Major, minor element chemistry and oxygen and hydrogen isotopic compositions of Marun oil-field brines, SW Iran: Source history and economic potential

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Cation and anion concentrations and oxygen and hydrogen isotopic ratios of brines in the Asmari Formation (Oligocene–early Miocene) from the Marun oil field of southwest Iran were measured to identify the origin of these brines (e.g. salt dissolution vs. seawater evaporation) as well as the involvement of water–rock reaction processes in their evolution. Marun brines are characterized by having higher concentrations of calcium (11 000–20 000 mg/L), chlorine (120 000–160 000 mg/L) and bromide (600–1000 mg/L) compared to modern seawater. Samples are also enriched in ^{18}O relative to seawater, fall to the right of the Global Meteoric Water Line and local rain water, and plot close to the halite brine trajectory on the δD versus $\delta^{18}O$ diagram. Geochemical characteristics of Marun brines are inconsistent with a meteoric origin, but instead correspond to residual evaporated seawater modified by water–rock interaction, most significantly dolomitization. In addition, anhydrite precipitation or sulphate reduction appears to be important in chemical modification of the Marun brines, as indicated by lower sulphate contents relative to evaporated seawater. Extensive dolomitization, the presence of anhydrite nodules and high salinity fluid inclusions in the upper parts of the Asmari Formation fit a model whereby the Marun brines likely originated from the seepage reflux of concentrated seawater during the deposition of the overlying Gachsaran Formation evaporites in the Miocene. Copyright © 2010 John Wiley & Sons, Ltd.

1. INTRODUCTION

Subsurface brines are important for both scientific and economic purposes. The geochemistry of brines is frequently used to study the brines' origin and evolution (Stueber and Walter, 1991; Hanor, 2001; Lowenstein *et al.*, 2003; McIntosh and Walter, 2005; Hanor and McIntosh, 2006; Kharaka *et al.*, 2006; Lowenstein and Risacher, 2009), also fingerprint formation waters in petroleum production and exploration (Wittrup *et al.*, 1987; Wittrup and Kyser, 1990; Rostron and Holmden, 2000), and to evaluate the flow path history and trapping of associated oil (Tóth, 1987; Verweij, 1993; Dahlberg, 1994; Hunt, 1996). In terms of economic importance, brines are used as sources of industrial minerals and chemical production (e.g. Hitchon and Holter, 1971; Ober, 2001; Rostron *et al.*, 2002).

Brines with high concentrations of calcium and sodium are found in various geological and geographical occurrences in Iran including brines associated with small oil springs in the north, and large oil fields in the south-southwest of Iran (Kaghaz-chi, 2000; Najafzadeh, 2000; Majlesi, 2001). In northern Iran geochemical studies of brines have revealed economic concentrations of iodine (65 ppm), 1120 times higher than that of seawater (Khajeh *et al.*, 2007). However, no detailed studies on the economic potential, chemical properties and the source of the oil-field brines in southern Iran have yet been performed.

The origin of brines (halite dissolution vs. seawater evaporation), the extent of chemical modification (e.g. water–rock interaction) and their migration history (e.g. *in situ* seawater evaporation or seepage from enclosing strata) are internationally significant problems in studying the

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genesis of oil-field brines. Thus, the objective of this paper is to present the chemistry of brines from the Asmari Formation from the Marun oil field in Iran to better understand the origin and evolutionary history of the brines and to evaluate their economic potential. To the authors' knowledge these represent the first published analyses from the second largest oil reservoir (Nehring, 1978) in the country.

2. GEOLOGY

The Marun oil field is located within an asymmetrical NW–SE trending anticline in southern Iran, within the Zagros Fold Belt (Figure 1). The Zagros Fold Belt was created as the consequence of Neo-Tethys closure and the collision of the Afro-Arabian continental lithosphere with the Iranian plates, whose convergence started in Late Cretaceous, accelerated during the late Miocene and Pliocene and continued up to the present day (Ricou, 1974; Berberian and King, 1981; Alavi, 2004; Stöcklin, 1968;). The Zagros Fold Belt consists of a package of folded and faulted rocks composed of 4–7 km of mainly Palaeozoic and Mesozoic successions overlain by 3–5 km of Cenozoic siliciclastic and carbonate rocks and resting on metamorphosed Proterozoic Pan-Africa basement (Brown and Jackson, 1960; Agar, 1987; Husseini, 1989). The resulting folding and deformation during successive Alpine orogenic pulses in the Zagros Fold Belt has also created large oil traps (Bordenave and Hegre, 2005; Wennberg et al., 2006), including that of the Marun oil traps.

There are three main elements (Figure 1) of the petroleum accumulation for the Marun oil field: the oil source (Pabdeh Formation), oil reservoir (Asmari Formation) and the seal (Gachsaran Formation). The Pabdeh Formation (Eocene) consists of about 800 m of thin-bedded, deep marine hemipelagic–pelagic calcareous shale, marl and limestone with subordinate argillaceous limestone (Alavi, 2004). This formation is very enriched in organic matter in some places and is known as a source rock for oil fields in the Zagros area (Kamali and Rezaee, 2003). Overlying the Pabdeh Formation and hosting the oil and brine in the Marun field is the Asmari Formation (Oligo-Miocene), the most important oil reservoir in SW Iran. It consists of approximately 400 m of limestone (grainstone, packestone and wackestone) and dolostone with subordinate intervals of sandstone and shale (Ehrenberg et al., 2006; Ahmadhadi et al., 2007; Jafarzadeh and Hosseini-Barzi, 2008). According to Horbury et al. (2004) and Pickard et al. (2005), the Asmari Formation in the Marun field is characterized by siliciclastic influx while it is dominated by carbonates in other locations. Dolomitization is also important at Marun field and is generally more extensive in the upper part of the Asmari reservoir (Aqrawi et al., 2006). In the Marun area, the Asmari
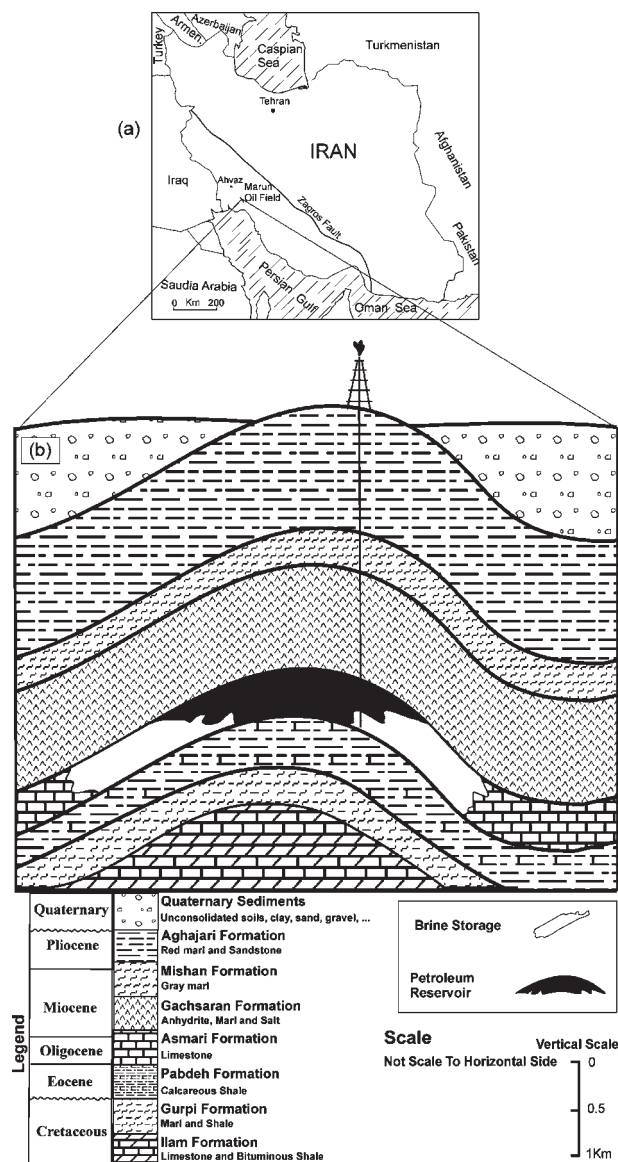

Figure 1. Schematic map showing the location of the Marun oil field (**a**) and the stratigraphy of the study area (**b**). The Marun oil field is hosted in the Asmari Formation (modified from Motiee, 1995; Alavi, 2004; Rudkiewicz et al., 2007).

Formation was deposited from Oligocene to early Miocene on a tropical platform, and in a NW–SE trending basin in the foreland of the Zagros orogenic belt (Sepehr and Cosgrove, 2004; Ehrenberg et al., 2006). Asmari Formation deposition was followed by the deposition of the Gachsaran evaporites (Miocene) which form a regional seal, and may have resulted from either the tectonic partitioning of the platform into sub-basins with restricted water circulation (Beydoun et al., 1992; Aqrawi, 1993; Bahadori and Koyi, 2004) or deposition in very shallow lagoon and sabkha environment in arid conditions (Gill and Ala, 1972; Motiee, 1995). The Gachsaran Formation (Figure 1) consists of multiple sequences of variable thickness and lithology including

evaporites, shale, marl, limestone and sandstone (Alavi, 2004). The cyclic deposition of the Gachsaran Formation in closed sub-basins implies their episodic subsidence (Bahadori and Koyi, 2004). Because of abundant evaporites and thus low permeability, the Ghachsaran Formation forms the caprock at many important oil fields including Marun.

3. SAMPLING AND ANALYTICAL METHODS

Brine samples were collected from three producing oil wells at depths of 3500–4000 m below sea level, in the central, east and western parts of the Marun oil field. Three additional samples were also used: one from a pool into which brines are poured, a nearby river and the Ahvaz rain station. The pH, Eh and temperature of the brines were measured at the site of sampling. Samples were filtered using standard 0.45 μm size Durapore syringe filters and splits were taken for anion, cation and stable isotope analyses. The splits for ICP were acidified with 3× distilled nitric acid (2.8 N) to lower the pH to approximately 1. The concentrations of the dissolved major and trace elements were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), respectively, through a commercial laboratory (Edmonton, Alberta). The protocol was APHA 3120B and USEPA ICP-MS 200. 8. Relative errors for the major and most trace elements do not exceed 5% ($\pm 1\sigma$) based on repeat runs and intermethod comparisons. Concentrations of Cl, Br, Na and I were determined by neutron activation analysis (NAA) at the SLOWPOKE Nuclear Reactor Facility, University of Alberta. Errors of the NAA determinations are 3% or less ($\pm 1\sigma$). Isotopic composition ($\delta^{18}O$ and δD) of samples was measured using a Gasbench and a DeltaPlus XP isotope ratio mass spectrometer (ThermoFinnigan, Germany) in the G.G. Hatch stable isotope laboratory at the University of Ottawa. Analytical precision for the $\delta^{18}O$ and δD of the water was ± 0.15 and ± 0.5‰, respectively.

4. RESULTS

Results of the analyses for the samples are shown (Table 1). Total dissolved solids (TDS) of the studied samples are

Table 1. Total dissolved solids (TDS), anion and cation concentration (mg/L) and oxygen and hydrogen isotopic compositions of the Marun oil-field brines

Sample	07MNA01/02	07MNA19/20	07MNA25/26	07MNA31/32	River water	Rain water-1	Rain water-2
pH	5.9	6.2	6.1	6.5			
Eh	80	78	72	44			
Temp (°C)	35	49	64	43			
Alkalinity		1240	1190	1350			
TDS	222 277	253 328	230 841	199 682			
As	1.13	1.43	1.22	0.89			
Ba	9.2	3.7	7.8	6.8			
B	146	117	120	127			
Br	781	980	830	574			
Ca	17 000	19 900	17 000	11 300			
Cl	134 100	155 700	141 000	120 900			
I	21.0	22.3	26.4	28.5			
Fe	67.8	16	38.2	23.7			
Pb	0.02	0.04	0.02	0.03			
Li	12.6	11.8	12.4	12.8			
Mg	1900	2610	2000	1400			
Mn	3.2	2	2.8	2.8			
Ni	0.14	0.17	0.17	0.16			
K	1600	1600	1600	1600			
Se	0.03	0.12	0.15	0.25			
Si	20	10	10	10			
Na	65 400	71 000	67 000	63 500			
Sr	1100	1240	1060	971			
S*	90	90	100	100			
Ta	0.027	0.014	0.028	0.026			
Zn	2.7	6.3	3.6	0.5			
δD_{SMOW}	−9.01	−2	−8	−3	−22	18.5	17
$\delta^{18}O_{SMOW}$	8.31	8	8	9	−5	1.6	1

For the nearby river and rain waters, only isotopic ratios have been measured.
S = Sulphur.

higher than 150 000 mg/L. The concentration of elements indicates that the Marun brines are enriched in Na + K, Ca and Cl and are thus considered Na–Ca–Cl-type brines (Lowenstein and Timofeeff, 2008).

Abundances of cations and anions in brines from the Marun oil-field relative to the average content of evaporated modern seawater are plotted in Figure 2. To calculate data for Figure 2, first the Cl concentration for each sample was divided by the average Cl concentration in seawater (i.e. 19 000 mg/L) to reach the concentration factor. The concentration in seawater of each element was multiplied by this concentration factor to obtain the concentration of elements in evaporated seawater. Marun data were then normalized to the evaporated seawater by dividing the concentration of elements in each sample to that of the evaporated seawater calculated in the last stage. It can be seen in Figure 2, calcium and Sr have higher concentrations in the Marun brines than in concentrated seawater. Marun brines have lower SO_4 compared to concentrated modern seawater (Figure 2), assuming all S is present as SO_4 and that no H_2S is present, as observed in the field. Iodine is concentrated while Si is depleted in the Marun brines with respect to concentrated modern seawater (Figure 2). The average Br concentrations in the Marun brines (790 mg/L) are approximately 1.6 times the concentration of this element in evaporated seawater ($\sim$480 mg/L). On the log Cl versus log Br diagram (Figure 3), the chemical composition of the studied brine plots close to the seawater evaporation trajectory (SET) and away from saturation with halite.

Compositions of $\delta^{18}O_{SMOW}$ and δD_{SMOW} in the Marun oil-field brines range between +7.74 to +8.31 and −2.25 to −9.01‰, respectively. These data fall to the right of the
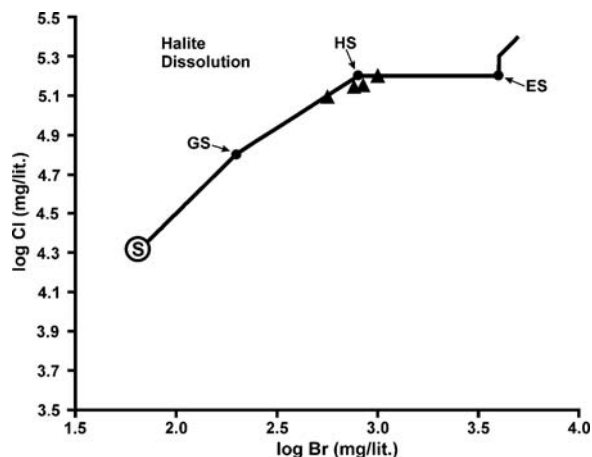

Figure 3. Log Cl versus log Br diagram showing the position of Marun brine samples (filled triangles) on the seawater evaporation trend line (Carpenter, 1978). S = seawater, GS = Gypsum saturation, HS = Halite saturation, ES = Epsomite saturation.

Global Meteoric Water Line (GMWL) as well as local rain water, and close to the halite brine trajectory (Figure 4). The oxygen and hydrogen isotopic ratios for the local river water plot close to the GMWL (Figure 4).

5. DISCUSSION

5.1. Seawater evaporation versus halite dissolution

Of particular interest in the study of brines is the origin of salinities higher than that of seawater. Hypotheses for the
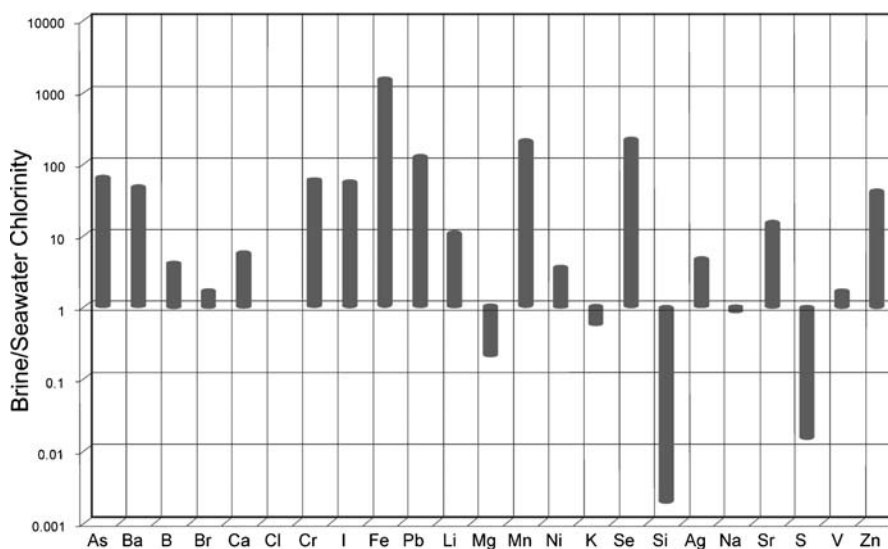

Figure 2. Elemental patterns of Marun oil-field brines normalized to seawater chlorinity (McCaffrey *et al.*, 1987).
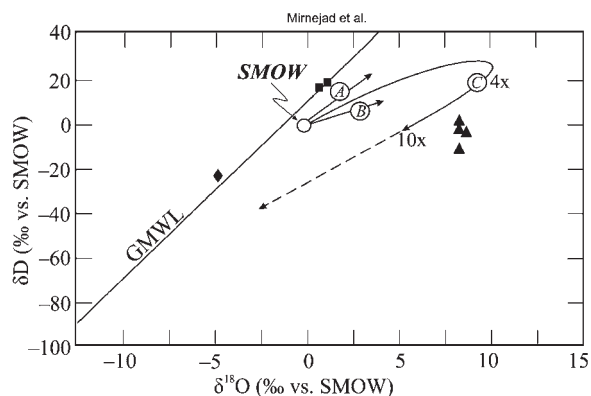
Figure 4. Marun oil-field brines (filled triangles) plot close to the trajectory line of evaporated seawater (Holser, 1979) and to the right of GMWL (Global Meteoric Water Line) on the δD versus δ^{18}O diagram. Local river water = filled diamond; local rain water = filled squares. Diagram after Knauth and Beeunas (1986). Curves A and B show initial evaporation under humid and arid conditions, respectively. Curve C is estimation of evaporating seawater through a concentration of 10× (Holser, 1979).
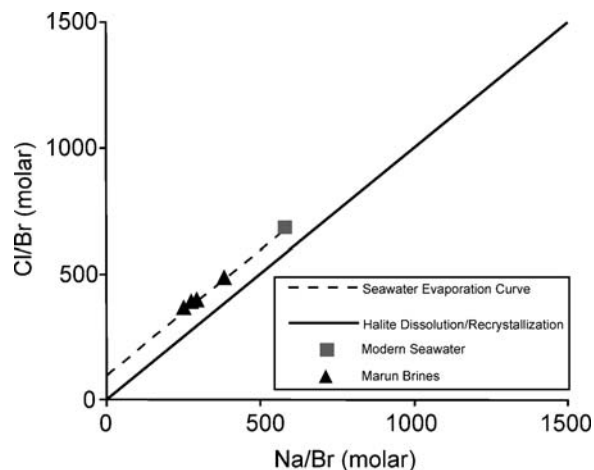

Figure 5. Marun oil-field brines (filled triangles) overlap the seawater evaporation trend line on the Cl/Br versus Na/Br diagram. Halite dissolution line and seawater curve after Walter *et al.* (1990).

source of high salinity formation water include salt dissolution (Land and Prezbindowski, 1981; Hanor and McIntosh, 2006; Schijf, 2007), and the burial of evapo-concentrated seawater (Carpenter, 1978; Lowenstein and Timofeeff, 2008).

Seawater dissolution of salt cannot be considered likely for Marun brines because the position of the Marun brines on the log Cl versus log Br diagram (Figure 3) suggests that the brines were derived from seawater by evaporation that proceeded well into the gypsum stability field and reached near the stage of halite precipitation (McCaffrey *et al.*, 1987). This indicates that the Marun brines developed during advanced stages of evaporation of seawater (Figure 3). Marun brines also plot to the left of the halite dissolution line and overlap the seawater evaporation curve on the Cl/Br versus Na/Br (molar ratios) diagram (Figure 5), suggesting that the salinity in these samples did not originate from dissolution of halite. The position of the data on the δD and δ^{18}O diagram (Figure 4) show that the Marun brines are enriched in ^{18}O relative to standard mid-ocean water (SMOW) and appear to be seawater concentrated at least 8 times by evaporation. This is also supported by the Br concentrations in the Marun brines (574–980 mg/L) which is 9–15 times more concentrated relative to the seawater Br (67 mg/L). According to Holser (1979) and Knauth and Beeunas (1986), D and ^{18}O in seawater are enriched progressively during evaporation. However, once seawater is concentrated to four times (and under certain conditions of humidity and chemical composition), both δD and δ^{18}O values of saline solutions define a 'hook' and reverse towards lower values (Sharp, 2005). Although processes such as exchange with hydrous minerals, loss of hydrogen-bearing gases (e.g. CH$_4$), and diffusion can increase the δD values of the water (Coplen and Hanshaw, 1973), it seems that

the latter processes were not influential in changing the hydrogen isotopic composition of the Marun brines because δD is not significantly different than the original seawater. With respect to high δ^{18}O values, it is possible that water–rock interaction that leads to evolved ^{18}O and little evolved D could also produce the trend for Marun brines as shown in Figure 4. As it is discussed in the next section, dolomitization of limestone was the likely water–rock interaction dominated in the Marun brines and such a process could have also created the observed O and D isotope values in the studied samples.

5.2. Diagenetic reactions

In addition to seawater evaporation, diagenetic brine–rock interactions (e.g. dolomitization and sulphate reduction/precipitation of anhydrite) can be important in controlling the chemistry of brines (Carpenter, 1978; Land and Prezbindowski, 1981; Spencer, 1987; Kharaka and Hanor, 2004). In a review of the chemistry of various basinal brines from the USA, Lowenstein and Timofeeff (2008) have shown that regardless of the age, host rock and chemistry of the original seawater, sulphate, Mg and K levels in basinal brines are below the concentrations expected from evaporation of seawater, and thus diagenetic brine–rock reactions seem important in controlling the chemical composition of basinal brines. Considering the chemical deviations of the Marun brines from the modern evaporated seawater (Figure 2), it is quite likely that water–rock interactions have played some role in modifying the chemical composition of the former.

Figure 6 shows ion–ion compositional plots of the Marun brines as well as the major ion evaporation paths of modern seawater. Marun brines show enrichments in Ca and
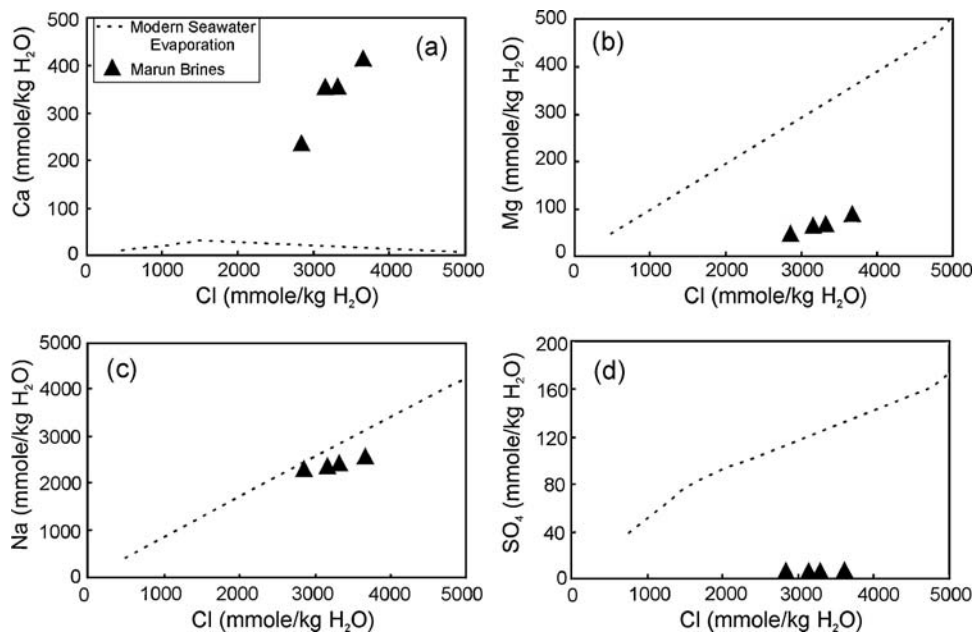
Figure 6. Concentrations of (**a**) Ca, (**b**) Mg, (**c**) Na, and (**d**) SO_4 versus Cl in the Marun brines (filled triangles). Evaporation pathway of modern seawater, obtained from Lowenstein (personal communications).

depletions in Mg compared to those predicted by simulated evaporation of modern seawater (Figure 6a and b). Although albitization of plagioclase has been invoked as a process to explain Ca enrichment in brines (Kharaka and Hanor, 2004), the lack of significant Na depletion in the Marun brines relative to the modern seawater paths on the Na versus Cl plot (Figure 6c) rules out albitization in the genesis of Marun brines. Dolomitization of limestone and precipitation of dolomite cement during burial can lead to excess Ca in brines as well as Mg loss from brines (Carpenter, 1978; Hardie, 1987). Michael *et al.* (2003) attributed the lower Mg and higher Ca contents of the brines in Alberta, Canada, relative to the evaporated seawater to the dolomitization process. The incorporation of Mg into the calcite crystal structure and thus release of Ca into the brines during the dolomitization process (Ehrenberg *et al.*, 2007) may also explain the higher Ca and lower Mg contents of the Marun brines than the evaporated seawater (Figure 6a and b). Stratigraphic columns and petrophysical data support dolomitization and the flow of large amounts of fluids in the upper parts of the Asmari Formation (Aqrawi *et al.*, 2006). In addition, our mass-balance calculations in which the sum of Ca and Mg in the Marun brines and in the evaporated seawater at the same levels of Cl were estimated, show that the total Ca + Mg (mole) in the Marun brines and in the evaporated seawater are the same ($\sim$5 moles), and thus replacement of calcite by dolomite has likely occurred through the reaction: $2CaCO_3(s) + Mg^{2+}(aq) \leftrightarrow (CaMg)(CO_3)_2(s) + Ca^{2+}(aq)$.

The Marun brines are depleted in SO_4 relative to that of the modern seawater (Figure 6d). As to the origin of lower SO_4 concentrations in the Marun brines compared to those predicted from evaporation of seawater, it seems likely that sulphate had been lost by some geochemical processes to account for the low sulphur content. Hanor (1987), Gavrieli *et al.* (1995) and Hanor and McIntosh (2006) argue that SO_4 depletion in brines can be caused by either biological/ chemical sulphate reduction or precipitation of gypsum as a result of dolomitization/extensive evaporation or both. In the Marun area, the regional geothermal gradient is 3.01°C per 100 m, which translates to Asmari reservoir's temperature of 105–120°C at a depth of 3500–4000 m. Such a temperature may have provided sufficient thermal energy for thermo-chemical sulphate reduction to occur in the brines. Alternatively, the presence of gypsum/anhydrite in the Gachsaran Formation and at the upper levels in the Asmari Formation (Bordenave, 2002; Ehrenberg *et al.*, 2007) may support the loss of sulphate by precipitation of $CaSO_4$.

Iodine concentration in Marun brines varies from 21 to 28.5 mg/L. Iodine has a high storage fixation coefficient with organic matter and it can also be absorbed by clays and carbon under certain conditions (Moran *et al.*, 1995). The rate of iodine absorption increases with increasing temperature and acidity, and decreases in the presence of inorganic salts ($CaCl_2$) (Collins and Egleson, 1967). It is possible that the clay minerals in the Asmari Formation may have taken up some of the iodine out of the system and thus has lowered the concentration of this element to the present values.

5.3. The migration history of the Marun brines

Most parts of the Asmari Formation were deposited in open-marine, high energy conditions at the margin of a NW trending basin (Alavi, 2004). Therefore, the high concentrations of Br and Cl in the Marun brines are not inherited from the sedimentary environment in which the lower Asmari Formation was deposited. Rather, the Marun brines originated from an evaporatively concentrated seawater that has entered the Oligo-Miocene host sediments. Several workers have already reported the widespread development of dolomites in the upper parts of the Asmari Formation (James and Wynd, 1965; McQuillan, 1985; Vaziri-Moghaddam et al., 2006; Mossadegh et al., 2009) and that the dolomitization intensifies towards the shelf-interior, the anhydrite cement and felty-textured nodule increases upwards in dolomitized beds, and the monophase high salinity fluid inclusions become ubiquitous in the upper dolomite succession beneath the Gachsaran Formation (Aqrawi et al., 2006; Ehrenberg et al., 2007). It is important to note that the dolomitized grains in the upper parts of the Asmari Formation show evidence for late-stage and post-sedimentary diagenetic modification by dolomitizing fluids (Aqrawi et al., 2006). In addition, the Sr isotope analysis reveals that some of the dolomite and anhydrite in the uppermost Asmari Formation have younger ages than the macrofossil age-depth trend, suggesting that dolomitization occurred after deposition and was influenced by seepage reflux of evaporatively concentrated seawater (Ehrenberg et al., 2007). A series of evaporite beds present in the overlying Gachsaran Formation indicate that evaporites were produced from concentrated seawater and in restricted basins (Aqrawi et al., 2006). By inference, it is proposed here that the concentrated seawaters that refluxed downward during basal Gachsaran evaporite deposition were trapped within the Asmari Formation during Miocene time, underwent interactions with the host rocks, and evolved into the Marun brines.

5.4. Economic potential of the Marun brines

In terms of economic potential, the average concentrations of many cations–anions (i.e. Br, Li, Mg, B, Na, K) from the Marun oil-field brines are too low to be considered of any industrial use. For example, Li, Br and B that are commercially extracted from Salar de Hombre Muerto, Argentina (Li: 914 ppm), Smackover Formation, Arkansas (Br: 3000–5000 ppm) and Searles Lake, California (B: 3000 ppm) (Rostron et al., 2002 and references therein) have substantially low concentrations in the Marun brines (Li: 12.4 ppm; Br: 791.2 ppm; B: 127.5 ppm). The only exception is I whose concentration in the Marun brines (24.5 ppm) is slightly lower than that in the commercial brines of

Tomigusku Formation, Japan (I: 85 ppm) (Rostron et al., 2002). Further geochemical analysis and economic appraisal of I from the Marun and other oil-field brines in southern Iran is encouraged.

6. CONCLUSIONS

Evaporated palaeo-seawater is the most probable precursor fluid of the present-day Marun oil-field brine, based on the chemical composition and isotopic signatures. Most cations and anions in Marun oil-field brines have abundances that are higher than those of modern seawater. Halogen systematics indicate a fluid concentrated past gypsum saturation, in addition, Br/Cl ratios point to the origin of the salinity from evaporatively concentrated seawater. The chemical deviation of the Marun brines from that of concentrated seawater point to the importance of other processes such as water–rock interaction in the evolution of the studied brines. While meteoric water influx and salt dissolution were not involved, processes like dolomitization, sulphate reduction and gypsum/anhydrite precipitation, as evidenced by lower Mg and SO_4 contents and greater Ca abundances than those expected from evaporation of seawater, can also be recognized in the genesis of the Marun brines. The Marun brines in the Asmari Formation likely originated from evaporated seawater that refluxed downwards during the overlying Gachasaran Formation evaporite deposition.

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