppm) with a salinity 6.2 times higher than seawater (Jamil, 1978), as for West Qurna oilfield, salinity 7.3 times higher than seawater and dominated by 191,700 ppm of chloride (Al-Marsoumi and Abdul-Wahab, 2005). These prior works utilized brine chemistry but did not address the evolution of the reservoir brine, as they relied mainly on cations and anions without considering isotopes. More recently, the boron stable isotope ratio of the brine from the Mishrif reservoir has given a seawater signature (Awadh et al., 2019a; Awadh et al., 2018) and highlighted the role of salinity in generating the formation pressure and controlling the fluid flow (Al-Mimar and Awadh, 2019). The developing of the oilfield brines over the geological time and its response to the flooding and diagenesis have a significant impact on petroleum reservoir quality, but this subject has not yet been investigated.

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75 The diagenetic effects on brine waters can be evaluated by comparing the Na, Ca and
76 Cl concentrations of the brine with those of seawater and with the so-called basinal fluid line
77 in the Ca-excess versus Na-deficit binary diagram (Davisson and Criss, 1996). However, in
78 this plot the interpretation could be misguided because: (i) the reference basinal fluid line
79 takes into account only plagioclase albitisation, often without checking the real
80 thermodynamic equilibria state of the involved waters; and ii) modelling involves the current
81 seawater composition disregarding that of past periods (Babel and Schreiber, 2014;
82 Lowenstein et al., 2003). A combination of isotope parameters as O-H stable isotope ratios
83 and $^{87}\text{Sr}/^{86}\text{Sr}$ was proposed by Danquigny et al. (2005) to evaluate the effect of water
84 flooding in the Mishrif Formation water of Qatar. However, in that work, seawater
85 evaporation, the isotope salt effect (Horita et al., 1993), and the contribution of radiogenic
86 strontium to the limestones of the Mishrif Formation were not considered.

75 The objectives of this research are: i) to investigate the origin of the oilfield waters; ii)
76 to evaluate the composition of oilfield waters over time; and iii) to trace the influence of
77 diagenesis and any geothermal effects on the brine. This investigation considers the above
78 described effects and processes in the Mishrif Formation brines by reinterpreting the
79 previously published main chemical constituents, along with new and original data on trace
80 elements, oxygen and hydrogen water isotope ratio, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, and thermodynamic
81 calculations. Moreover, the previously published data of boron isotope ratio $\delta^{11}\text{B}$ (Awadh et
82 al., 2019a; Awadh et al., 2018) are here reinterpreted as a geothermometer tool, and are
83 results compared with those obtained from chemical geothermometers. The main research
84 contribution is to obtain better understanding of the oilfield brines evolution.

97 **2. Geological setting**

98 *2.1. Oilfield locations, main geological features and tectonics*

99 The studied oilfields, Rumaila South (RU), Rumaila North (R), West Qurna (WQ), Zubair
100 (ZB) and Majnoon (MJ) are located in southern part of Iraq (Jassim and Buday, 2006) (Fig.
101 1A). The Mesopotamian zone extends from middle to southern Iraq as a relatively flat terrain
102 with a gradient of less than 10 cm/km in the north-west to the Arabian Gulf. The zone was
103 probably uplifted during Hercynian deformation but was subject to subsidence from the Late
104 Permian onwards (Jassim and Buday, 2006). The oilfields are located in the Zubair zone
105 (Grabowski Jr., 2014; Sadooni and Aqrabi, 2000), southern part of the Mesopotamia plain
106 (Fig. 1A), an area characterized by the presence of a gentle subsurface succession of
107 anticlinal and synclinal structures. These structures form giant hydrocarbon traps: Rumaila
108 South (37 km length, 16 km width), Rumaila North (40 km, 13.5 km), West Qurna (35 km, 8
109 km) and Majnoon (48 km, 10 km).

110 From the interpretation of gravity and magnetic data, Alyasi et al. (2014) mentioned
111 that the presence of anticlinal structures is due to the effect of the evaporites of the Late
112 Jurassic Gotnia Formation and Late Ediacaran – Early Cambrian Hormuz Formation in
113 addition to other tectonic forces, where salts moves upward by buoyant forces and the denser
114 rocks remain below them. To the north of the Arabian Gulf, huge salt-gypsum domes are
115 exposed at a surface coexisting with a mixture of igneous and metamorphic rocks peeled off
116 from the Precambrian crystalline basement (Mortazavi et al., 2017). Jabal Sanam is one of the
117 salt diapirs in southern Iraq / northern Kuwait border (Fig. 1); it is an extension of the
118 Hormuz Formation, located in Iran at the northern part of the Arabian Gulf, which contains
119 more than 200 salt domes composed of sequences of evaporates, shales, siltstones and
120 carbonates (Mortazavi et al., 2017). The role of tectonic events (extensional faulting) and
121 differential loading of sedimentary cover above the mobile salt layer are the main triggering
122 factors of the salt diapirism (Singh, 2012). In particular, the Permo-Triassic Tethyan rifting,
123 the Cretaceous-Paleogene obduction and the compressive events associated with basement

124 reactivation of north-south Arabian trends could have started the episodic salt diapir activity
125 in the area of this study (Singh, 2012). However, traces of a neotectonic reactivation were
126 also documented (Sissakian et al., 2017).

127 The Zubair zone is a southern part of the Mesopotamian Basin that is located close to
128 the junction of the Arabian Shelf and Iranian continental block. Collision of these plates at
129 the Mesozoic-Cenozoic boundary produced the Zagros Foredeep fault and the Mesopotamian
130 Basin, which is a member of the Arabian Gulf Basin (Konyuhov and Maleki, 2006). During
131 the Mesozoic and Cenozoic, the study area was a tropical region, with organic-rich
132 carbonates or organic-rich argillaceous sediments being deposited. Good-quality source rocks
133 were preserved in different intervals of geological time, particularly during the Mesozoic. For
134 example (Fig. 1B): the Alan Formation in the Middle Jurassic; the Sargelu, Najmah and
135 Sulaiy formations are the source rocks in the Upper Jurassic; the Yamama Formation is a
136 reservoir and productive carbonate and the Zubair Formation is a reservoir and productive
137 sand in the Lower Cretaceous; the Ratawi, Shuaiba and Nahr Umr formations are carbonate
138 reservoirs in the Lower Cretaceous. The Mauddud, Ahmadi and Rumaila formations are the
139 mainly carbonate reservoirs in the Cenomanian. The Mishrif Formation is a main carbonate
140 reservoir of the Cenomanian-Turonian (Fig. 1B). The Khasib and Tanuma formations are
141 poor reservoirs. Tectonic fracturing of younger higher carbonate permits vertical migration of
142 hydrocarbons into anticlines under efficient evaporitic seals. The regional evaporite seal is
143 Gotnia Formation in the Upper Jurassic, and Fat'ha Formation in the Tertiary (Fig. 1B).

144 *2.2. Stratigraphy, paleogeography and mineralogy*

145 The Mishrif Formation is the main productive reservoir in southern Iraq, the United Arab
146 Emirates, Oman, and Qatar. It was deposited in a shallow environment on the Rumaila
147 Formation conformity. Its upper contact is unconformable with the Khasib Formation,
148 representing a regression in the Turonian-Campanian age (Al-Mimar et al., 2018;

149 Awadeesian et al., 2019). It is represented by a unique lithostratigraphic unit regionally
150 deposited in a fluctuating environment of shallow to deep-water reflecting the tectonic
151 activity in the area (Alsharhan and Nairn, 1988). The carbonate rocks are composed of
152 bioclastic particles (algae, rudist and coral reef) and represent the main facies of the Mishrif
153 Formation. In terms of mineralogy, the Mishrif Formation is mainly composed of calcite
154 (90% av.), with heterogeneous distribution of small amounts of dolomite, kaolinite, chlorite,
155 authigenic quartz and clays (smectites and mixed layers) that do not exceed 10% (Al-Mimar
156 et al., 2018). Southwardly, facies change to distal mid-ramp and proximal mid-ramp deposits
157 and grade into outer-ramp deposits (Aqrawi et al., 1998). Eastwardly, close to the Zagros
158 Foredeep Fault (ZFF) on the border with Iran, the Mishrif Formation is thicker (up to 400 m)
159 and deeper (up to 3000 m) (Abbas and Mahdi, 2019; Mahdi et al., 2013). In particular, thick
160 lagoonal units were deposited in the Majnoon field, implying a paleogeographic change in the
161 eastern part of the study area where carbonate production caught up with the rising sea level
162 until the filling of accommodation space with lagoonal deposits (Mahdi et al., 2013). The
163 movement of the Hormuz Formation's salts was particularly important in southern Iraq
164 (Murriss, 1980). Sadooni (2005) suggested that rudist build-ups in the Basrah area nucleated
165 on the crests of growing salt structures. When the build-ups reached wave-base, they were
166 eroded and rudist fragments were reworked, transported and dispersed to form bioclastic
167 packstone/grainstones (Aqrawi et al., 2010).

3. Methodology

3.1. Chemical and isotope analyses

170 Physicochemical parameters and major ion composition of five formation water samples
171 from Rumaila South (RU287), Rumaila North (R590), West Qurna (WQ87), Majnoon
172 (MJ20), and Zubair (ZB140) oilfields were reprised from Awadh et al. (2018) (mean values

173 and standard deviations at N = 28) and reinterpreted to investigate diagenesis and the
174 temperature of the system using geothermometry. In this study, trace elements (total sulphur,
175 Ba, Li, Fe, Mn, Rb, Sr) were analysed at the ALS Group Laboratory in Seville (Spain) using
176 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; ALS analytical code
177 ME-ICP14L) after filtration and acidification by nitric acid. The dissolved silica as SiO₂(aq)
178 was analysed using the heteropoly blue spectrophotometric method (Clesceri et al., 1999) on
179 filtered and diluted (1:5 by 18 MOhm ASTM Type 1 water) samples. The delta isotope
180 values of hydrogen and oxygen of water molecules in ‰ versus V-SMOW reference standard
181 $\delta^2\text{H}(\text{H}_2\text{O})_c$ and $\delta^{18}\text{O}(\text{H}_2\text{O})_c$, respectively, were obtained; where subscript ‘c’ represents the
182 ‘composition’ scale (Horita et al., 1993). These isotope measurements were conducted by the
183 H₂-H₂O and CO₂-H₂O gas equilibration isotope ratio mass spectrometry (IRMS) method on
184 the vacuum-distilled samples (Boschetti et al., 2011). The salt effect parameter $10^3\ln\Gamma$ of the
185 brines was calculated taking into account the chemical composition and the temperature of
186 the samples by PHREEQCI code, version 3, with the Pitzer thermodynamic database
187 (Boschetti et al., 2011; Horita et al., 1993; Parkhurst and Appelo, 2013). According to Horita
188 et al. (1993), the delta activity of hydrogen and oxygen, $\delta^2\text{H}(\text{H}_2\text{O})_a$ and $\delta^{18}\text{O}(\text{H}_2\text{O})_a$,
189 respectively, was obtained summing the salt effect parameter and the delta isotope
190 composition of hydrogen and oxygen.

191 The strontium isotope ratios, $^{87}\text{Sr}/^{86}\text{Sr}$, of the brines were obtained using thermal
192 ionization mass spectrometry (TIMS). Prior to the analytical process, separation of Sr from
193 the matrix bulk elements, and especially from Rb, was executed using heat plate evaporation
194 with Teflon® vials at 80°C, followed by chromatographic extraction using Sr-Resin™
195 (TrisKem International) (crown-ether (4, 4' (5')-di-t-butylcyclohexano-18-crown-6). The
196 final Sr fraction was recovered from the bulk using HNO₃ 0.05M as eluent, then evaporated
197 on a heat plate at 80°C and introduced into the mass spectrometer. Possible ^{87}Rb interferences

198 were corrected in the Sr analysis and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was normalised in order to correct for
199 mass fractionation, taking into account a reference value of $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. The $^{87}\text{Sr}/^{86}\text{Sr}$
200 results were normalised to NBS SRM 987 (National Bureau of Standards Standard Reference
201 Material 987 – strontium carbonate). Internal precision was 3×10^{-6} .

202 *3.2. Thermodynamic calculations*

203 PHREEQCI code and Pitzer thermodynamic dataset were also used to define:

- 204 i) the mineral-water saturation indices $SI = \log(\text{IAP}/K)$, where IAP and K are the ion
205 activity product of the dissolved constituents and K is the mineral solubility product in a
206 specific reaction, respectively, and the partial pressure of carbon dioxide by the Peng–
207 Robinson equation of state (Parkhurst and Appelo, 2013);
- 208 ii) a geothermal model based on multimineral equilibria.

209 Results were compared to previously published chemical and isotopic
210 geothermometers specific for sedimentary brines (Boschetti et al., 2015; Kharaka and
211 Mariner, 1989; Sanjuan et al., 2014). The calculated activity of the dissolved constituents was
212 also used to calculate the saturation index of a carbonate solid solution made of calcite,
213 magnesite, rhodochrosite, siderite and strontianite by EQ3/6 code, version 8 (Wolery and
214 Jarek, 2003).

215 The Geochemist's Workbench® code (GWB), version 7.0.6 (Bethke and Yeakel,
216 2008), was used to calculate the evaporation path of Cretaceous seawater using the React
217 tool, HMW thermodynamic database, and the main chemical composition of seawater during
218 that period (Bäbel and Schreiber, 2014). According to Bäbel and Schreiber (2014), a chloride
219 concentration of present-day seawater ($565 \text{ mmol kg}^{-1} \text{ H}_2\text{O}$) was taken as a reference; then
220 chloride concentration was charge-balanced, taking into account other main constituents and
221 $\text{pH} = 7.5$ (Hönisch et al., 2012), and a $\log\text{PCO}_2(\text{g}) = -3$ was settled during evaporation. This

222 latter corresponded to a mean concentration of 1000 ppmv of CO₂ in the Cretaceous
223 atmosphere (Hönisch et al., 2012; Wang et al., 2014).

224 Finally, activity diagrams using a thermodynamic database of the minerals and
225 dissolved constituents, recalculated at a pressure of 20 MPa, were plotted using the Act tool
226 of the GWB-code (Boschetti et al., 2016). The Rxn tool of the same code was also used to
227 check the thermodynamic equilibria of specific reactions.

228 **4. Results and Discussion**

229 The physicochemical and isotope parameters are reported in Table 1. The recalculated main
230 chemical composition in equivalents per liter of formation water from the southern region of
231 Iraq shows a Cl-Na composition. In particular, the Na/Cl equivalent ratios range span
232 between 0.77 and 0.91, with a mean of 0.83 ± 0.05 , which is similar to that of present-day
233 seawater (0.86). The Ca/(SO₄ + HCO₃) equivalent ratios of the brines are largely over 1, with
234 a mean of 44 ± 19 and a range between 15 and 78. Therefore, brines can be classified also as
235 Ca-Cl, according to Rosenthal (1997). The mean measured temperature of the water sampled
236 in the Mishrif Formation is 65 ± 2 °C (N = 28) (Awadh et al., 2018). Between the
237 investigated trace elements, the concentration of barium and manganese are higher in
238 Majnoon (5.43 and 4.47 mg/l, respectively) in comparison with the range of the samples from
239 the other oilfields (1.44-1.79 and 0.10-0.13 mg/l, respectively). All samples showed
240 supersaturation in calcite, aragonite, and dolomite (Table 2). Barite and anhydrite are also
241 supersaturated in all but one sample (RU287). Finally, waters are in equilibrium with
242 chalcedony and oversaturated in quartz.

243 *4.1 Chemical composition: diagenesis and geothermometry*

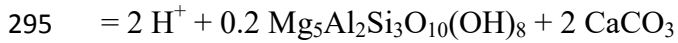
244 According to the previous published works on southern Iraq oilfields (Awadh et al., 2019a;
245 Awadh et al., 2018), the above described chemical ratios of Na/Cl = 0.83 ± 0.05 and Ca/(SO₄

246 + HCO₃) = 44 ± 19 are typical of marine origin formation waters that have undergone
247 chemical modification due to diagenesis (Boschetti et al., 2011; Rosenthal, 1997). The
248 Langelier–Ludwig and brine differentiation diagrams (Boschetti, 2011; Hounslow, 1995) of
249 Figure 2 depict the distinct composition of the oilfield brines in comparison with the local
250 shallow groundwater (Hamdan, 2017) and surface waters (Al-Mallah, 2014; ROPME, 2011;
251 Rzóška, 1980). Surface water (Ghalib and Almallah, 2017), water produced from crude oil
252 dehydration (Al-Shamkhani, 2013) or a mixture of both were used in the oilfields for water-
253 flooding purposes. In Figure 2A, the brine samples from this study and literature are grouped
254 in a narrow field, whereas in the brine differentiation plot (Figure 2B), brines are displaced
255 between the evaporation curve of Cretaceous seawater and the produced waters from
256 dehydrators (Al-Furaiji, 2016; Al-Shamkhani, 2013). Similarly to the Cretaceous formation
257 brines in Venezuela (Boschetti et al., 2016), most of the studied brines affected by diagenesis
258 show a Ca-excess and Na-deficit and seem to follow the typical Ca-Na exchange trend of the
259 so-called basinal fluid line (Davisson and Criss, 1996) (Figure 3). Sample RU287 was
260 probably affected by dolomitization and then by mixing with waters produced from crude
261 dehydrators (“produced water” field in Figure 3). The hottest (115°C) water sample from the
262 deeper Zubair sandstone indicates that the chemical effects of Ca-Na reactions (Al-Marsoumi
263 and Abdul-Wahab, 2005), most probably due to albitisation, are more pronounced at higher
264 temperatures (Figure 3A). Different from the Mishrif Formation, albite was found in the
265 Zubair Formation (Al-Ziayyir, 2018). Moreover, from a theoretical point of view, the
266 diagenetic effects could be more or less pronounced if the variability of the seawater
267 composition in the past was considered. If Cretaceous seawater is used as a reference instead
268 of present-day seawater, the oilfield brines are more clustered towards the axes origin of
269 Figure 3B (which coincides with the composition of less saline surface water) or towards the
270 “produced water” fields. The dolomitization process seems to have had a greater role in the

271 Ca-excess of the waters (Figure 3B). However, the geothermal modelling indicated in Figure
272 4, also suggests that calcite-dolomite equilibration occurred along with chalcedony instead of
273 quartz. In that diagram, all but one sample are clustered between 50 and 75°C isotherms, a
274 range that includes the temperatures of $64 \pm 5^\circ\text{C}$ (N = 9) and $64 \pm 7^\circ\text{C}$ (N = 5) obtained by
275 Mg-Li and chalcedony geothermometers, respectively — the latter corrected for dissolved
276 silica activity and pressure (Kharaka and Mariner, 1989) (Table 2). The exception is
277 represented by sample MJ20 (Majnoon oilfield), which is shifted towards the quartz-dolomite
278 (ordered) model (Figure 4) and shows the lowest temperature from quartz and chalcedony
279 from geothermometric equations (Table 2). Such an apparent convergence between quartz
280 and chalcedony is probably attributable to the greater depth and pressure in the MJ20
281 borehole (Table 1), conditions that could enhance simultaneous equilibria between the fluid
282 and the two mineral phases (Giggenbach, 1991). For the MJ20 sample, a mean value of
283 70.5°C between the geothermometric equations of quartz and chalcedony shows a good
284 agreement with the 68°C obtained from the Mg-Li geothermometer (Table 2).

285 Globally, the mean inferred temperature of the brines are quite similar to the mean
286 temperature measured at depth, confirming that the present-day borehole temperatures are not
287 so different from those reached during Neogene burial (Abeed et al., 2013). Sample MJ20 is
288 an exception, showing a temperature 10°C higher. This is probably due to the effect of
289 greater borehole depth (Fig. 1B) and pressure. The Majnoon oilfield had the highest
290 measured values (Table 1). Activity diagrams of Figures 5A and 5B show that Mg
291 concentration in the brine seems to be limited by dolomite and by chlorite. To check the
292 coexistence of the minerals, the thermodynamics of the following reaction have been
293 calculated (Supplementary File 1):





296 At P = 20 MPa and buffering conditions of Figure 5A, except for Mg which has been
297 buffered by clinocllore, $\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$, instead of dolomite. The above reaction is in
298 equilibria at 64°C using $\log[\text{Ca}^{2+}/(\text{H}^+)^2] = 11.11$ and $\log[\text{SiO}_2(\text{aq})] = -3.32$, which
299 corresponds to the mean activity values of all investigated samples (Supplementary File 1).
300 Therefore, this corroborates not only that dolomite and chlorite could coexist in the studied
301 basin, but also the temperature values obtained by geothermometers, in particular those by
302 Li-Mg and chalcedony equations (Table 2).

303 Figure 5 also shows that the Ca/Na ratio is probably controlled by smectite instead of
304 albite. The role of clays on the control of Na amount in solution by Ca-Na exchange or Na
305 adsorption could also explain the lower temperatures of 42 ± 6 °C obtained using the Na/Li
306 geothermometer (Kharaka and Mariner, 1989; Sanjuan et al., 2014) (Table 2). Similarly, the
307 values obtained from the boron isotope geothermometer gave an underestimation of the brine
308 temperature (Table 2). This could be due to a higher $\delta^{11}\text{B}$ value in Cretaceous seawater (up to
309 3‰ higher than the present; Lemarchand et al. 2002), together with a fractionation effect due
310 to evaporation up to halite saturation (approximately +4‰) (Vengosh et al. 1992). Actually,
311 by subtracting a value of 7‰ from the original values of the brines, a mean temperature of 64
312 ± 6 °C was obtained from the boron isotope geothermometric equation (Boschetti et al.,
313 2015), which matches with that obtained by the calcite-dolomite-chlorite-kaolinite equilibria.

314 4.2. Oxygen and hydrogen stable isotope ratios

315 The isotope composition value — i.e. not considering the salt effect according to Horita et al.
316 (1993) — of the studied formation water is similar to that of the Mishrif Formation values
317 from the Qatar oilfield values (Danquigny et al., 2005) (Figure 6). However, the calculation
318 of isotope activity due to the salt effect reveals a high enrichment in $\delta^2\text{H}$ (up to +8.3‰) and a

319 slight depletion in $\delta^{18}\text{O}$ (up to -0.3‰) in comparison to the analysed isotope composition. As
320 presented in Figure 6, the isotope composition of the formation waters from the samples
321 analyzed in this study fall close to the final part of the hook path derived from experimental
322 seawater evaporation (e.g. Gonfiantini et al., 2018), thus confirming the marine origin of
323 these samples, as previously inferred by the boron isotope (Awadh et al., 2018). It should be
324 noted that the experimental hook paths of the evaporated seawater are generally analysed
325 from salt pans without the addition of either new marine or meteoric water (i.e. closed
326 system) (Gonfiantini, 1965; Gonfiantini et al., 2018). This could be the reason why the
327 isotope activity values of the brine — i.e. considering the salt effect according to Horita et al.
328 (1993) — do not fall on the hook path (Figure 6). In Figure 6, the Iraq meteoric water line
329 (IMWL) and its prediction interval (parallel dashed lines with $\delta^2\text{H} \pm 10.3$ ‰ from IMWL)
330 were recalculated from the rainwater isotope data of Ali et al. (2015) using the error-in-
331 variable (EIV) regression method (Boschetti et al., 2019). The extrapolation of the best fit
332 line of the brine samples meets the prediction interval of the meteoric water line just between
333 rain waters collected from Başrah city (Fig. 1) plus other southern Iraq areas (Al-Kinani et
334 al., 2018; Ali et al., 2015; Jassem et al., 2018) and evaporated river samples from the Tigris
335 and Euphrates (Jassem et al., 2018) (Figure 6). Sample RU287 shows the highest contribution
336 of modern fresh water. It should also be remarked that, in comparison with other samples, the
337 RU287 brine displays barite supersaturation (Table 2), which is probably due to the effect of
338 mixing between brines and local water of meteoric origin or reinjected produced waters as a
339 consequence of the water flooding (Ghalib and Almallah, 2017; Sorbie and Mackay, 2000).
340 This is in line with the previously described chemical diagrams. On the opposite side, the
341 extrapolated best fit line of the isotope activity of the brines meets the hooked evaporation
342 path of seawater just on the top of the hump (Figure 6), which approximatively corresponds
343 to gypsum saturation (Holser, 1979; Knauth and Beeunas, 1986).

344 Evaporated seawater samples from present-day sabkha and lagoon environments (i.e.
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2 345 open systems) show $\delta^{18}\text{O}$ up to +6.5‰, which is similar to those determined in the formation
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4 346 brines of this study, but with $\delta^2\text{H}$ enrichment up to approximately +30‰ (McKenzie et al.,
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7 347 1980; Nadler and Magaritz, 1980; Robinson and Gunatilaka, 1991). Lower deuterium values
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10 348 are mainly due to mixing with evaporated surface waters or groundwater of meteoric origin
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12 349 (McKenzie et al., 1980; Robinson and Gunatilaka, 1991); whereas, flooding and mixing of
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14 350 evaporated solution with new seawater inputs could shift the composition back to the starting
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17 351 values (i.e. near V-SMOW) (Nadler and Magaritz, 1980) (Figure 6). A similar effect was
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19 352 observed in Miocene brines by comparison with $\delta^{18}\text{O}$ from coeval gypsum, with the
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22 353 exception of the formation waters affected by a positive $\delta^{18}\text{O}$ -shift as result of diagenetic
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24 354 water-rock interaction with limestones (Boschetti et al., 2011). In a similar way, and
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27 355 assuming that starting seawater during the Phanerozoic has remained isotopically similar to
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29 356 the present-day V-SMOW value (i.e. 0‰ both for oxygen and for hydrogen stable isotope
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32 357 ratios) (Gregory and Taylor Jr, 1981; Ryb and Eiler, 2018; Sessions, 2016), the ^{18}O
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34 358 enrichment of formation waters as observed in samples MJ20, ZB140, and R590 could be due
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37 359 to water–rock interaction. Therefore, water-rock interaction and dilution seem to be the main
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39 360 processes that affected in a significant manner the isotope composition of the studied brines.
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42 361 Such a diagenetic effect was also hypothesised for the Mishrif Formation in Qatar
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44 362 where limestones value ranges between $+24.4 \text{ ‰} < \delta^{18}\text{O} \text{ (V-SMOW)} < +27.4 \text{ ‰}$, formation
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47 363 brines $\delta^{18}\text{O}$ up to +5‰ (V-SMOW), and temperatures between 50 and 70°C have been
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50 364 measured (Deville de Periere, 2011). As the isotope values of the limestones from the same
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52 365 formation in southern Iraq are within the range of those measured in Qatar, i.e. $+25.2 \text{ ‰} <$
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54 366 $\delta^{18}\text{O} \text{ (V-SMOW)} < +27.4 \text{ ‰}$ (Taha and Abdullah, 2019), the diagenetic effect can be
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57 367 hypothesised also for this area. Considering a mean value $\delta^{18}\text{O}(\text{H}_2\text{O})_a = +3.9 \text{ ‰}$ (V-SMOW)
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59 368 for the brine samples that fall within the diagenetic arrow in Figure 6 and a mean value of
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369 $\delta^{18}\text{O}$ (limestones) equal to +26.5 ‰ (V-SMOW) of the Mishrif Formation in southern Iraq, it
370 is possible to calculate an oxygen isotope fractionation factor of $1000\ln\alpha$ (calcite-water) =
371 +22.3 ‰. This latter value corresponds to a temperature between 56°C (Kim and O'Neil,
372 1997) and 69°C (Zheng, 1999). Other isotope effects due to clays and crude are probably not
373 quantitatively important or less pronounced than the salt effect. Indeed, a fractionation
374 between water and hydrocarbons should generate in brines a shift towards $\delta^2\text{H}$ values higher
375 than seawater (e.g., Horita, 2009), but this is not the case (Figure 6). Furthermore, the amount
376 of clays minerals in the Mishrif Formation are probably insufficient to generate a significant
377 isotope effect on the $\delta^2\text{H}$ of the waters.

378 *4.3. Strontium isotope ratio*

379 The strontium isotope ratios of the four brine samples analysed are $0.707713 < {}^{87}\text{Sr}/{}^{86}\text{Sr} <$
380 0.707749 (WQ87, RU287, ZB140, R590), which corresponds to a marine strontium of late
381 Cenomanian–early Maastrichtian age (McArthur, 2010; McArthur et al., 2012); with the
382 sample at the Majnoon oilfield (MJ20) showing the highest value of 0.708043. The Mishrif
383 reservoir is Cenomanian–Turonian; therefore, the strontium isotope ratio should theoretically
384 not be greater than 0.707314 ± 0.000005 (McArthur, 2010; McArthur et al., 2012). The
385 higher strontium isotope ratios in formation waters could suggest a contribution of more
386 radiogenic strontium from injected waters when compared to the more saline and enriched
387 brines (Danquigny et al., 2005), but in this case the oxygen and hydrogen stable isotope ratios
388 are not less than the other samples. Moreover, it should be also noted that ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ values up
389 to 0.707869 have been detected in the brines from the Mishrif Formation in Qatar (Al Khalij
390 offshore field; Danquigny et al. 2005) and up to 0.70878 in the carbonate matrix of the coeval
391 Sarvak Formation in southern Iran (Hajikazemi et al., 2012). Such elevated values detected at
392 the disconformity surfaces of the formations are probably due to the contribution of meteoric
393 water during diagenesis (e.g., Hajikazemi et al. 2012). However, the combination of high

394 manganese and radiogenic strontium contributions to the limestones of the Sarvak Formation
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2 395 of southern Iran were also attributed to different sources: i) a Cenomanian-Turonian subaerial
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4 396 exposure; ii) diagenetic fluids; and iii) detritus (Navidtalab et al., 2016). Actually, all the
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6 397 inspected brines of this study are undersaturated with respect to pure rhodocrosite ($SI = -3.9 \pm$
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9 398 0.8), but in equilibrium with carbonate solid solution ($SI = -0.082 \pm 0.261$) (Table 2). In
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11 399 particular, despite its high Mn activity, the Majnoon brine MJ20 showed a slight
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13 400 undersaturation in that solid solution. Therefore, the higher Mn concentration (up to 4 mg/l)
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15 401 and radiogenic strontium at that brine could be acquired by limestone dissolution in a
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17 402 disconformity layers. Alternatively, as suggested by the lowest gypsum and anhydrite
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19 403 saturation indices of the Majnoon sample (Table 2), it cannot be excluded that there was a
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21 404 contribution of radiogenic strontium-rich sulphate minerals from Cambrian salt domes (up to
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23 405 0.7092) (McArthur et al., 2012). Salt domes characterise the fold settings in the oilfields of
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25 406 southern Iraq (Al-Ameri et al., 2011; Al-Mimar and Awadh, 2019). The doming triggered
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27 407 local uplift and emergence of paleo-exposure surfaces (Rahimpour-Bonab et al., 2013), thus
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29 408 the shallow back shoal/lagoonal depositional environment of Mishrif limestones at the
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31 409 Majnoon oilfield and the salt domes seem to be related (Aqrawi et al., 2010; Mahdi et al.,
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33 410 2013). Moreover, “hydrothermal fluids” with temperatures up to 80°C were hypothesized to
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35 411 form diagenetic cements (i.e., blocky calcite), dolomite and coarse crystalline pyrite during
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37 412 deeper burial of the Sarvak Formation (Hajikazemi et al., 2017). Therefore, the chemical,
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39 413 thermal and isotopic anomalies of the Majnoon brine suggest that it is the hottest fluid
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41 414 probably related to the higher geothermal gradient of a deeper structure as the ZFF (Basilici
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43 415 et al., 2020; Bordenave, 2008; Bordenave and Hegre, 2010).

54 416 **5. Conclusions**

57 417 This paper presented the first data on isotope ratios of oxygen, hydrogen, and strontium of
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59 418 oilfield waters from southern Iraq, along with new trace element data and a reinterpretation of
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419 previous published chemistry. Processes like diagenesis and seawater evaporation that
420 typically occur in these fluids can be distinguished using classical ‘basinal fluid’ chemical
421 diagrams. Mishrif Formation waters are Cretaceous connate brines and the different chemical
422 composition of seawater of that period needs to be taken into account for a more correct
423 interpretation. The Ca-excess versus Na-deficit composition of these kinds of fluids are
424 usually explained by albitisation. However, it was verified by activity plots that in the Mishrif
425 limestone reservoir the Na/Ca exchange that occurs in brines is mainly due to water-smectite
426 equilibrium.

427 The values $\delta^2\text{H}$ and $\delta^{18}\text{O}$ obtained on selected samples show that oxygen isotope
428 composition of the brines was isotopically more affected by equilibria with limestone than
429 evaporation. The global effect of the water-rock interaction is an ^{18}O -enrichment of the
430 brines. Locally, dilution by present-day water of meteoric origin and shift towards the local
431 meteoric water line also detected, probably as consequence of water-flooding (Rumaila
432 South, sample RU287). Furthermore, it is also shown that isotope data cannot be separated
433 from the interpretation of the chemical composition of sedimentary brines. The contribution
434 of the salt effect on the stable isotope ratios of water molecules, i.e. $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$, needs
435 to be evaluated because this parameter could vary the results during fractionation processes
436 such as seawater evaporation and diagenesis. Hydrogen isotope ratios are probably more
437 affected by the salt effect than other fractionations. Furthermore, taking into account the salt
438 effect, the temperature range inferred from carbonate-water oxygen isotope ratio fractionation
439 is comparable to that obtained from the chemical geothermometers, i.e. between 50 and 75°C.
440 According to Abeed et al. (2013), these evaluations confirm that the present-day borehole
441 temperatures are not so different from those reached during Neogene burial.

442 More recent mixing processes such as water floods could be detected by a comparison
443 with the composition of the formation brine, waters produced from crude dehydrators, and

1 444 the local waters of meteoric origin. The strontium isotope ratio confirms the interaction of
2 445 Cretaceous limestone for most of the studied samples, suggesting a late Cenomanian–early
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4 446 Maastrichtian age, and an input of more radiogenic strontium in the Majnoon oilfield (MJ20
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7 447 sample). The brine sample from this latter oilfield showed a particular geochemical
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9 448 characteristic. Despite the lower temperature measured at the MJ20 borehole (60°C), the
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11 449 slightly higher temperature obtained by the Li-Mg, Na-Li and $\delta^{11}\text{B}$ geothermometers (up to
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13 450 74°C) is probably due to the deeper structure of that oilfield, which is closer to the ZFF. The
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15 451 more radiogenic strontium ratio at Majnoon could be related to: i) debris input in the
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17 452 limestone, which could explain also the high Mn content; or ii) interaction with local
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19 453 Cambrian sulphates. An inspection of additional samples, sulphur stable isotope ratio
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21 454 ($^{34}\text{S}/^{32}\text{S}$) and radiogenic isotope of the halogens (^{139}I , ^{36}Cl) could improve the knowledge of
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23 455 the past water flow events and clarify the relationship between the high Mn concentration /
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25 456 high radiogenic strontium in the Cretaceous limestones and the salt domes.
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41 461 constructive comments and suggestions.
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46 **Captions**

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48 463 **Table 1** – Physicochemical parameters, major ion composition, trace elements concentration,
49 464 and isotopic results from Awadh et al. (2018) and this study.

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51 465 **Table 2** – Geothermometric results in Celsius degree (°C); mineral saturation indices (SI),
52 466 and carbon dioxide partial pressure as $\log\text{P}(\text{CO}_2)\text{g}$ obtained by PHREECI code, version 3,
53 467 along with Pitzer thermodynamic dataset at the measured temperature and water pressure
54 468 conditions (Table 1). EQ 3/6 code was also used to calculate the saturation indexes of
55 469 carbonates solid solution.
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58 470 **Figure 1** – A) Location map showing the studied oilfields at the Zubair zone, within the
59 471 southern part of the Mesopotamia plain and to the southwest of the Zagros Foredeep Fault
60 472 (ZFF); Stratigraphic correlation of the five oilfield wells penetrating four formations
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473 (Rumaila, Mishrif, Khasib, and Tanuma) in which there is a well from each oilfield (RU287
474 from Rumaila South, R590 from Rumaila North, WQ87 from West Qurna, MJ20 from
475 Majnoon, and ZB140 from Zubair oilfield); B) Typical section represents the stratigraphic
476 setting in the study area.

477 **Figure 2** – Langelier–Ludwig (A) and Brine Differentiation Plot (B) of the oilfield brines of
478 southern Iraq (Al-Mallah, 2014; Al-Marsoumi and Abdul-Wahab, 2005; Awadh et al., 2019b;
479 Awadh et al., 2018; Jamil, 1978) compared with shallow groundwater (Hamdan, 2017), Shatt
480 Al-Arab River (ROPME, 2011), Shatt Al-Basrah Canal, or ‘Main Drain’ (Al-Mallah, 2014)
481 and seawater. In both diagrams, concentration of the dissolved species are in equivalent/liter;
482 dashed ellipses depict the trend of the Tigris–Euphrates River system at Qurna and Shatt Al-
483 Arab River during the 60s (Rzóska, 1980). In (B), Mishrif Formation’s brine waters from
484 Awadh et al. (2018) are distinguished by black triangles; the five samples reprised in this
485 study are highlighted by white crosses. The brine data from other references (Al-Mallah,
486 2014; Al-Marsoumi and Abdul-Wahab, 2005; Awadh et al., 2019b; Jamil, 1978) are
487 represented by white triangles. Produced waters from hydrocarbon dehydrators are also
488 shown for comparison (dashed field) (Al-Furaiji, 2016; Al-Shamkhani, 2013). Arrows depict
489 possible mixing trends. In the inset, the original fields of the diagram along with evaporation
490 paths of present-day (Boschetti, 2011; Hounslow, 1995) and Cretaceous seawater (this study)
491 are shown. G and H depict the gypsum and halite saturation points, respectively.

492 **Figure 3** – $\text{Ca-excess} = 2 \times [\text{Ca}_{\text{meas}} - (\text{Ca}/\text{Cl})_{\text{SW}} \times \text{Cl}_{\text{meas}}]/40.08$ vs. $\text{Na-deficit} = [(\text{Na}/\text{Cl})_{\text{SW}} \times$
493 $\text{Cl}_{\text{meas}} - \text{Na}_{\text{meas}}] / 22.99$ diagram for oilfield waters from southern Iraq, where meas =
494 measured, SW = seawater and Ca, Na and Cl are elemental concentrations in mg/l (Davisson
495 and Criss, 1996). The 1Ca-2Na or 1Ca-1Na exchange arrows depict the possible paths of
496 formation fluids in sedimentary basins during plagioclase albitisation (Davisson and Criss,
497 1996). In (A) and (B) diagrams, present-day and Cretaceous seawater were used as SW-
498 composition, respectively. In both: light gray ellipse at the origin of the plot represents the
499 initial seawater composition (i.e. before evaporation), local groundwater and surface waters
500 composition; dashed and dot-dashed lines depict the evaporation paths of Cretaceous and
501 present-day seawaters, respectively. Other symbols and fields as in Figure 2.

502 **Figure 4** – Base-10 logarithm of silicium versus calcium/magnesium ratio diagram of the
503 Mishrif Formation’s brines from southern Iraq (molar concentration). Dashed curves depict
504 the simultaneous equilibria of calcite-dolomites plus quartz (light gray) or chacedony (black)
505 calculated by PHREEQCI code and pitzer thermodynamic dataset (Parkhurst and Appelo,
506 2013) at the mean pressure of the five samples (27.8 MPa; Table 1).

507 **Figure 5** – Activity plots for the system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ at $P = 200$
508 bar and $50 < T < 75$ °C. In (A), the activity of dissolved silica has been fixed at the mean
509 value detected in the waters, i.e.: $\log[\text{SiO}_2(\text{aq})] = -3.32$, whereas in (B) it was buffered by
510 chalcedony. In both diagrams: water activity at $\log[\text{H}_2\text{O}] = -0.0855$ (mean value of the local
511 brines); aluminium buffered by kaolinite; magnesium and HCO_3^- buffered by dolomite and
512 calcite, respectively.

513 **Figure 6** – $\delta^2\text{H}(\text{H}_2\text{O})$ vs. $\delta^{18}\text{O}(\text{H}_2\text{O})$ diagram. Samples from this study are differentiated for
514 isotope composition (white-crossed gray triangles) and isotope activity (white-crossed black
515 triangles): the former represent analytical results of water samples after vacuum distillation
516 and IRMS; the latter represent isotope composition plus the theoretical salt effect (Horita et
517 al., 1993) (Table 1). Water isotope composition of brines from the Mishrif Formation in
518 Qatar are also shown for comparison (open triangles) (Danquigny et al., 2005). Dotted lines
519 depict the linear best fits of the two ways of representation of isotope ratios in brines.

520 Evaporated seawaters from a closed (Gonfiantini et al., 2018) and open (McKenzie et al.,
1 521 1980; Nadler and Magaritz, 1980; Robinson and Gunatilaka, 1991) system are shown for
2 522 comparison. The previous published data on isotope composition of the Arabian Gulf
3 523 seawater and its evaporated composition are depicted by the field with waves and forward-
4 524 back curved arrows, respectively (Bagheri et al., 2014; McKenzie et al., 1980; Robinson and
5 525 Gunatilaka, 1991; Yurtsever, 1994). Rainwater samples (drops) from southern Iraq (Al-
6 526 Kinani et al., 2018; Ali et al., 2015; Jassem et al., 2018) and northern Kuwait (Hadi et al.,
7 527 2016) are also shown for comparison. Tigris and Euphrates samples are represented by open
8 528 squares; samples out of the IMWL's (Iraq meteoric water line) prediction interval are
9 529 evaporated surface water samples (arrow with slope ~ 4.3) (Ali et al., 2015; Jassem et al.,
10 530 2018).

11 531 **Supplementary File 1** - Calculation of the thermodynamic equilibria by Rxn tool of The
12 532 Geochemist's Workbench® code (Bethke and Yeakel, 2008) and P = 20 MPa thermodynamic
13 533 dataset (Boschetti et al., 2016). To reduce the variables, the activity of calcium and hydrogen
14 534 was rewritten as log-ratio in the reaction and automatically rebalanced by the tool.

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1 **Chemical and isotope composition of the oilfield brines from Mishrif**

2 **Formation (southern Iraq): Diagenesis and geothermometry**

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26 Abstract

27 This paper focuses on the geochemical composition and isotope geochemistry of brines in the
28 Cenomanian–Turonian carbonate Mishrif reservoir of southern Iraq. Main dissolved
29 constituents, trace elements, $\delta^2\text{H}$ and $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, mineral saturation indices and
30 thermodynamic calculations were investigated in formation waters from the Mishrif
31 Formation to obtain a better understanding of brine evolution and diagenetic effects over
32 geological time. Previous published $\delta^{11}\text{B}$ data were also reinterpreted as a geothermometer
33 tool. The results are compared with previous published data for local oilfields and coeval
34 formations in the Arabian Gulf. The Mishrif brine has a marine origin and is diagenetically
35 modified to Ca-excess and Na-deficit. Formation waters are quartz supersaturated and are in
36 equilibrium with chalcedony and calcite-dolomite in the temperatures range of 50–75°C,
37 which is also confirmed by calcite-water oxygen isotope fractionation and $\delta^{11}\text{B}$
38 geothermometer. The potential role of clays in conditioning brine chemistry during diagenetic
39 processes was highlighted by activity diagrams; in particular, their adsorption/exchange
40 effect on sodium could explain the lower temperature obtained by the Na/Li geothermometer
41 (42 ± 6 °C). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values show that oxygen isotope composition of the brines
42 was isotopically more affected by interaction with limestone during diagenesis than seawater
43 evaporation. The main effect is an ^{18}O -enrichment on the brine starting from the SMOW
44 value. Locally, dilution by present-day meteoric water was also detected (Rumaila South),
45 which is shifted towards the local meteoric water line. The strontium isotope ratios range
46 from 0.707713 to 0.707749 and correspond to a marine strontium of late Cenomanian–early
47 Maastrichtian age, except for the Majnoon sample, which shows a more radiogenic value
48 (0.708043). Radiogenic strontium and gypsum and anhydrite saturation indices of the
49 Majnoon sample could indicate the contribution of calcium and sulphate from the strontium-
50 rich sulphate minerals of the Cambrian salt domes occurring in the oilfields of southern Iraq.

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The higher manganese concentration (4 mg/l) and the slightly higher temperature inferred by geothermometers (up to 74 °C) in comparison with present-day could indicate that the Majnoon brine is a hot fluid, probably related to a deeper structure such as the Zagros Foredeep Fault.

Keywords: Oilfield waters; chemical composition; geothermometry; oxygen and hydrogen stable isotope ratios; strontium isotopes.

1. Introduction

In the Jurassic–Cretaceous petroleum system of southern Iraq, hydrocarbons are mainly trapped in Lower Cretaceous sandstone and carbonate reservoirs. Crude oil is generated from the organic-rich Upper Jurassic (Sargelu and Sulaiy formations) changing the Lower Cretaceous carbonates of the Yamama Formation and the Zubair Formation, a clastics reservoir (Abeed et al., 2012; Abeed et al., 2013). The chemical composition of formation waters from the Yamama reservoir in the Zubair and North/South Rumaila oilfields is mainly composed of chloride (up to 143,589 ppm) with a salinity 6.2 times higher than seawater (Jamil, 1978), as for West Qurna oilfield, salinity 7.3 times higher than seawater and dominated by 191,700 ppm of chloride (Al-Marsoumi and Abdul-Wahab, 2005). These prior works utilized brine chemistry but did not address the evolution of the reservoir brine, as they relied mainly on cations and anions without considering isotopes. More recently, the boron stable isotope ratio of the brine from the Mishrif reservoir has given a seawater signature (Awadh et al., 2019a; Awadh et al., 2018) and highlighted the role of salinity in generating the formation pressure and controlling the fluid flow (Al-Mimar and Awadh, 2019). The developing of the oilfield brines over the geological time and its response to the flooding and diagenesis have a significant impact on petroleum reservoir quality, but this subject has not yet been investigated.

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75 The diagenetic effects on brine waters can be evaluated by comparing the Na, Ca and
76 Cl concentrations of the brine with those of seawater and with the so-called basinal fluid line
77 in the Ca-excess versus Na-deficit binary diagram (Davisson and Criss, 1996). However, in
78 this plot the interpretation could be misguided because: (i) the reference basinal fluid line
79 takes into account only plagioclase albitisation, often without checking the real
80 thermodynamic equilibria state of the involved waters; and ii) modelling involves the current
81 seawater composition disregarding that of past periods (Babel and Schreiber, 2014;
82 Lowenstein et al., 2003). A combination of isotope parameters as O-H stable isotope ratios
83 and $^{87}\text{Sr}/^{86}\text{Sr}$ was proposed by Danquigny et al. (2005) to evaluate the effect of water
84 flooding in the Mishrif Formation water of Qatar. However, in that work, seawater
85 evaporation, the isotope salt effect (Horita et al., 1993), and the contribution of radiogenic
86 strontium to the limestones of the Mishrif Formation were not considered.

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The objectives of this research are: i) to investigate the origin of the oilfield waters; ii)
to evaluate the composition of oilfield waters over time; and iii) to trace the influence of
diagenesis and any geothermal effects on the brine. This investigation considers the above
described effects and processes in the Mishrif Formation brines by reinterpreting the
previously published main chemical constituents, along with new and original data on trace
elements, oxygen and hydrogen water isotope ratio, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, and thermodynamic
calculations. Moreover, the previously published data of boron isotope ratio $\delta^{11}\text{B}$ (Awadh et
al., 2019a; Awadh et al., 2018) are here reinterpreted as a geothermometer tool, and are
results compared with those obtained from chemical geothermometers. The main research
contribution is to obtain better understanding of the oilfield brines evolution.

2. Geological setting

2.1. Oilfield locations, main geological features and tectonics

99 The studied oilfields, Rumaila South (RU), Rumaila North (R), West Qurna (WQ), Zubair
100 (ZB) and Majnoon (MJ) are located in southern part of Iraq (Jassim and Buday, 2006) (Fig.
101 1A). The Mesopotamian zone extends from middle to southern Iraq as a relatively flat terrain
102 with a gradient of less than 10 cm/km in the north-west to the Arabian Gulf. The zone was
103 probably uplifted during Hercynian deformation but was subject to subsidence from the Late
104 Permian onwards (Jassim and Buday, 2006). The oilfields are located in the Zubair zone
105 (Grabowski Jr., 2014; Sadooni and Aqrabi, 2000), southern part of the Mesopotamia plain
106 (Fig. 1A), an area characterized by the presence of a gentle subsurface succession of
107 anticlinal and synclinal structures. These structures form giant hydrocarbon traps: Rumaila
108 South (37 km length, 16 km width), Rumaila North (40 km, 13.5 km), West Qurna (35 km, 8
109 km) and Majnoon (48 km, 10 km).

110 From the interpretation of gravity and magnetic data, Alyasi et al. (2014) mentioned
111 that the presence of anticlinal structures is due to the effect of the evaporites of the Late
112 Jurassic Gotnia Formation and Late Ediacaran – Early Cambrian Hormuz Formation in
113 addition to other tectonic forces, where salts moves upward by buoyant forces and the denser
114 rocks remain below them. To the north of the Arabian Gulf, huge salt-gypsum domes are
115 exposed at a surface coexisting with a mixture of igneous and metamorphic rocks peeled off
116 from the Precambrian crystalline basement (Mortazavi et al., 2017). Jabal Sanam is one of the
117 salt diapirs in southern Iraq / northern Kuwait border (Fig. 1); it is an extension of the
118 Hormuz Formation, located in Iran at the northern part of the Arabian Gulf, which contains
119 more than 200 salt domes composed of sequences of evaporates, shales, siltstones and
120 carbonates (Mortazavi et al., 2017). The role of tectonic events (extensional faulting) and
121 differential loading of sedimentary cover above the mobile salt layer are the main triggering
122 factors of the salt diapirism (Singh, 2012). In particular, the Permo-Triassic Tethyan rifting,
123 the Cretaceous-Paleogene obduction and the compressive events associated with basement

124 reactivation of north-south Arabian trends could have started the episodic salt diapir activity
125 in the area of this study (Singh, 2012). However, traces of a neotectonic reactivation were
126 also documented (Sissakian et al., 2017).

127 The Zubair zone is a southern part of the Mesopotamian Basin that is located close to
128 the junction of the Arabian Shelf and Iranian continental block. Collision of these plates at
129 the Mesozoic-Cenozoic boundary produced the Zagros Foredeep fault and the Mesopotamian
130 Basin, which is a member of the Arabian Gulf Basin (Konyuhov and Maleki, 2006). During
131 the Mesozoic and Cenozoic, the study area was a tropical region, with organic-rich
132 carbonates or organic-rich argillaceous sediments being deposited. Good-quality source rocks
133 were preserved in different intervals of geological time, particularly during the Mesozoic. For
134 example (Fig. 1B): the Alan Formation in the Middle Jurassic; the Sargelu, Najmah and
135 Sulaiy formations are the source rocks in the Upper Jurassic; the Yamama Formation is a
136 reservoir and productive carbonate and the Zubair Formation is a reservoir and productive
137 sand in the Lower Cretaceous; the Ratawi, Shuaiba and Nahr Umr formations are carbonate
138 reservoirs in the Lower Cretaceous. The Mauddud, Ahmadi and Rumaila formations are the
139 mainly carbonate **reservoirs** in the Cenomanian. The Mishrif Formation is a main carbonate
140 reservoir of the Cenomanian-Turonian (Fig. 1B). The Khasib and Tanuma formations are
141 poor reservoirs. Tectonic fracturing of younger higher carbonate permits vertical migration of
142 hydrocarbons into anticlines under efficient evaporitic seals. The regional evaporite seal is
143 Gotnia Formation in the Upper Jurassic, and Fat'ha Formation in the **Tertiary** (Fig. 1B).

144 *2.2. Stratigraphy, paleogeography and mineralogy*

145 The Mishrif Formation is the main productive reservoir in southern Iraq, the United Arab
146 Emirates, Oman, and Qatar. It was deposited in a shallow environment on the Rumaila
147 Formation conformity. Its upper contact is unconformable with the Khasib Formation,
148 representing a regression in the Turonian-Campanian age (Al-Mimar et al., 2018;

149 Awadeesian et al., 2019). It is represented by a unique lithostratigraphic unit regionally
150 deposited in a fluctuating environment of shallow to deep-water reflecting the tectonic
151 activity in the area (Alsharhan and Nairn, 1988). The carbonate rocks are composed of
152 bioclastic particles (algae, rudist and coral reef) and represent the main facies of the Mishrif
153 Formation. In terms of mineralogy, the Mishrif Formation is mainly composed of calcite
154 (90% av.), with heterogeneous distribution of small amounts of dolomite, kaolinite, chlorite,
155 authigenic quartz and clays (smectites and mixed layers) that do not exceed 10% (Al-Mimar
156 et al., 2018). Southwardly, facies change to distal mid-ramp and proximal mid-ramp deposits
157 and grade into outer-ramp deposits (Aqrawi et al., 1998). Eastwardly, close to the Zagros
158 Foredeep Fault (ZFF) on the border with Iran, the Mishrif Formation is thicker (up to 400 m)
159 and deeper (up to 3000 m) (Abbas and Mahdi, 2019; Mahdi et al., 2013). In particular, thick
160 lagoonal units were deposited in the Majnoon field, implying a paleogeographic change in the
161 eastern part of the study area where carbonate production caught up with the rising sea level
162 until the filling of accommodation space with lagoonal deposits (Mahdi et al., 2013). The
163 movement of the Hormuz Formation's salts was particularly important in southern Iraq
164 (Murriss, 1980). Sadooni (2005) suggested that rudist build-ups in the Basrah area nucleated
165 on the crests of growing salt structures. When the build-ups reached wave-base, they were
166 eroded and rudist fragments were reworked, transported and dispersed to form bioclastic
167 packstone/grainstones (Aqrawi et al., 2010).

3. Methodology

3.1. Chemical and isotope analyses

170 Physicochemical parameters and major ion composition of five formation water samples
171 from Rumaila South (RU287), Rumaila North (R590), West Qurna (WQ87), Majnoon
172 (MJ20), and Zubair (ZB140) oilfields were reprised from Awadh et al. (2018) (mean values

173 and standard deviations at N = 28) and reinterpreted to investigate diagenesis and the
174 temperature of the system using geothermometry. In this study, trace elements (total sulphur,
175 Ba, Li, Fe, Mn, Rb, Sr) were analysed at the ALS Group Laboratory in Seville (Spain) using
176 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES; ALS analytical code
177 ME-ICP14L) after filtration and acidification by nitric acid. The dissolved silica as SiO₂(aq)
178 was analysed using the heteropoly blue spectrophotometric method (Clesceri et al., 1999) on
179 filtered and diluted (1:5 by 18 MOhm ASTM Type 1 water) samples. The delta isotope
180 values of hydrogen and oxygen of water molecules in ‰ versus V-SMOW reference standard
181 $\delta^2\text{H}(\text{H}_2\text{O})_c$ and $\delta^{18}\text{O}(\text{H}_2\text{O})_c$, respectively, were obtained; where subscript ‘c’ represents the
182 ‘composition’ scale (Horita et al., 1993). These isotope measurements were conducted by the
183 H₂-H₂O and CO₂-H₂O gas equilibration isotope ratio mass spectrometry (IRMS) method on
184 the vacuum-distilled samples (Boschetti et al., 2011). The salt effect parameter $10^3\ln\Gamma$ of the
185 brines was calculated taking into account the chemical composition and the temperature of
186 the samples by PHREEQCI code, version 3, with the Pitzer thermodynamic database
187 (Boschetti et al., 2011; Horita et al., 1993; Parkhurst and Appelo, 2013). According to Horita
188 et al. (1993), the delta activity of hydrogen and oxygen, $\delta^2\text{H}(\text{H}_2\text{O})_a$ and $\delta^{18}\text{O}(\text{H}_2\text{O})_a$,
189 respectively, was obtained summing the salt effect parameter and the delta isotope
190 composition of hydrogen and oxygen.

191 The strontium isotope ratios, $^{87}\text{Sr}/^{86}\text{Sr}$, of the brines were obtained using thermal
192 ionization mass spectrometry (TIMS). Prior to the analytical process, separation of Sr from
193 the matrix bulk elements, and especially from Rb, was executed using heat plate evaporation
194 with Teflon® vials at 80°C, followed by chromatographic extraction using Sr-Resin™
195 (TrisKem International) (crown-ether (4, 4’ (5’)-di-t-butylcyclohexano-18-crown-6). The
196 final Sr fraction was recovered from the bulk using HNO₃ 0.05M as eluent, then evaporated
197 on a heat plate at 80°C and introduced into the mass spectrometer. Possible ^{87}Rb interferences

198 were corrected in the Sr analysis and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was normalised in order to correct for
199 mass fractionation, taking into account a reference value of $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. The $^{87}\text{Sr}/^{86}\text{Sr}$
200 results were normalised to NBS SRM 987 (National Bureau of Standards Standard Reference
201 Material 987 – strontium carbonate). Internal precision was 3×10^{-6} .

202 *3.2. Thermodynamic calculations*

203 PHREEQCI code and Pitzer thermodynamic dataset were also used to define:

- 204 i) the mineral-water saturation indices $SI = \log(\text{IAP}/K)$, where IAP and K are the ion
205 activity product of the dissolved constituents and K is the mineral solubility product in a
206 specific reaction, respectively, and the partial pressure of carbon dioxide by the Peng–
207 Robinson equation of state (Parkhurst and Appelo, 2013);
- 208 ii) a geothermal model based on multimineral equilibria.

209 Results were compared to previously published chemical and isotopic
210 geothermometers specific for sedimentary brines (Boschetti et al., 2015; Kharaka and
211 Mariner, 1989; Sanjuan et al., 2014). The calculated activity of the dissolved constituents was
212 also used to calculate the saturation index of a carbonate solid solution made of calcite,
213 magnesite, rhodochrosite, siderite and strontianite by EQ3/6 code, version 8 (Wolery and
214 Jarek, 2003).

215 The Geochemist's Workbench® code (GWB), version 7.0.6 (Bethke and Yeakel,
216 2008), was used to calculate the evaporation path of Cretaceous seawater using the React
217 tool, HMW thermodynamic database, and the main chemical composition of seawater during
218 that period (Bäbel and Schreiber, 2014). According to Bäbel and Schreiber (2014), a chloride
219 concentration of present-day seawater ($565 \text{ mmol kg}^{-1} \text{ H}_2\text{O}$) was taken as a reference; then
220 chloride concentration was charge-balanced, taking into account other main constituents and
221 $\text{pH} = 7.5$ (Hönisch et al., 2012), and a $\log\text{PCO}_2(\text{g}) = -3$ was settled during evaporation. This

222 latter corresponded to a mean concentration of 1000 ppmv of CO₂ in the Cretaceous
223 atmosphere (Hönisch et al., 2012; Wang et al., 2014).

224 Finally, activity diagrams using a thermodynamic database of the minerals and
225 dissolved constituents, recalculated at a pressure of 20 MPa, were plotted using the Act tool
226 of the GWB-code (Boschetti et al., 2016). The Rxn tool of the same code was also used to
227 check the thermodynamic equilibria of specific reactions.

228 **4. Results and Discussion**

229 The physicochemical and isotope parameters are reported in Table 1. The recalculated main
230 chemical composition in equivalents per liter of formation water from the southern region of
231 Iraq shows a Cl-Na composition. In particular, the Na/Cl equivalent ratios range span
232 between 0.77 and 0.91, with a mean of 0.83 ± 0.05 , which is similar to that of present-day
233 seawater (0.86). The Ca/(SO₄ + HCO₃) equivalent ratios of the brines are largely over 1, with
234 a mean of 44 ± 19 and a range between 15 and 78. Therefore, brines can be classified also as
235 Ca-Cl, according to Rosenthal (1997). The mean measured temperature of the water sampled
236 in the Mishrif Formation is 65 ± 2 °C (N = 28) (Awadh et al., 2018). Between the
237 investigated trace elements, the concentration of barium and manganese are higher in
238 Majnoon (5.43 and 4.47 mg/l, respectively) in comparison with the range of the samples from
239 the other oilfields (1.44-1.79 and 0.10-0.13 mg/l, respectively). All samples showed
240 supersaturation in calcite, aragonite, and dolomite (Table 2). Barite and anhydrite are also
241 supersaturated in all but one sample (RU287). Finally, waters are in equilibrium with
242 chalcedony and oversaturated in quartz.

243 *4.1 Chemical composition: diagenesis and geothermometry*

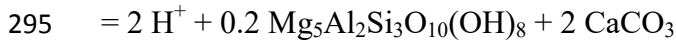
244 According to the previous published works on southern Iraq oilfields (Awadh et al., 2019a;
245 Awadh et al., 2018), the above described chemical ratios of Na/Cl = 0.83 ± 0.05 and Ca/(SO₄

246 + HCO₃) = 44 ± 19 are typical of marine origin formation waters that have undergone
247 chemical modification due to diagenesis (Boschetti et al., 2011; Rosenthal, 1997). The
248 Langelier–Ludwig and brine differentiation diagrams (Boschetti, 2011; Hounslow, 1995) of
249 Figure 2 depict the distinct composition of the oilfield brines in comparison with the local
250 shallow groundwater (Hamdan, 2017) and surface waters (Al-Mallah, 2014; ROPME, 2011;
251 Rzóska, 1980). Surface water (Ghalib and Almallah, 2017), water produced from crude oil
252 dehydration (Al-Shamkhani, 2013) or a mixture of both were used in the oilfields for water-
253 flooding purposes. In Figure 2A, the brine samples from this study and literature are grouped
254 in a narrow field, whereas in the brine differentiation plot (Figure 2B), brines are displaced
255 between the evaporation curve of Cretaceous seawater and the produced waters from
256 dehydrators (Al-Furaiji, 2016; Al-Shamkhani, 2013). Similarly to the Cretaceous formation
257 brines in Venezuela (Boschetti et al., 2016), most of the studied brines affected by diagenesis
258 show a Ca-excess and Na-deficit and seem to follow the typical Ca-Na exchange trend of the
259 so-called basinal fluid line (Davisson and Criss, 1996) (Figure 3). Sample RU287 was
260 probably affected by dolomitization and then by mixing with waters produced from crude
261 dehydrators (“produced water” field in Figure 3). The hottest (115°C) water sample from the
262 deeper Zubair sandstone indicates that the chemical effects of Ca-Na reactions (Al-Marsoumi
263 and Abdul-Wahab, 2005), most probably due to albitisation, are more pronounced at higher
264 temperatures (Figure 3A). Different from the Mishrif Formation, albite was found in the
265 Zubair Formation (Al-Ziayyir, 2018). Moreover, from a theoretical point of view, the
266 diagenetic effects could be more or less pronounced if the variability of the seawater
267 composition in the past was considered. If Cretaceous seawater is used as a reference instead
268 of present-day seawater, the oilfield brines are more clustered towards the axes **origin of**
269 **Figure 3B** (which coincides with the composition of less saline surface water) or towards the
270 “produced water” fields. The dolomitization process seems to have had a greater role in the

271 Ca-excess of the waters (Figure 3B). However, the geothermal modelling indicated in Figure
272 4, also suggests that calcite-dolomite equilibration occurred along with chalcedony instead of
273 quartz. In that diagram, all but one sample are clustered between 50 and 75°C isotherms, a
274 range that includes the temperatures of $64 \pm 5^\circ\text{C}$ (N = 9) and $64 \pm 7^\circ\text{C}$ (N = 5) obtained by
275 Mg-Li and chalcedony geothermometers, respectively — the latter corrected for dissolved
276 silica activity and pressure (Kharaka and Mariner, 1989) (Table 2). The exception is
277 represented by sample MJ20 (Majnoon oilfield), which is shifted towards the quartz-dolomite
278 (ordered) model (Figure 4) and shows the lowest temperature from quartz and chalcedony
279 from geothermometric equations (Table 2). Such an apparent convergence between quartz
280 and chalcedony is probably attributable to the greater depth and pressure in the MJ20
281 borehole (Table 1), conditions that could enhance simultaneous equilibria between the fluid
282 and the two mineral phases (Giggenbach, 1991). For the MJ20 sample, a mean value of
283 70.5°C between the geothermometric equations of quartz and chalcedony shows a good
284 agreement with the 68°C obtained from the Mg-Li geothermometer (Table 2).

285 Globally, the mean inferred temperature of the brines are quite similar to the mean
286 temperature measured at depth, confirming that the present-day borehole temperatures are not
287 so different from those reached during Neogene burial (Abeed et al., 2013). Sample MJ20 is
288 an exception, showing a temperature 10°C higher. This is probably due to the effect of
289 greater borehole depth (Fig. 1B) and pressure. The Majnoon oilfield had the highest
290 measured values (Table 1). Activity diagrams of Figures 5A and 5B show that Mg
291 concentration in the brine seems to be limited by dolomite and by chlorite. To check the
292 coexistence of the minerals, the thermodynamics of the following reaction have been
293 calculated (Supplementary File 1):





296 At P = 20 MPa and buffering conditions of Figure 5A, except for Mg which has been
297 buffered by clinocllore, $\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$, instead of dolomite. The above reaction is in
298 equilibria at 64°C using $\log[\text{Ca}^{2+}/(\text{H}^+)^2] = 11.11$ and $\log[\text{SiO}_2(\text{aq})] = -3.32$, which
299 corresponds to the mean activity values of all investigated samples (Supplementary File 1).
300 Therefore, this corroborates not only that dolomite and chlorite could **coexist** in the studied
301 basin, but also the temperature values obtained by geothermometers, in particular those by
302 Li-Mg and chalcedony equations (Table 2).

303 Figure 5 also shows that the Ca/Na ratio is probably controlled by smectite instead of
304 albite. The role of clays on the control of Na amount in solution by Ca-Na exchange or Na
305 adsorption could also explain the lower temperatures of 42 ± 6 °C obtained using the Na/Li
306 geothermometer (Kharaka and Mariner, 1989; Sanjuan et al., 2014) (Table 2). Similarly, the
307 values obtained from the boron isotope geothermometer **gave an** underestimation of the brine
308 temperature (Table 2). This could be due to a higher $\delta^{11}\text{B}$ value in Cretaceous seawater (up to
309 3‰ higher than the present; Lemarchand et al. 2002), together with a fractionation effect due
310 to evaporation up to halite saturation (approximately +4‰) (Vengosh et al. 1992). Actually,
311 by subtracting a value of 7‰ from the original values of the brines, a mean temperature of 64
312 ± 6 °C was obtained from the boron isotope geothermometric equation (Boschetti et al.,
313 2015), which matches with that obtained by the calcite-dolomite-chlorite-kaolinite equilibria.

314 4.2. Oxygen and hydrogen stable isotope ratios

315 The isotope composition value — i.e. not considering the salt effect according to Horita et al.
316 (1993) — of the studied formation water is similar to that of the Mishrif Formation values
317 from the Qatar oilfield values (Danquigny et al., 2005) (Figure 6). However, the calculation
318 of isotope activity due to the salt effect reveals a high enrichment in $\delta^2\text{H}$ (up to +8.3‰) and a

319 slight depletion in $\delta^{18}\text{O}$ (up to -0.3‰) in comparison to the analysed isotope composition. As
320 presented in Figure 6, the isotope composition of the formation waters from the samples
321 analyzed in this study fall close to the final part of the hook path derived from experimental
322 seawater evaporation (e.g. Gonfiantini et al., 2018), thus confirming the marine origin of
323 these samples, as previously inferred by the boron isotope (Awadh et al., 2018). It should be
324 noted that the experimental hook paths of the evaporated seawater are generally analysed
325 from salt pans without the addition of either new marine or meteoric water (i.e. closed
326 system) (Gonfiantini, 1965; Gonfiantini et al., 2018). This could be the reason why the
327 isotope activity values of the brine — i.e. considering the salt effect according to Horita et al.
328 (1993) — do not fall on the hook path (Figure 6). In Figure 6, the Iraq meteoric water line
329 (IMWL) and its prediction interval (parallel dashed lines with $\delta^2\text{H} \pm 10.3$ ‰ from IMWL)
330 were recalculated from the rainwater isotope data of Ali et al. (2015) using the error-in-
331 variable (EIV) regression method (Boschetti et al., 2019). The extrapolation of the best fit
332 line of the brine samples meets the prediction interval of the meteoric water line just between
333 rain waters collected from Başrah city (Fig. 1) plus other southern Iraq areas (Al-Kinani et
334 al., 2018; Ali et al., 2015; Jassem et al., 2018) and evaporated river samples from the Tigris
335 and Euphrates (Jassem et al., 2018) (Figure 6). Sample RU287 shows the highest contribution
336 of modern fresh water. It should also be remarked that, in comparison with other samples, the
337 RU287 brine displays barite supersaturation (Table 2), which is probably due to the effect of
338 mixing between brines and local water of meteoric origin or reinjected produced waters as a
339 consequence of the water flooding (Ghalib and Almallah, 2017; Sorbie and Mackay, 2000).
340 This is in line with the previously described chemical diagrams. On the opposite side, the
341 extrapolated best fit line of the isotope activity of the brines meets the hooked evaporation
342 path of seawater just on the top of the hump (Figure 6), which approximatively corresponds
343 to gypsum saturation (Holser, 1979; Knauth and Beeunas, 1986).

344 Evaporated seawater samples from present-day sabkha and lagoon environments (i.e.
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2 345 open systems) show $\delta^{18}\text{O}$ up to +6.5‰, which is similar to those determined in the formation
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4 346 brines of this study, but with $\delta^2\text{H}$ enrichment up to approximately +30‰ (McKenzie et al.,
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7 347 1980; Nadler and Magaritz, 1980; Robinson and Gunatilaka, 1991). Lower deuterium values
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10 348 are mainly due to mixing with evaporated surface waters or groundwater of meteoric origin
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12 349 (McKenzie et al., 1980; Robinson and Gunatilaka, 1991); whereas, flooding and mixing of
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14 350 evaporated solution with new seawater inputs could shift the composition back to the starting
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17 351 values (i.e. near V-SMOW) (Nadler and Magaritz, 1980) (Figure 6). A similar effect was
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19 352 observed in Miocene brines by comparison with $\delta^{18}\text{O}$ from coeval gypsum, with the
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22 353 exception of the formation waters affected by a positive $\delta^{18}\text{O}$ -shift as result of diagenetic
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24 354 water-rock interaction with limestones (Boschetti et al., 2011). In a similar way, and
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27 355 assuming that starting seawater during the Phanerozoic has remained isotopically similar to
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29 356 the present-day V-SMOW value (i.e. 0‰ both for oxygen and for hydrogen stable isotope
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32 357 ratios) (Gregory and Taylor Jr, 1981; Ryb and Eiler, 2018; Sessions, 2016), the ^{18}O
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34 358 enrichment of formation waters as observed in samples MJ20, ZB140, and R590 could be due
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37 359 to water–rock interaction. Therefore, water-rock interaction and dilution seem to be the main
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39 360 processes that affected in a significant manner the isotope composition of the studied brines.
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42 361 Such a diagenetic effect was also hypothesised for the Mishrif Formation in Qatar
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44 362 where limestones value ranges between $+24.4 \text{ ‰} < \delta^{18}\text{O} \text{ (V-SMOW)} < +27.4 \text{ ‰}$, formation
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47 363 brines $\delta^{18}\text{O}$ up to +5‰ (V-SMOW), and temperatures between 50 and 70°C have been
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50 364 measured (Deville de Periere, 2011). As the isotope values of the limestones from the same
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52 365 formation in southern Iraq are within the range of those measured in Qatar, i.e. $+25.2 \text{ ‰} <$
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54 366 $\delta^{18}\text{O} \text{ (V-SMOW)} < +27.4 \text{ ‰}$ (Taha and Abdullah, 2019), the diagenetic effect can be
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57 367 hypothesised also for this area. Considering a mean value $\delta^{18}\text{O}(\text{H}_2\text{O})_a = +3.9 \text{ ‰}$ (V-SMOW)
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59 368 for the brine samples that fall within the diagenetic arrow in Figure 6 and a mean value of
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369 $\delta^{18}\text{O}$ (limestones) equal to +26.5 ‰ (V-SMOW) of the Mishrif Formation in southern Iraq, it
370 is possible to calculate an oxygen isotope fractionation factor of $1000\ln\alpha$ (calcite-water) =
371 +22.3 ‰. This latter value corresponds to a temperature between 56°C (Kim and O'Neil,
372 1997) and 69°C (Zheng, 1999). Other isotope effects due to clays and crude are probably not
373 quantitatively important or less pronounced than the salt effect. Indeed, a fractionation
374 between water and hydrocarbons should generate in brines a shift towards $\delta^2\text{H}$ values higher
375 than seawater (e.g., Horita, 2009), but this is not the case (Figure 6). Furthermore, the amount
376 of clays minerals in the Mishrif Formation are probably insufficient to generate a significant
377 isotope effect on the $\delta^2\text{H}$ of the waters.

378 4.3. Strontium isotope ratio

379 The strontium isotope ratios of the four brine samples analysed are $0.707713 < {}^{87}\text{Sr}/{}^{86}\text{Sr} <$
380 0.707749 (WQ87, RU287, ZB140, R590), which corresponds to a marine strontium of late
381 Cenomanian–early Maastrichtian age (McArthur, 2010; McArthur et al., 2012); with the
382 sample at the Majnoon oilfield (MJ20) showing the highest value of 0.708043. The Mishrif
383 reservoir is Cenomanian–Turonian; therefore, the strontium isotope ratio should theoretically
384 not be greater than 0.707314 ± 0.000005 (McArthur, 2010; McArthur et al., 2012). The
385 higher strontium isotope ratios in formation waters could suggest a contribution of more
386 radiogenic strontium from injected waters when compared to the more saline and enriched
387 brines (Danquigny et al., 2005), but in this case the oxygen and hydrogen stable isotope ratios
388 are not less than the other samples. Moreover, it should be also noted that ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ values up
389 to 0.707869 have been detected in the brines from the Mishrif Formation in Qatar (Al Khalij
390 offshore field; Danquigny et al. 2005) and up to 0.70878 in the carbonate matrix of the coeval
391 Sarvak Formation in southern Iran (Hajikazemi et al., 2012). Such elevated values detected at
392 the disconformity surfaces of the formations are probably due to the contribution of meteoric
393 water during diagenesis (e.g., Hajikazemi et al. 2012). However, the combination of high

394 manganese and radiogenic strontium contributions to the limestones of the Sarvak Formation
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3 395 of southern Iran were also attributed to different sources: i) a Cenomanian-Turonian subaerial
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5 396 exposure; ii) diagenetic fluids; and iii) detritus (Navidtalab et al., 2016). Actually, all the
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7 397 inspected brines of this study are undersaturated with respect to pure rhodocrosite ($SI = -3.9 \pm$
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10 398 0.8), but in equilibrium with carbonate solid solution ($SI = -0.082 \pm 0.261$) (Table 2). In
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12 399 particular, despite its high Mn activity, the Majnoon brine MJ20 showed a slight
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14 400 undersaturation in that solid solution. Therefore, the higher Mn concentration (up to 4 mg/l)
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16 401 and radiogenic strontium at that brine could be acquired by limestone dissolution in a
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18 402 disconformity layers. Alternatively, as suggested by the lowest gypsum and anhydrite
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20 403 saturation indices of the Majnoon sample (Table 2), it cannot be excluded that there was a
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22 404 contribution of radiogenic strontium-rich sulphate minerals from Cambrian salt domes (up to
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24 405 0.7092) (McArthur et al., 2012). Salt domes characterise the fold settings in the oilfields of
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26 406 southern Iraq (Al-Ameri et al., 2011; Al-Mimar and Awadh, 2019). The doming triggered
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28 407 local uplift and emergence of paleo-exposure surfaces (Rahimpour-Bonab et al., 2013), thus
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30 408 the shallow back shoal/lagoonal depositional environment of Mishrif limestones at the
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32 409 Majnoon oilfield and the salt domes seem to be related (Aqrawi et al., 2010; Mahdi et al.,
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34 410 2013). Moreover, “hydrothermal fluids” with temperatures up to 80°C were hypothesized to
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36 411 form diagenetic cements (i.e., blocky calcite), dolomite and coarse crystalline pyrite during
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38 412 deeper burial of the Sarvak Formation (Hajikazemi et al., 2017). Therefore, the chemical,
39
40 413 thermal and isotopic anomalies of the Majnoon brine suggest that it is the hottest fluid
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42 414 probably related to the higher geothermal gradient of a deeper structure as the ZFF (Basilici
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44 415 et al., 2020; Bordenave, 2008; Bordenave and Hegre, 2010).

54 416 **5. Conclusions**

57 417 This paper presented the first data on isotope ratios of oxygen, hydrogen, and strontium of
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59 418 oilfield waters from southern Iraq, along with new trace element data and a reinterpretation of
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419 previous published chemistry. Processes like diagenesis and seawater evaporation that
420 typically occur in these fluids can be distinguished using classical ‘basinal fluid’ chemical
421 diagrams. Mishrif Formation waters are Cretaceous connate brines and the different chemical
422 composition of seawater of that period needs to be taken into account for a more correct
423 interpretation. The Ca-excess versus Na-deficit composition of these kinds of fluids are
424 usually explained by albitisation. However, it was verified by activity plots that in the Mishrif
425 limestone reservoir the Na/Ca exchange that occurs in brines is mainly due to water-smectite
426 equilibrium.

427 The values $\delta^2\text{H}$ and $\delta^{18}\text{O}$ obtained on selected samples show that oxygen isotope
428 composition of the brines was isotopically more affected by equilibria with limestone than
429 evaporation. The global effect of the water-rock interaction is an ^{18}O -enrichment of the
430 brines. Locally, dilution by present-day water of meteoric origin and shift towards the local
431 meteoric water line also detected, probably as consequence of water-flooding (Rumaila
432 South, sample RU287). Furthermore, it is also shown that isotope data cannot be separated
433 from the interpretation of the chemical composition of sedimentary brines. The contribution
434 of the salt effect on the stable isotope ratios of water molecules, i.e. $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$, needs
435 to be evaluated because this parameter could vary the results during fractionation processes
436 such as seawater evaporation and diagenesis. Hydrogen isotope ratios are probably more
437 affected by the salt effect than other fractionations. Furthermore, taking into account the salt
438 effect, the temperature range inferred from carbonate-water oxygen isotope ratio fractionation
439 is comparable to that obtained from the chemical geothermometers, i.e. between 50 and 75°C.
440 According to Abeed et al. (2013), these evaluations confirm that the present-day borehole
441 temperatures are not so different from those reached during Neogene burial.

442 More recent mixing processes such as water floods could be detected by a comparison
443 with the composition of the formation brine, waters produced from crude dehydrators, and

1 444 the local waters of meteoric origin. The strontium isotope ratio confirms the interaction of
2 445 Cretaceous limestone for most of the studied samples, suggesting a late Cenomanian–early
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4 446 Maastrichtian age, and an input of more radiogenic strontium in the Majnoon oilfield (MJ20
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7 447 sample). The brine sample from this latter oilfield showed a particular geochemical
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9 448 characteristic. Despite the lower temperature measured at the MJ20 borehole (60°C), the
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11 449 slightly higher temperature obtained by the Li-Mg, Na-Li and $\delta^{11}\text{B}$ geothermometers (up to
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13 450 74°C) is probably due to the deeper structure of that oilfield, which is closer to the ZFF. The
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15 451 more radiogenic strontium ratio at Majnoon could be related to: i) debris input in the
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17 452 limestone, which could explain also the high Mn content; or ii) interaction with local
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19 453 Cambrian sulphates. An inspection of additional samples, sulphur stable isotope ratio
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21 454 ($^{34}\text{S}/^{32}\text{S}$) and radiogenic isotope of the halogens (^{139}I , ^{36}Cl) could improve the knowledge of
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23 455 the past water flow events and clarify the relationship between the high Mn concentration /
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25 456 high radiogenic strontium in the Cretaceous limestones and the salt domes.
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46 **Captions**

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48 463 **Table 1** – Physicochemical parameters, major ion composition, trace elements concentration,
49 464 and isotopic results from Awadh et al. (2018) and this study.

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51 465 **Table 2** – Geothermometric results in Celsius degree (°C); mineral saturation indices (SI),
52 466 and carbon dioxide partial pressure as $\log\text{P}(\text{CO}_2)\text{g}$ obtained by PHREECI code, version 3,
53 467 along with Pitzer thermodynamic dataset at the measured temperature and water pressure
54 468 conditions (Table 1). EQ 3/6 code was also used to calculate the saturation indexes of
55 469 carbonates solid solution.
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58 470 **Figure 1** – A) Location map showing the studied oilfields at the Zubair zone, within the
59 471 southern part of the Mesopotamia plain and to the southwest of the Zagros Foredeep Fault
60 472 (ZFF); Stratigraphic correlation of the five oilfield wells penetrating four formations
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473 (Rumaila, Mishrif, Khasib, and Tanuma) in which there is a well from each oilfield (RU287
474 from Rumaila South, R590 from Rumaila North, WQ87 from West Qurna, MJ20 from
475 Majnoon, and ZB140 from Zubair oilfield); B) Typical section represents the stratigraphic
476 setting in the study area.

477 **Figure 2** – Langelier–Ludwig (A) and Brine Differentiation Plot (B) of the oilfield brines of
478 southern Iraq (Al-Mallah, 2014; Al-Marsoumi and Abdul-Wahab, 2005; Awadh et al., 2019b;
479 Awadh et al., 2018; Jamil, 1978) compared with shallow groundwater (Hamdan, 2017), Shatt
480 Al-Arab River (ROPME, 2011), Shatt Al-Basrah Canal, or ‘Main Drain’ (Al-Mallah, 2014)
481 and seawater. In both diagrams, concentration of the dissolved species are in equivalent/liter;
482 dashed ellipses depict the trend of the Tigris–Euphrates River system at Qurna and Shatt Al-
483 Arab River during the 60s (Rzóska, 1980). In (B), Mishrif Formation’s brine waters from
484 Awadh et al. (2018) are distinguished by black triangles; the five samples reprised in this
485 study are highlighted by white crosses. The brine data from other references (Al-Mallah,
486 2014; Al-Marsoumi and Abdul-Wahab, 2005; Awadh et al., 2019b; Jamil, 1978) are
487 represented by white triangles. Produced waters from hydrocarbon dehydrators are also
488 shown for comparison (dashed field) (Al-Furaiji, 2016; Al-Shamkhani, 2013). Arrows depict
489 possible mixing trends. In the inset, the original fields of the diagram along with evaporation
490 paths of present-day (Boschetti, 2011; Hounslow, 1995) and Cretaceous seawater (this study)
491 are shown. G and H depict the gypsum and halite saturation points, respectively.

492 **Figure 3** – $\text{Ca-excess} = 2 \times [\text{Ca}_{\text{meas}} - (\text{Ca}/\text{Cl})_{\text{SW}} \times \text{Cl}_{\text{meas}}]/40.08$ vs. $\text{Na-deficit} = [(\text{Na}/\text{Cl})_{\text{SW}} \times$
493 $\text{Cl}_{\text{meas}} - \text{Na}_{\text{meas}}] / 22.99$ diagram for oilfield waters from southern Iraq, where meas =
494 measured, SW = seawater and Ca, Na and Cl are elemental concentrations in mg/l (Davisson
495 and Criss, 1996). The 1Ca-2Na or 1Ca-1Na exchange arrows depict the possible paths of
496 formation fluids in sedimentary basins during plagioclase albitisation (Davisson and Criss,
497 1996). In (A) and (B) diagrams, present-day and Cretaceous seawater were used as SW-
498 composition, respectively. In both: light gray ellipse at the origin of the plot represents the
499 initial seawater composition (i.e. before evaporation), local groundwater and surface waters
500 composition; dashed and dot-dashed lines depict the evaporation paths of Cretaceous and
501 present-day seawaters, respectively. Other symbols and fields as in Figure 2.

502 **Figure 4** – Base-10 logarithm of silicium versus calcium/magnesium ratio diagram of the
503 Mishrif Formation’s brines from southern Iraq (molar concentration). Dashed curves depict
504 the simultaneous equilibria of calcite-dolomites plus quartz (light gray) or chacedony (black)
505 calculated by PHREEQCI code and pitzer thermodynamic dataset (Parkhurst and Appelo,
506 2013) at the mean pressure of the five samples (27.8 MPa; Table 1).

507 **Figure 5** – Activity plots for the system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$ at $P = 200$
508 bar and $50 < T < 75$ °C. In (A), the activity of dissolved silica has been fixed at the mean
509 value detected in the waters, i.e.: $\log[\text{SiO}_2(\text{aq})] = -3.32$, whereas in (B) it was buffered by
510 chalcedony. In both diagrams: water activity at $\log[\text{H}_2\text{O}] = -0.0855$ (mean value of the local
511 brines); aluminium buffered by kaolinite; magnesium and HCO_3^- buffered by dolomite and
512 calcite, respectively.

513 **Figure 6** – $\delta^2\text{H}(\text{H}_2\text{O})$ vs. $\delta^{18}\text{O}(\text{H}_2\text{O})$ diagram. Samples from this study are differentiated for
514 isotope composition (white-crossed gray triangles) and isotope activity (white-crossed black
515 triangles): the former represent analytical results of water samples after vacuum distillation
516 and IRMS; the latter represent isotope composition plus the theoretical salt effect (Horita et
517 al., 1993) (Table 1). Water isotope composition of brines from the Mishrif Formation in
518 Qatar are also shown for comparison (open triangles) (Danquigny et al., 2005). Dotted lines
519 depict the linear best fits of the two ways of representation of isotope ratios in brines.

520 Evaporated seawaters from a closed (Gonfiantini et al., 2018) and open (McKenzie et al.,
1 521 1980; Nadler and Magaritz, 1980; Robinson and Gunatilaka, 1991) system are shown for
2 522 comparison. The previous published data on isotope composition of the Arabian Gulf
3 523 seawater and its evaporated composition are depicted by the field with waves and forward-
4 524 back curved arrows, respectively (Bagheri et al., 2014; McKenzie et al., 1980; Robinson and
5 525 Gunatilaka, 1991; Yurtsever, 1994). Rainwater samples (drops) from southern Iraq (Al-
6 526 Kinani et al., 2018; Ali et al., 2015; Jassem et al., 2018) and northern Kuwait (Hadi et al.,
7 527 2016) are also shown for comparison. Tigris and Euphrates samples are represented by open
8 528 squares; samples out of the IMWL's (Iraq meteoric water line) prediction interval are
9 529 evaporated surface water samples (arrow with slope ~ 4.3) (Ali et al., 2015; Jassem et al.,
10 530 2018).

11 531 **Supplementary File 1** - Calculation of the thermodynamic equilibria by Rxn tool of The
12 532 Geochemist's Workbench® code (Bethke and Yeakel, 2008) and P = 20 MPa thermodynamic
13 533 dataset (Boschetti et al., 2016). To reduce the variables, the activity of calcium and hydrogen
14 534 was rewritten as log-ratio in the reaction and automatically rebalanced by the tool.

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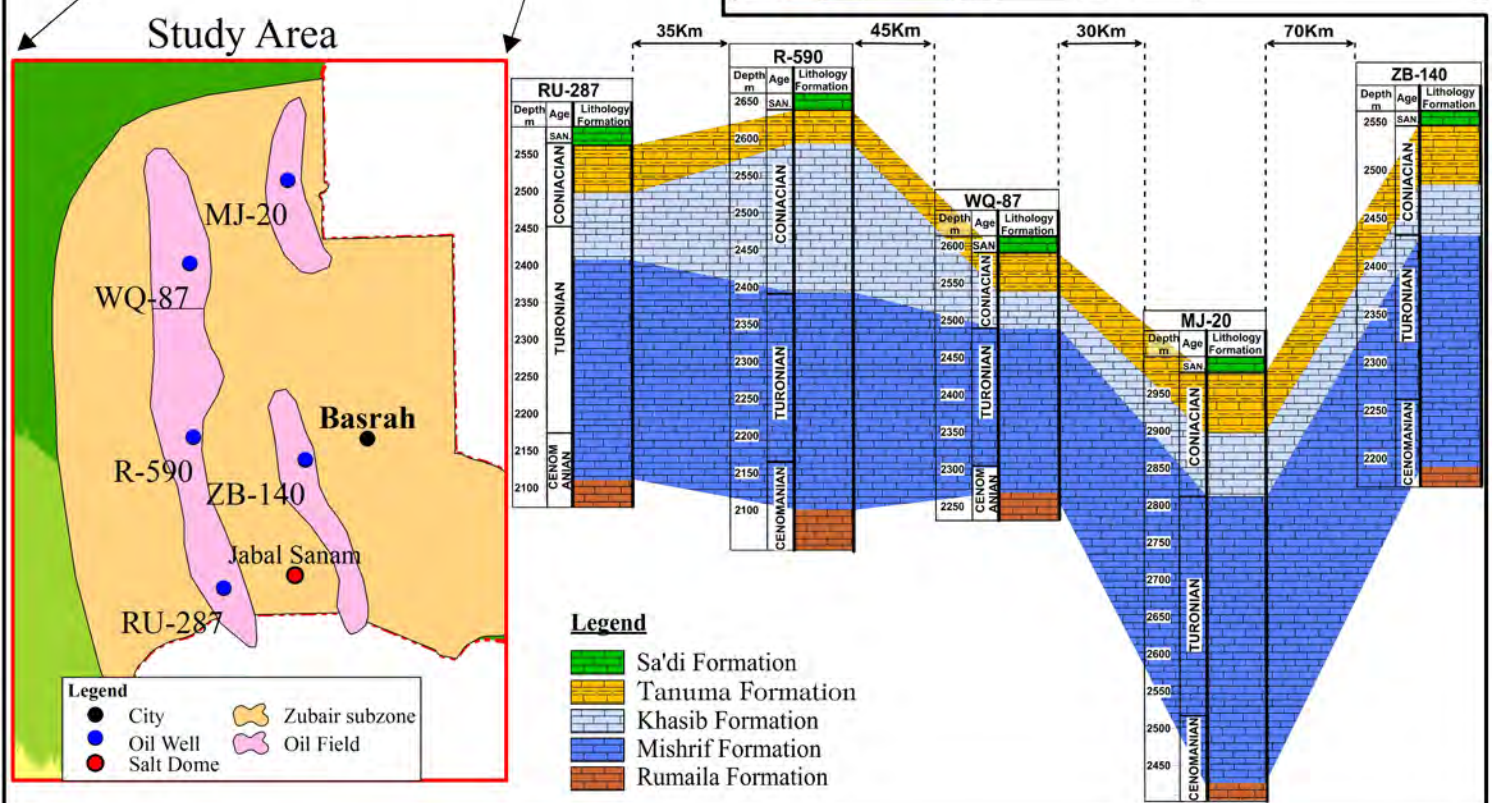
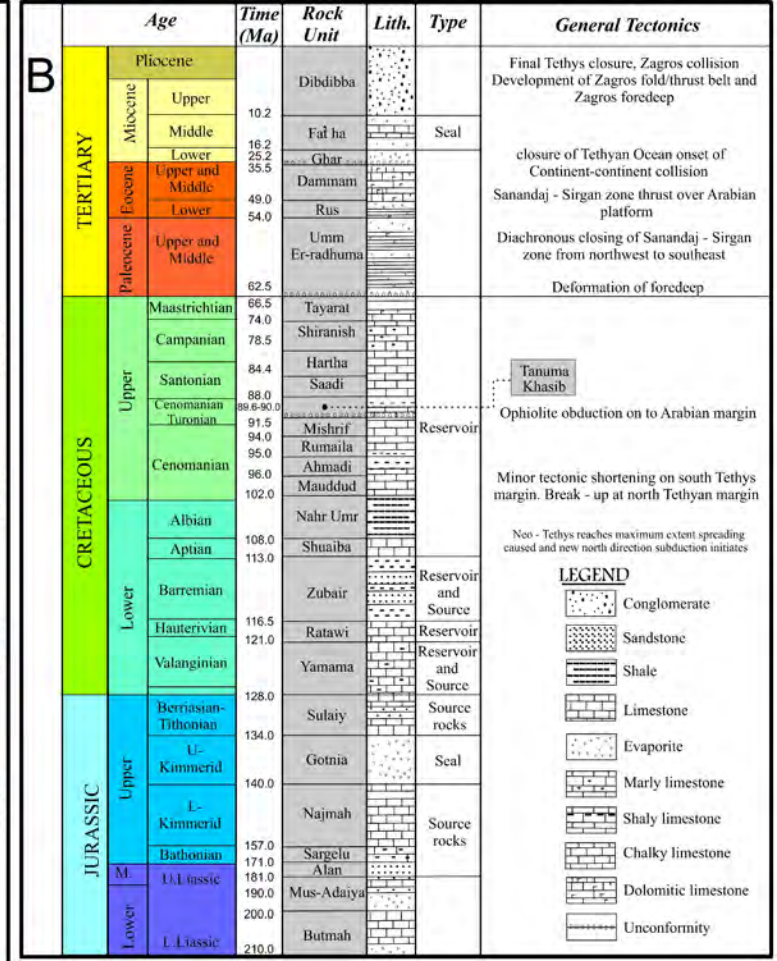
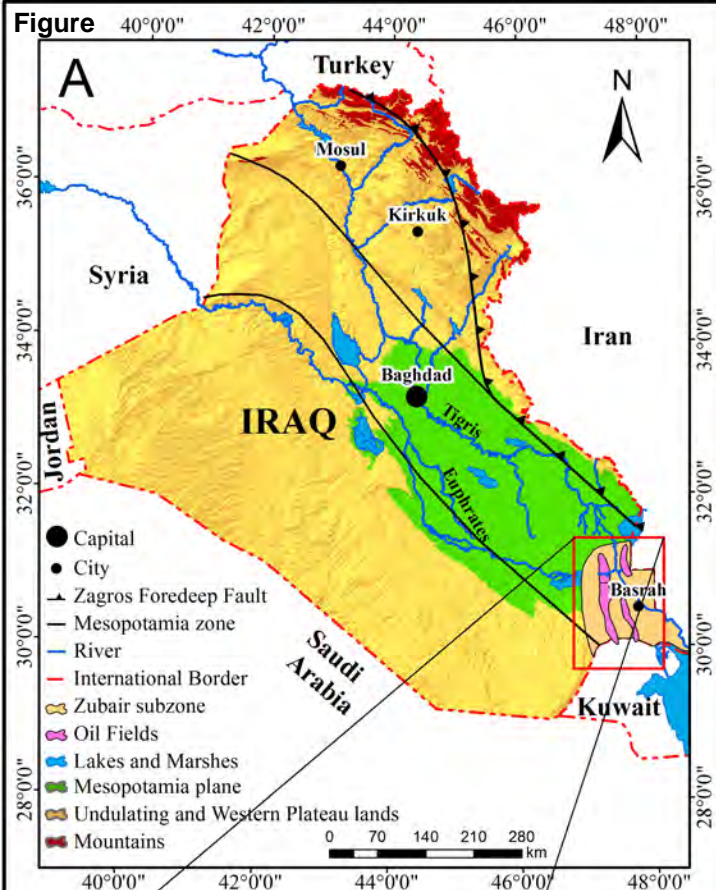
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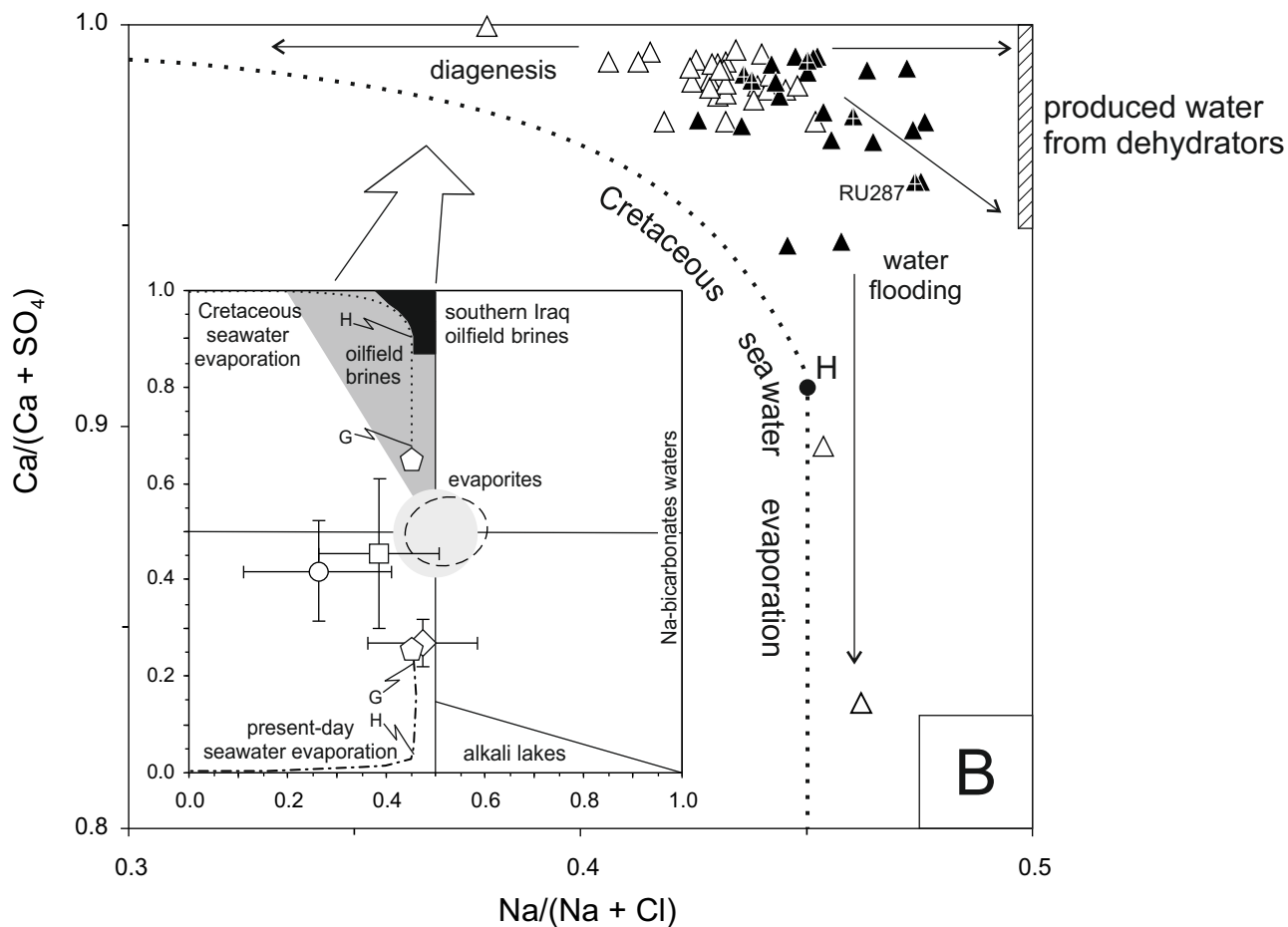
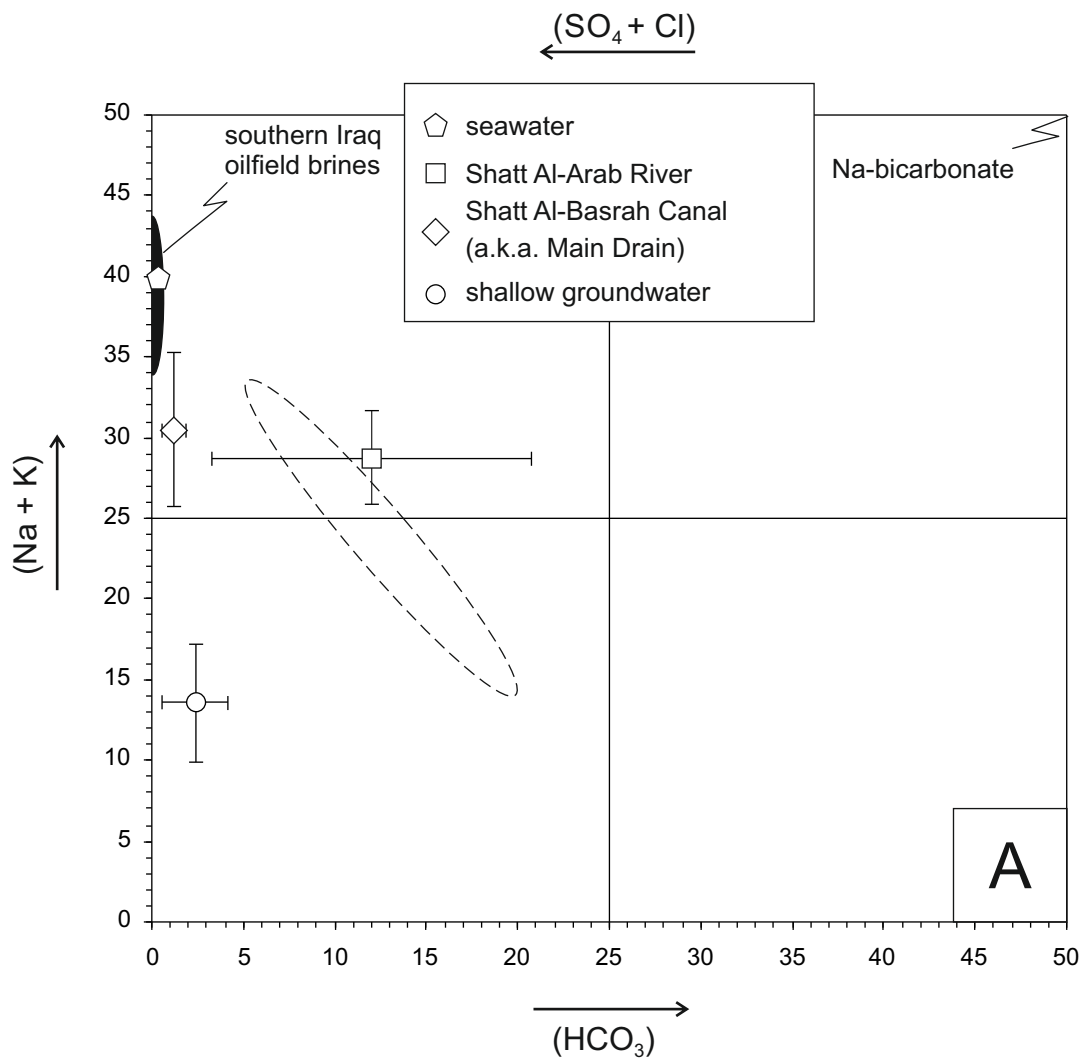
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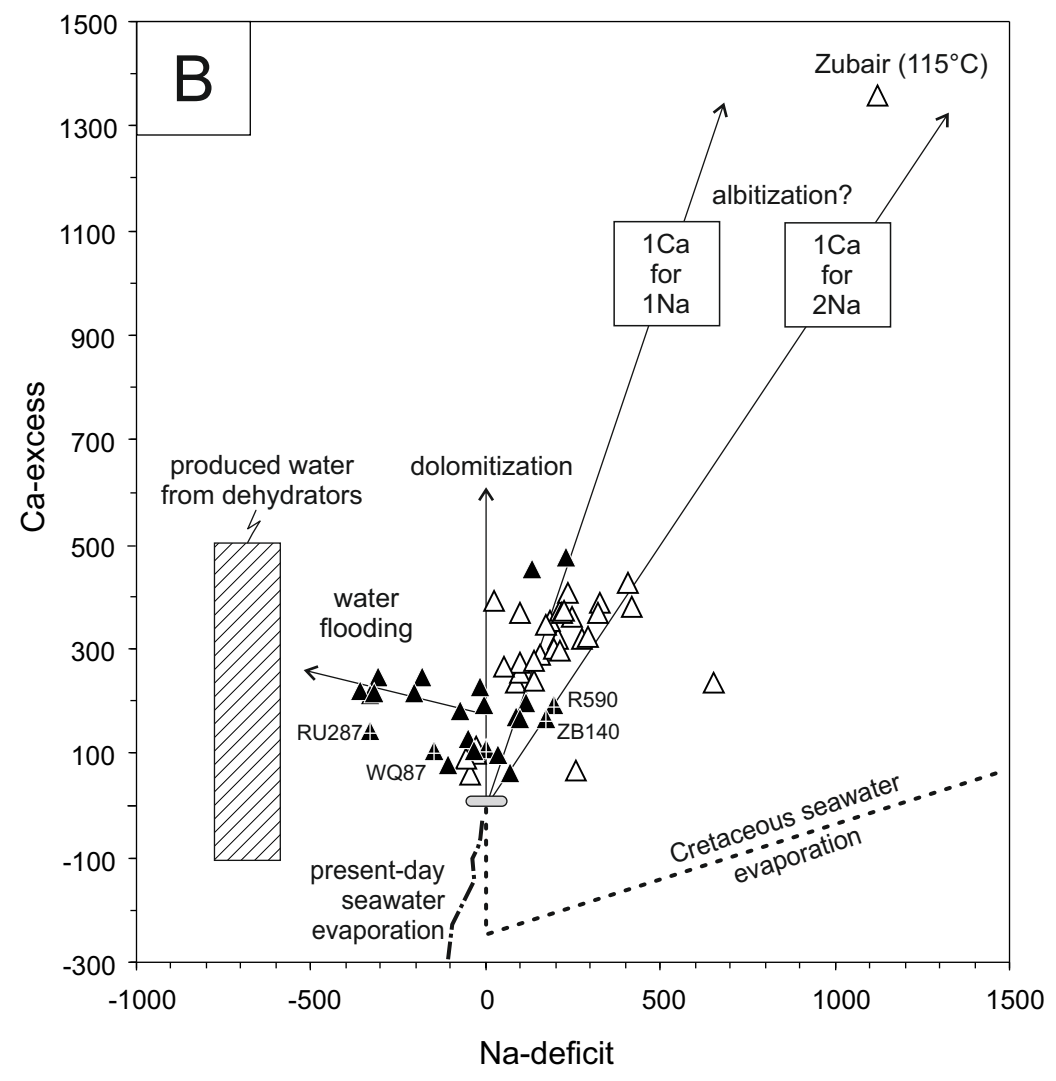
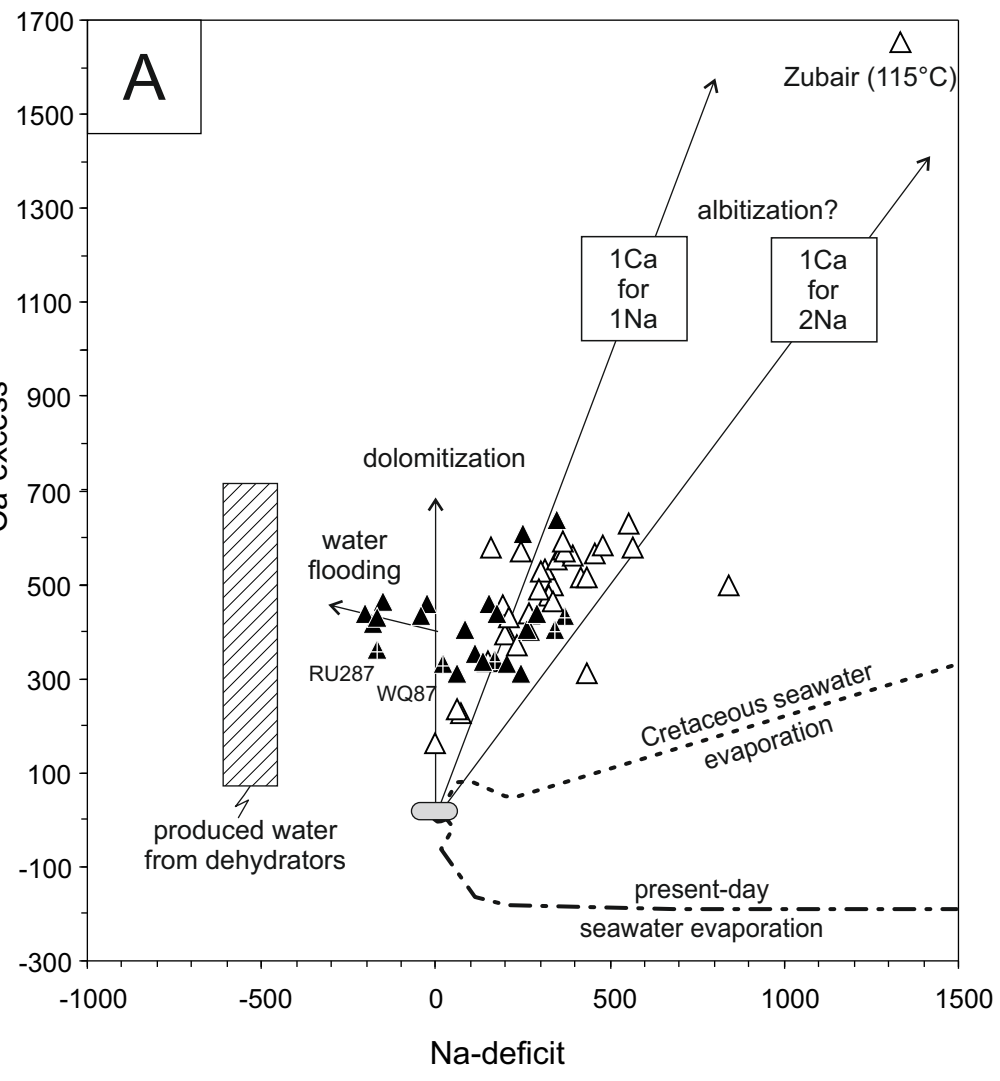
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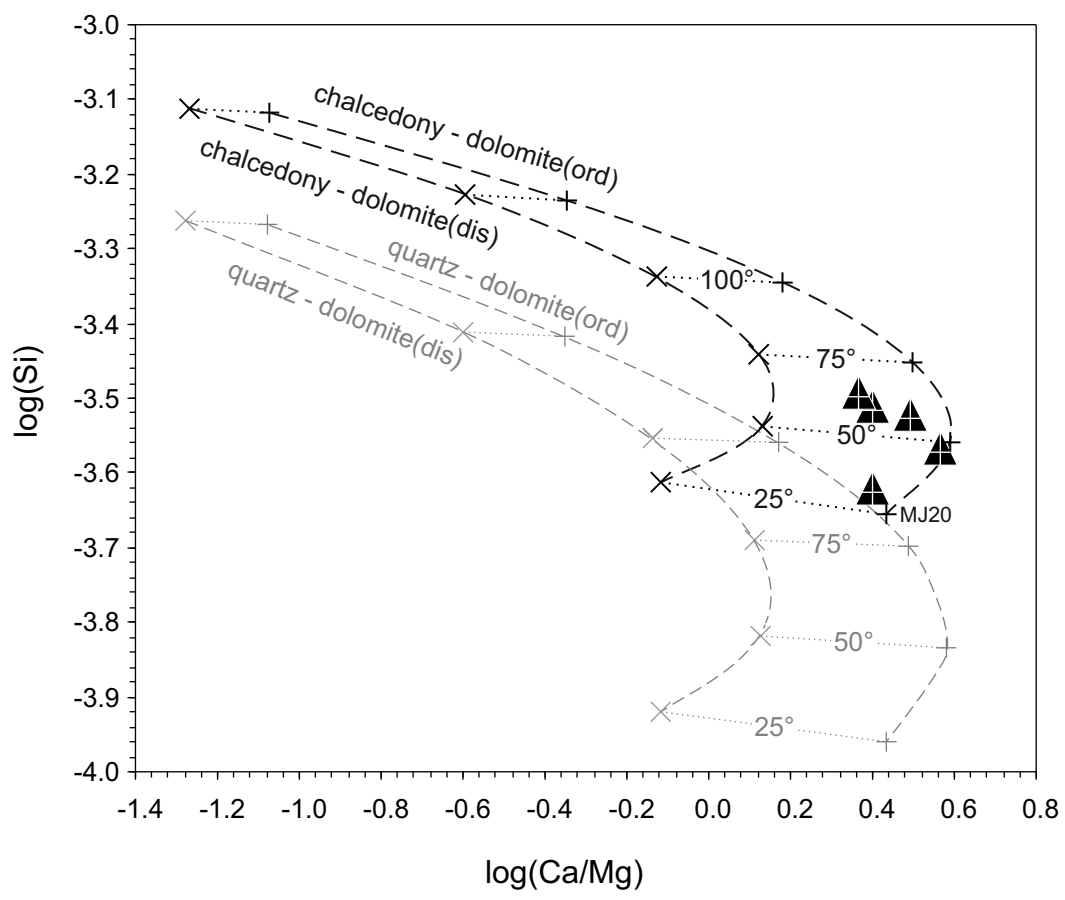


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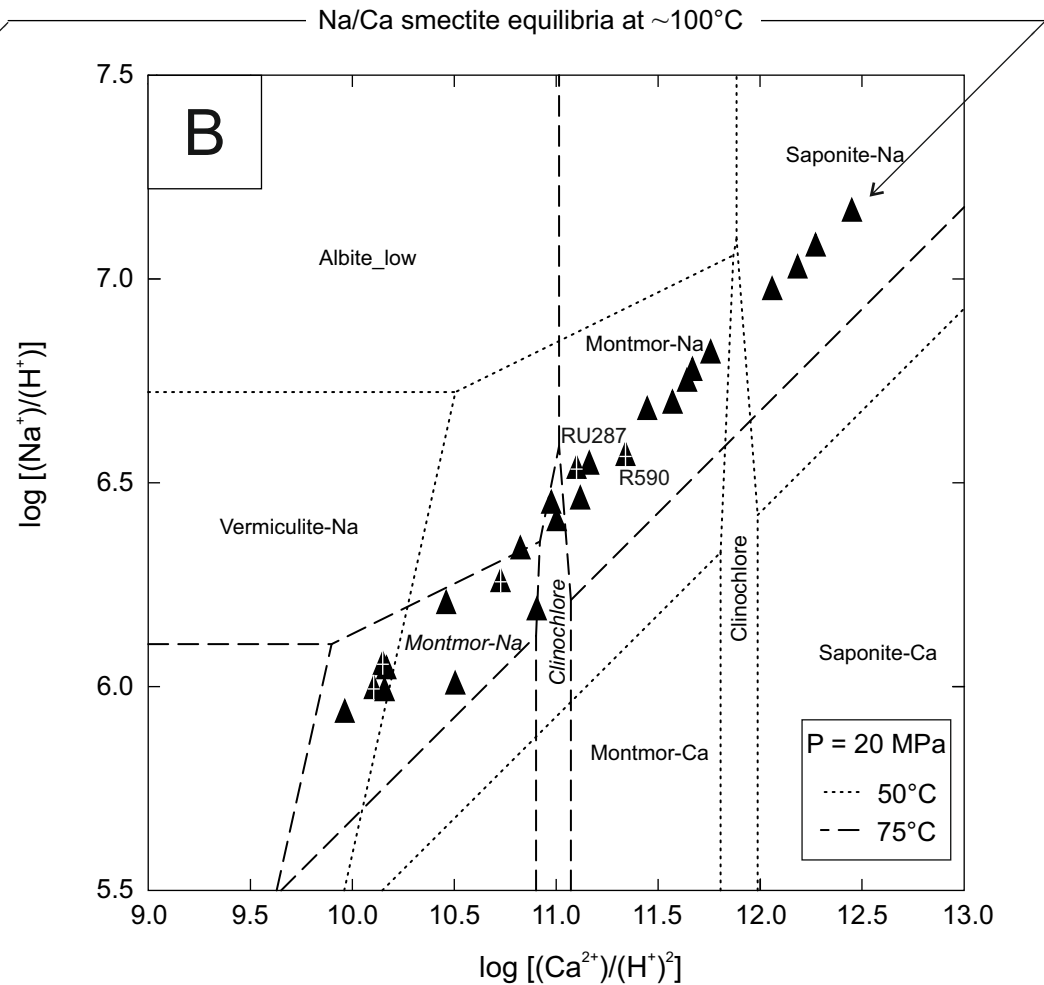
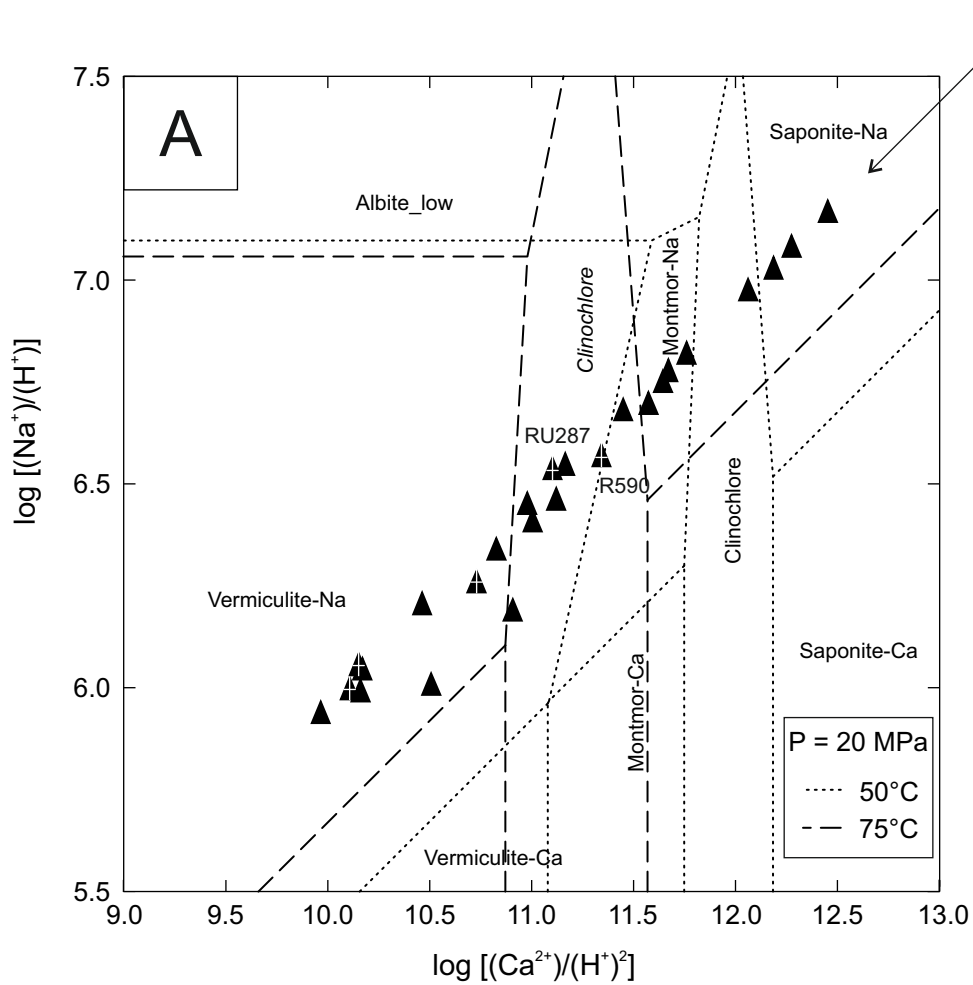
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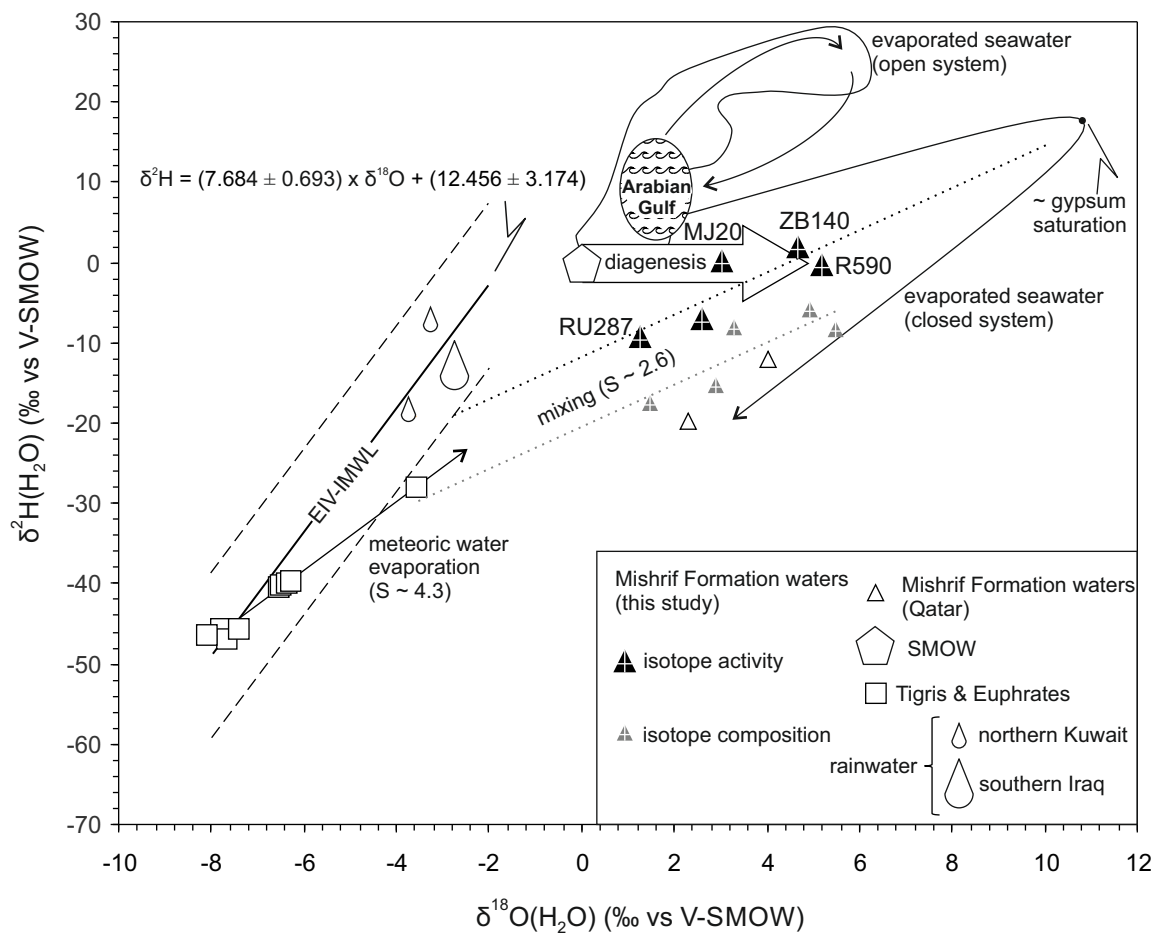


Table 1

borehole code	unit	RU287	R590	WQ87	MJ20	*ZB140	mean	±	std.dev.	CV %	N	reference
depth oil	m	2438	2682	2295	2836	2464	2412	±	118	5	28	Awadh et al. 2018
depth water	m	2700	2362	2316	2646	2377	2588	±	151	6	28	Awadh et al. 2018
oil pressure	kPa	29027	27717	25511	28613	27614	26977	±	1139	4	28	Awadh et al. 2018
water pressure	kPa	28751	30337	24759	32095	28269	28185	±	2292	8	28	Awadh et al. 2018
Temperature	°C	66	65	67	60	64	65	±	2	3	28	Awadh et al. 2018
pH		6.0	6.1	5.5	5.5	5.8	6.0	±	0.4	6	28	Awadh et al. 2018
Eh (S ^{-II} /S ^{VI} redox couple)	V	-	-0.165	-0.118	-0.120	-0.140	-0.144	±	0.023	-16	8	this study
TDS	mg/l	235500	255997	248000	249123	246798	243342.75	±	21229	9	28	Awadh et al. 2018
Na	mg/l	83500	77987	82413	80945	77994	78508	±	8561	11	28	Awadh et al. 2018
Ca	mg/l	10300	11980	9870	10105	11356	11417	±	1351	12	28	Awadh et al. 2018
Mg	mg/l	2000	2895	2587	2445	1880	2391	±	543	23	28	Awadh et al. 2018
K	mg/l	1750	2740	1800	2290	480	1709	±	767	45	28	Awadh et al. 2018
Cl	mg/l	143000	155341	148900	152410	154260	145857	±	14281	10	28	Awadh et al. 2018
SO ₄	mg/l	1000	360	550	213	385	595	±	347	58	28	Awadh et al. 2018
HCO ₃	mg/l	200	120	162	416	196	208	±	89	43	28	Awadh et al. 2018
sulfide as S	mg/l	-	144	68	64	86	103	±	38	37	8	this study
Li	mg/l	4.20	4.06	3.88	5.28	3.09	4.35	±	0.90	21	9	this study
Ba	mg/l	1.77	1.79	1.71	5.43	1.44	2.28	±	1.73	76	9	this study
Sr	mg/l	392	384	365	330	299	371	±	47	13	9	this study
Rb	mg/l	0.80	0.90	0.80	0.80	0.80	0.86	±	0.09	10	9	this study
Fe	mg/l	0.20	0.25	0.22	0.25	0.18	0.25	±	0.04	16	9	this study
Mn	mg/l	0.12	0.12	0.13	4.47	0.10	0.82	±	1.52	184	9	this study
SiO ₂	mg/l	15.5	17.0	16.5	13.0	15.0	15.4	±	1.6	10	5	this study
B	mg/l	31.1	28.1	30.8	21.9	24.9	27.4	±	3.9	14	5	Awadh et al. 2018
δ ¹¹ B	‰	35.8	35.9	35.8	33.7	35.6	35.4	±	0.9	3	5	Awadh et al. 2018
δ ¹⁸ O(H ₂ O)c	‰	1.47	5.48	2.89	3.30	4.94	3.6	±	1.6	45	5	this study
δ ² H(H ₂ O)c	‰	-17.4	-8.4	-15.3	-8.1	-5.8	-11.0	±	5.0	-46	5	this study
10 ³ lnΓ(¹⁸ O)	‰	-0.23	-0.29	-0.31	-0.26	-0.26	-0.27	±	0.03	-11	5	this study

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$10^3 \ln \Gamma(^2\text{H})$	‰	8.0	8.0	8.3	8.3	7.8	8.1 ± 0.2	3	5	this study
$\delta^{18}\text{O}(\text{H}_2\text{O})_a$	‰	1.24	5.19	2.58	3.04	4.68	3.35 ± 1.60	48	5	this study
$\delta^2\text{H}(\text{H}_2\text{O})_a$	‰	-9.40	-0.42	-6.99	0.18	1.93	-2.94 ± 4.95	-168	5	this study
$^{87}\text{Sr}/^{86}\text{Sr}$		0.707729	0.707749	0.707724	0.708043	0.707713	0.707792 ± 0.000141	0.02	5	this study

* boron concentration and stable isotope ratio from ZB142 borehole (*in italic*).

- not measured or not detected.

Table 2

	RU287	R590	WQ87	MJ20	ZB140	mean	±	std.dev.	CV %	N	
	geothermometers [°C]										reference
Li-Mg	65	61	61	68	59	64	±	5	8	9	Kharaka and Mariner 1989 (equation 19 in that work)
Li-Mg	64	59	59	68	57	63	±	6	9	9	Kharaka and Mariner 1989 (equation 18 in that work)
*Quartz	97	97	101	86	89	94	±	6	7	5	Kharaka and Mariner 1989 (table 6.4, equation 1 in that work)
*Chalcedony	67	66	71	55	58	64	±	7	10	5	Kharaka and Mariner 1989 (table 6.4, equation 2 in that work)
Na-Li	40	41	38	47	34	42	±	6	13	9	Kharaka and Mariner 1989 (table 6.4, equation 8 in that work)
Na-Li	40	41	39	48	34	42	±	6	13	9	Sanjuan et al. 2014 (equation 9 in that work)
δ ¹¹ B	19	18	19	32	20	21	±	6	27	5	Boschetti et al. 2015
†δ ¹¹ B-corrected	61	61	61	74	61	64	±	6	9	5	Boschetti et al. 2015; this work
B	73	70	72	62	66	68	±	5	7	5	Boschetti et al. 2016 (equation 3 in that work)
♣mean	66	63	65	68	60						
♣std.dev.	4	4	6	4	3						
	saturation indexes [SI = (logIAP)/(logK)]										code
calcite	1.1	1.0	0.58	0.87	0.92	1.1	±	0.4	34	28	PHREEQCI
aragonite	0.77	0.69	0.24	0.54	0.59	0.78	±	0.38	48	28	PHREEQCI
magnesite	-0.13	-0.27	-0.56	-0.40	-0.44	-0.18	±	0.33	-179	28	PHREEQCI
rhodochrosite	-4.04	-4.31	-4.60	-2.70	-4.31	-3.9	±	0.8	-22	9	PHREEQCI
siderite	-3.16	-3.44	-3.80	-3.40	-3.51	-3.4	±	0.3	-10	9	PHREEQCI
strontianite	-1.19	-1.49	-1.78	-1.55	-1.55	-1.4	±	0.4	-25	9	PHREEQCI
♣carbonates-SS	0.22	0.11	-0.44	-0.21	-0.089	-	±	0.261	-319	5	EQ3/6
dolomite-disordered	1.5	1.4	0.55	1.1	1.0	1.5	±	0.8	52	28	PHREEQCI
dolomite-ordered	1.9	1.8	0.95	1.5	1.4	1.9	±	0.8	41	28	PHREEQCI
quartz	0.30	0.30	0.33	0.25	0.24	0.28	±	0.03	12	5	PHREEQCI
chalcedony	-0.024	-	0.0088	-	-0.082	-	±	0.040	-100	5	PHREEQCI
anhydrite	0.094	-0.36	-0.13	-0.65	-0.33	-0.21	±	0.28	-134	28	PHREEQCI
gypsum	-0.15	-0.58	-0.39	-0.82	-0.54	-0.43	±	0.27	-63	28	PHREEQCI
barite	0.061	-0.42	-0.21	-	-0.43	-0.45	±	0.58	-129	9	PHREEQCI
halite	-0.44	-0.50	-0.41	-0.47	-0.53	-0.50	±	0.15	-31	28	PHREEQCI
logP(CO ₂)g	-0.45	-0.77	-0.050	0.352	-0.25	-0.46	±	0.41	-91	28	PHREEQCI

* the equation takes into account the effects of pressure and salinity on mineral solubility;

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- † before calculation, both the effect due to Cretaceous seawater (-3‰) and evaporation (-4‰) were subtracted from the values of the brine samples (Table 1);
- ♣ all geothermometric results were considered, except those from Na-Li equations and uncorrected $\delta^{11}\text{B}$. For MJ20, the standard deviation was calculated considering the central value of the temperature obtained by quartz and calcedony equation (see Fig. 4 and text for details).
- ♣ calcite, magnesite, siderite, strontianite and rhodocrosite solid solution.

Supplementary Material (for online publication only)

[Click here to download Supplementary Material \(for online publication only\): Supplementary File 1.docx](#)

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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