Origin and evolution of formation water from the Ordovician carbonate reservoir in the Tazhong area, Tarim Basin, NW China

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\textbf{A R T I C L E  I N F O}

Keywords:
- Formation water
- Fluid migration
- Water-rock interaction
- Thermochemical sulfate reduction
- Environmental isotopes
- Tarim Basin

\textbf{A B S T R A C T}

Chemistry, H, O and Sr isotopes of formation waters were determined from the Ordovician carbonate reservoirs in the Tazhong area, Tarim basin. The aim is to elucidate their origin and migration and their alteration by thermochemical sulfate reduction (TSR) and water-rock interactions. The waters were originated from evaporated seawater, and are enriched in Ca and Sr, and depleted in Mg and SO\textsubscript{4} compared with the seawater evaporation trajectory (SET), thus are considered to result from dolomitization, anhydrite dissolution and in situ TSR. $\delta^{18}$O values show positive shift due to water-rock interactions, and $\delta^{87}$Sr values show negative shift with increasing TSR extents or total thiaadamantanes concentrations of the associated oils, likely resulting from hydrogen isotope exchange with TSR-H\textsubscript{2}S. However, the 6D-$\delta^{18}$O relationship was mainly controlled by the mixing with paleo-meteoric water with 6D of $-50\%$ and $\delta^{18}$O of $-7.5\%$. Paleo-meteoric water may have leached the Silurian siliciclastic rocks and thus has $\delta^{87}$Sr/$\delta^{86}$Sr up to 0.715. Upper Ordovician (O2j) formation water shows more negative 6D and $\delta^{18}$O values, higher $\delta^{87}$Sr/$\delta^{86}$Sr ratios and lower total dissolved solids (TDS) than the O1y water, which may have resulted from mixing of paleo-meteoric water. Lower Ordovician (O1y) formation water shows $\delta^{87}$Sr/$\delta^{86}$Sr ratio of 0.7095–0.7105, TDS from 160 to 240 g/l, and Sr concentrations from 300 to 1000 mg/L, which may have resulted from mixing with hydrothermal fluid up-migrated from Ediacaran and Lower Cambrian siliciclastic rocks. Significant mixings with paleo-meteoric water and hydrothermal fluid occurred at paleo-highland at the east of No.1 Fault-Slope Zone and active faulting zone near No.10 Structural Belt, respectively. Hydrothermal fluid and oils probably shared similar migration pathways in No.10 Structural Belt. Formation water geochemistry may thus provide clues to constraint on petroleum migration.

1. Introduction

Although the importance of subsurface formation water for hydrocarbon migration, mineralization and hydrogeology has been widely recognized (Worden et al., 1999; Moldvanyi et al., 1993; Cowie et al., 2014; Bagheri et al., 2014), in most instances, the origin and evolution history of formation water remain controversial. Chemical and isotopic compositions are widely employed in sedimentary basins to investigate the origins, migration pathways and water-rock interactions over geological time. Origins of formation water have previously been attributed to halite dissolution, evaporation concentrated seawater and meteoric water (Clayton et al., 1966; Holser et al., 1986; Walter et al., 1990; Birkle and Maruri, 2003; Elias et al., 2007; Lowenstein et al., 2003; Panno et al., 2013).

Cl/Br and Na/Br ratios are used as indicators for seawater evaporation and halite dissolution-precipitation, because Br is a conservative element for most water-rock interactions except halite (Carpenter, 1978; Walter et al., 1990; Stueber and Walter, 1991; Warner et al., 2012). $\delta^{87}$Sr/$\delta^{86}$Sr ratios of formation water are only influenced by the input of radiogenic $\delta^{87}$Sr rather than temperature, pressure or phase that can impact the element and/or stable isotope composition. Therefore, $\delta^{87}$Sr/$\delta^{86}$Sr ratios are used to constrain the origin of formation water and interpret regional scale hydrogeochemical processes, such as fluid flow issues (Burnaby et al., 2004; Chacko and Deines, 2008; Frost and Touer, 2004; Luz et al., 2009; Pennisi and Leeman, 2000).

Tazhong area is the most complex zone for petroleum exploration in the Tarim Basin. It has been modified by the Caledonian, Hercynian, Indosinian, Yanshanian and Himalayan tectonic movements since the Ordovician, increasing difficulties to illustrate the origin and evolution history of formation water. Cai et al. (2001b) identified three end member water in the basin, including high salinity Cambrian evaporitic water, paleo-meteoric water and highly radiogenic shale-derived water from the Awati Sag. More recently, more than 40 new wells have been

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drilled, from which new formation water, associated petroleum and 
H_2S gas were produced from the Ordovician Lianglitage (O_3l) and 
Yingshan (O_1–2y) Formations (Cai et al., 2015b), thus providing new 
constraints on the origin and migration in this area. Xiang et al. (2010) 
proposed that water chemistry of the Ordovician formation water in 
Tazhong area was altered by thermochemical sulfate reduction (TSR) 
by showing the relationships of H_2S concentrations to CO_2, SO_4^{2−}, Ca^{2+} 
and HCO_3^{−} concentrations. However, H_2S concentrations were shown 
to increase due to release from formation water, and thus cannot be 
simply used to indicate the extents of TSR (Cai et al., 2013; 2015b). 
Instead, thiaadamantanes (TAs) have been measured from the asso-
ciated oils and their concentrations have been used to indicate TSR 
extents (Cai et al., 2016), thus providing possibilities to discuss TSR 
effects on formation water chemical and isotopic compositions.

In this study, we integrated water chemistry, H, O and Sr isotopic 
compositions of the Ordovician formation water in Tazhong area. 
Specifically, we try to address the following questions: (1) What is 
characteristics of the water, and any difference between O_3l and O_1–2y 
water? (2) What is the origin of the water? (3) Whether and how did 
water-rock interactions, TSR and fluid mixing change formation water 
chemistry, H, O and Sr isotopic compositions? (4) Can formation water 
geochemistry be used to trace fluid mixing and oil migration?

Fig. 1. (a) Map of Tarim Basin showing tectonic units and location of Tazhong Uplift; (b) Map of study area showing geological tectonics and location of wells from which formation water samples were collected.
2. Geological setting

Tazhong area (or Central Tarim) is located in the center of Tazhong Uplift, Tarim Basin, northwest China. It is surrounded by the Manjiaer Sag, South Depression, Bachu Uplift and Tadong Uplift (Fig. 1a). It can be divided into the No.1 Fault-slope Zone, North Slope, No.10 Structural Belt, Central Faulted Horst Belt, South Slope and East Burial Hill Zone (Fig. 1b). Tazhong Uplift is one of the major petroleum production areas in the Tarim Basin. Oils and natural gases have been found in the Cambrian-Ordovician carbonate reservoirs and the Silurian-Carboniferous clastic reservoirs (Lu et al., 2004).

Tazhong Uplift has undergone Caledonian, Hercynian, Indosinian, Yanshanian and Himalayan tectonic movements since the Ordovician. During the Cambrian to Early Ordovician, central faulted horst belt was formed, resulting in an eastward-dipped paleo-geomorphology (Chen, 2005; Lin et al., 2009; Zhang, 2006). During the Middle-Late
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* TAs or thiaadamantanes are from Cai et al. (2016); H₂S from Cai et al. (2015b) and – represents no data available.
Orどzic deposits and the Cambrian-Ordovician Faults, Late Ordovician Thrust Faults and Silurian-Devonian Strike-Slip Faults (Li et al., 2013). These faults and unconformities served as conduits for oil and gas migration from the Lower Cambrian source rocks (Cai et al., 2001a, 2009a, 2009b, 2015a; Pang et al., 2013).

The geological record of the Tazhong Uplift can be divided into several tectonic events and related stratigraphic sequences (Fig. 2). The Lower Ediacaran is composed of morainic conglomerates and neritic facies sandstones and mudstones. The Upper Ediacaran consists of platform dolomite, micrite and lagoonal facies. The Lower Cambrian section comprises platform to platform-marginal thick dolomites; the Middle Cambrian is composed of supratidal anhydritic dolomites and anhydrite. Bedded anhydrite 44–98 m thick is present in the eastern ZS1 and ZS5 wells (Cai et al., 2015b). The Ordovician is predominantly composed of thick dolomite, packstone, and bioclastic limestone deposited in an open-platform environment with intercalated reef and shoal deposits. The Silurian and Devonian are composed of marine sandstone and mudstone. Carboniferous sandstones consist of littoral and neritic clastic deposits with intercalated micritic and bioclastic limestone. The Permian consists of marine-terrestrial transition facies gray or brown sandstone and mudstone with intercalated volcanics. The Mesozoic and Cenozoic are mainly composed of terrestrial sandstones and mudstones.

3. Sample collection and analysis

Water samples were obtained through drill-stem testing (DST) or repeat formation testing (RFT) from oil or water intervals and filtered through a 0.45 μm filter. Samples were not collected until Cl concentrations remained constant (10%) over 3 measurements per 8 h. Samples from TZ201-1H and TZ623-H2 with producing gas/water ratios higher than 50,000 m3/m3 were only measured on 87Sr/86Sr, in case condensed water changes chemical and hydrogen and oxygen isotopic compositions of the formation water. pH was measured using an electrode method within 2 h after sampling in the field. Major ion chemistry was measured by titration with Cl and SO4 by AgNO3 and BaCl2 potentiometric titration and Ca and Mg by ethylenediaminetetraacetic acid (EDTA) titration. The K+Na concentration was calculated from charge balances. After being acidified to pH less than 6, formation water was analyzed for dissolved metals K and Sr using a Jarrel-Ash 110 ± 1155V inductively coupled plasma atomic emission spectrometry (ICP-AES) instrument in the Institute of Ecology, the Chinese Academy of Sciences. Precision of the analyses is 5% for Sr and 8% for K, based upon replicate analyses. The Na concentrations were calculated by K +Na minus K. Based upon replicates, the precision for Cl measurement is better than 1.5%, for SO4 is 3%, for Mg 3% when Mg concentrations are higher than 500 mg/L and better than 6% in the Mg range from 300 to 500 mg/L. The precision for Ca is better than 3% when Ca concentrations are higher than 100 mg/L, and is better than 5% in the Ca range from 500 to 1000 mg/L. All the above measurement is done using a gravimetric method according to Clescerl et al. (1999). After filtration with a 0.45-μm filter, 0.5 ml of the water was dried at 180 °C until a constant weight was reached.

δD, δ18O and 87Sr/86Sr analyses were performed in the Stable Isotope Laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences. δD and δ18O were determined using methods of reduction on highly purified metallic Zn at 390 °C and CO2 equilibration, respectively. D/H and 18O/16O ratios were measured on a MAT251 mass spectrometer, and the results were reported relative to SMOW, with standard deviation of ±1 to 2‰ for δD and ±0.2 to 0.3‰ for δ18O, respectively. For determination of 87Sr/86Sr, sufficient formation water or solution was acidified to pH < 2 using 100% HCl. The 87Sr/86Sr ratios were measured on a Finnigan MAT-262 mass spectrometer and corrected relative to the NBS-987 standard with a measured average value of 0.710255 ± 0.000010. The precision for 87Sr/86Sr measurement is 0.00003–0.00007.

4. Results

Chemical and isotopic compositions of formation water from the study area are shown in Table 1. The water shows a variable chemical composition, pH values from 5.4 to 7.4 with an average of 6.7, and total dissolved solids (TDS) from 75 to 233 g/L with an average of 144 g/L, being 2–7 times more saline than seawater. O1− formation water has TDS from 123 to 233 g/L and a mean value of 182 g/L, and are higher than the O3l water which range from 75 to 129 g/L with a mean value of 99 g/L.

Na concentrations range from 7 to 67 g/L with an average of 42 g/L. Cl concentrations range from 45 to 143 g/L with an average of 83 g/L. Concentrations of other anions, such as SO4 and HCO3, are much lower than Cl (Table 1). Ca, the second most predominant cation, has concentrations from 3 to 48 g/L with an average of 14 g/L.

The O1− and O3l samples have δD values between −47.3 and −23.1‰ and −53.0 and −30.3‰, respectively, and δ18O values ranging from 2.69 to 9.01‰ and −2.63 to 1.27‰, respectively. δ18O values from the O1− formation water have higher than the O3l (Fig. 8). δ18O values of O1− samples are more positive than seawater, while most δ18O values of O3l samples are more negative than seawater.

87Sr/86Sr/Sr ratios from the O1− samples range from 0.07937 to 0.71031 with an average of 0.70973 and are lower than O3l samples which range from 0.71058 to 0.71305 with an average of 0.71141. Sr concentrations of O1− formation water range from 264 to 1043 mg/L, with an average value of 582 mg/L. Sr concentrations of O3l formation water range from 173 to 258 mg/L with an average of 212 mg/L (Table 1).

5. Discussion

5.1. Relationship between formation water and evaporated seawater

The origin of salinity in formation water from sedimentary basins has historically attributed to subaerial evaporation of seawater (Carpenter, 1978) and/or dissolution of evaporite (Land and Prezbindowski, 1981; Birkle et al., 2009). Modern seawater has a TDS of about 35.2 g/L and is dominated by Na+(10.7 g/L) and Cl− (19.3 g/L). Brines that evaporated beyond halite saturation level show a Na/Cl molar ratio lower than seawater (0.86) since the halite precipitation absorbs Na and Cl in 1:1 M ratio and consequently decreases the Na/Cl ratio (Bagheri et al., 2014). In contrast, the dissolution of halite will provide solute with Na/Cl molar ratio close to 1, which is slightly higher than that of seawater (Li and Jiang, 2013). The formation water in this study has Na/Cl molar ratios from 0.37 to 0.92 with an average of 0.79 (Table 1), most of which are close to seawater (Fig. 3), indicating an origin dominated by evaporated seawater.

Abnormally low Na/Cl molar ratios have been observed in TZ26-H9 (0.37) and ZG432 (0.39). They are located in the eastern side of No.1 Fault-Slope Zone and the central part of No.10 Structural Belt (Fig. 1b). Do these abnormal Na/Cl molar ratios result from halite precipitation? Formation water after halite precipitation is expected to have lower Na/Cl and Cl/Br molar ratios and high Cl concentrations saturated with halite. However, 1) Cl/Br molar ratios of Paleozoic formation
water are close to seawater (Cai et al., 2001b); 2) no halite is found in the area (Fig. 2). These two facts rules out the possibility that the abnormally low Na/Cl molar ratios resulted from halite precipitation. Other processes will be discussed in the next part.

5.2. Water-rock interactions

Seawater evaporation trajectory (SET) has been extensively used to determine the origin of water salinity and water-rock interactions (Cai and Mei, 1997; Birkle et al., 2009; Cai et al., 2001b; 2006). Fig. 4 shows variations of ions to Cl relative to the SET. Ca is plot above the SET and thus rich relative to seawater evaporation while Mg and SO₄ are depleted.

5.2.1. Albitization

Cations of formation water can be changed significantly by water-rock interactions. Most of the Ordovician formation water has Na plotted on the SET (Fig. 4a) and only ZG432 and TZ26-H9 water are depleted in Na. In sedimentary basins, water-rock interactions involving sodium are either albitization of plagioclase and K-feldspar or halite dissolution and precipitation (Davisson and Criss, 1996). Dissolution or precipitation of halite has been excluded as the origin as discussed in the last section. Thus, albitization of plagioclase or K-feldspar is most likely. The albitization with an exchange of 2 Na⁺ for 1 Ca²⁺ or 1 Na⁺ for 1 Ca²⁺ can result in Na depletion and Ca enrichment in basin fluid (Davisson and Criss, 1996). Davisson and Criss (1996) found a linear relationship between Na_deficit and Ca_excess for many basins, which was named as Basinal Fluid Line (BFL):

$$C_{a_{\text{excess}}} = 0.967 \text{Na}_{\text{deficit}} + 140.3 \quad (R = 0.98)$$

The excess of Ca and the deficit of Na are defined as follows:

$$C_{a_{\text{excess}}} = C_{a_{\text{meas}}} - (C_{a_{\text{meas}}} - C_{a_{\text{meas}}}) \times 2/40.08$$

$$\text{Na}_{\text{deficit}} = (\text{Na}_{\text{meas}} - C_{a_{\text{meas}}}) \times 1/22.99$$

Na_{deficit} and Ca_{excess} are plotted on Fig. 5. Ca excess and Na deficit can be found both in O₁₋₂y and O₁ formation water (Fig. 5). The samples are plotted on the Basinal Fluid Line (BFL) showing an exchange of 2 Na⁺ for 1 Ca²⁺. Albitization of plagioclase by 2 Na⁺ for 1 Ca²⁺ exchange could be responsible for the water. Plagioclase occurs in clastic rocks, and formation water from the Silurian to Carboniferous

**Fig. 3.** Relationship between Na/Cl molar ratios and Cl concentrations of Ordovician formation water. The solid line is the Na/Cl=0.86 line defined by seawater. Evaporation of seawater will increase the Cl concentrations coupled with unchanged Na/Cl molar ratios.

**Fig. 4.** Relationships of formation water Cl to Na, Ca, Mg, K, Sr and SO₄ relative to seawater evaporation trajectory (SET). H means halite, and SW means seawater.
clastic rocks is characterized by Na⁺ depletion and Ca²⁺ enrichment due to albitization (Cai et al., 2001b). Thus, the Na-deficit water in the Ordovician carbonate reservoirs may have mixed with formation water from clastic rocks in the Silurian to Carboniferous, or hydrothermal fluid from the Ediacaran and Lower Cambrian as initially proposed based on cement and vein geochemistry (Cai et al., 2008).

O₁₋₂y samples are broadly parallel to SET and slightly enriched in K. However, some of O₁ samples are slightly depleted in K relative to SET (Fig. 4d). K feldspar precipitation and illitization will decrease K concentration, while K feldspar dissolution and albitization will increase K concentration (Birks et al., 2009).

5.2.2. Dolomitization

Ca/Cl molar ratios of the Ordovician formation water range from 0.05 to 0.34 with an average of 0.12, which is 500% enrichment relative to seawater (0.02). Ordovician formation water has an average Na/Cl molar ratio of 0.79, being 8% depleted comparing to seawater (0.86). Hence, only about 4% Ca enrichment is produced according to the 2 Na⁺ for 1 Ca²⁺ albitization. Dolomitization of carbonates is considered to be the main mechanism for Ca enrichment coupled with Mg depletion (Fig. 4b, c), which is widely reported in many basins (Bottomley et al., 1999; Stueber and Walter, 1991). Mean Mg/Cl molar ratio of 0.01 yields 90% Mg depletion relative to seawater (0.1). Assuming that dolomitization is the only process accounting for the depletion of Mg in the formation water, 90% Ca enrichment is expected from dolomitization. Hence, other sources must have contributed Ca leading to Ca enrichment up to 500% in these formation water, and are likely from dissolution of anhydrite, gypsum and/or calcite.

5.2.3. TSR effects on formation water SO₄ and D values

All the water samples show a strong depletion in SO₄ with the water in the O₁₋₂y being more depleted than in the O₁ (Fig. 4e). In situ thermochemical sulfate reduction (TSR, reaction 1), redox reactions between dissolved sulfates and petroleum at temperatures > 120 °C (Cai et al., 2001a; 2003), is likely to have resulted in the SO₄ depletion and H₂S generation as supported by the ubiquitous distribution of H₂S in the Ordovician reservoir (Cai et al., 2001a; 2015b).

\[
\text{MgSO}_4 + \text{Ca}^{2+} + \text{petroleum} \rightarrow \text{Mg}^{2+} + \text{CaCO}_3 + \text{H}_2\text{S} + \text{altered petroleum}
\]  

H₂S in the O₁ reservoir is less than 4.7%, while H₂S in O₁₋₂y reservoir can reach up to about 15% (Cai et al., 2015b). SO₄ depletion and H₂S enrichment probably resulted from TSR in situ (Fig. 6a). H₂S has been shown to dissolve in formation water, precipitate as pyrite and have been incorporated into oils and solid bitumens producing alklythiolanes, alkylthiols and alkyl 2-thiaadamantanes in the area, thus H₂S concentrations cannot be used to reflect TSR extents in this case (Cai et al., 2015b; 2016). Thiaadamantanes (TAs) concentrations in petroleum are considered to better reflect TSR extents (Wei et al., 2012; Cai et al., 2016), and show increase with decreasing SO₄ concentration in the formation water (Fig. 6b). O₁ formation water show less SO₄ depletion than O₁₋₂y water (Fig. 4e), which means that TSR in O₁ reservoir is weaker. Overall, TSR is considered to be the main reason for the SO₄ depletion in the Ordovician formation water.

The water with the most negative δD value has the highest TAs and H₂S concentrations, indicating that δD values shifted negatively with increasing TSR extents (Fig. 7c and d). This probably resulted from isotopic exchanges between formation water and TSR-H₂S. Liquid hydrocarbons have δD values ranging from ~250 to ~50‰ (Bai et al., 2014; Radke et al., 2005; Liu et al., 2006) and gaseous hydrocarbons are usually lower than ~100‰ (Hu et al., 2013; Liu et al., 2016; Xiao, 2012). Therefore, the H₂S is expected to have much more negative δD values than formation water if it was derived from TSR by petroleum as suggested by Cai et al. (2001a; 2005 and, 2016).

Much poorer correlation exists between δ¹⁸O and H₂S (Fig. 7e) and especially between δ¹⁸O and TAs (not shown), indicating that δ¹⁸O values of the formation water were not altered by TSR. This observa-
tion is different from Jiang et al. (2015b), in which water was proposed to have been generated during TSR and thus decreased formation water salinities and δ¹⁸O values. The differences may be ascribed as different hydrocarbons involved in TSR. Liquid hydrocarbons were involved in TSR in this case (Cai et al., 2015b; 2016) whilst methane-dominated TSR occurred in NE Sichuan basin (Cai et al., 2004; 2013; Jiang et al., 2015b). Water was proposed to have been generated

Fig. 7. Crossplots showing, (a) A positive relationship between formation water δ¹⁸O and TDS; (b) No relationship between formation water δD and TDS; (c) A weak negative relationship between formation water δD and oil TAs; (d) A weak relationship between δD and H₂S when H₂S concentration is higher than 2%; (e) No relationship between δ¹⁸O and H₂S concentration.

Fig. 8. Relationship between δD and δ¹⁸O of Ordovician formation water. The regression line represents the mixing relationship between paleo-meteoric water and Ordovician formation water. Arrows indicate the expected shifts in δD and δ¹⁸O during evaporation, water-rock interactions, water-H₂S hydrogen isotope exchange. Global Meteoric Water Line (GMWL) is from Craig (1961) and seawater evaporation trajectory (SET) is from Moldvanyi et al. (1993).

Fig. 9. ⁸⁷Sr/⁸⁶Sr vs 1000/Sr crossplot showing two mixing trends in the Ordovician formation water in the Tazhong Uplift. Line 1 represents formation water mixed with paleo-meteoric water. Line 2 represents formation water mixed with hydrothermal water.

Fig. 10. ⁸⁷Sr/⁸⁶Sr vs TDS crossplot showing two mixing trends. Line 1 represents formation water mixed with paleo-meteoric water. Line 2 represents formation water mixed with hydrothermal water.
during TSR only by methane via reaction (2) not by C4+ hydrocarbons via reaction (3) (Pan et al., 2006).

\[
\text{CH}_4 + \text{Mg}^{2+} + \text{SO}_4^{2-} = \text{MgCO}_3 + \text{H}_2\text{S} + \text{H}_2\text{O} \quad (2)
\]

\[
4\text{C}_4\text{H}_12 + 5\text{Mg}^{2+} + 5\text{SO}_4^{2-} + \text{H}_2\text{O} = 5\text{MgCO}_3 + 8\text{CH}_4 + 5\text{H}_2\text{S} + 3\text{CO}_2 \quad (3)
\]

5.3. Meteoric water mixing indicated by δD and δ18O values

Most of the hydrogen and oxygen isotope data plot below the Global Meteoric Water Line (GMWL: δD = 8δ18O + 10; Craig, 1961) (Fig. 8), and thus are considered as typical formation water (Kharaka et al., 1987). A least square fit to the data intersects the global meteoric water line (GMWL) yielding an intercept at approximately −50‰ (δD) and −7.5‰ (δ18O). This may indicate that meteoric water, as suggested by the intercept, have mixed with formation water that originated from evaporated seawater. The regression line (dotted line) represents the mixing between meteoric water and formation water. O3l water shows lower δD, δ18O values and are closer to the intercept than the O1–2y water, which is supported by lower TDS in the O3l water (Figs. 7a, b and 8). Therefore, formation water of O3l mixed with the meteoric water to greater degree than the O1–2y water.

Aksu River and Tarim River in the Tarim Basin represent modern meteoric water, and show δD and δ18O values range from −78.0 to −54.9‰ and from −11.1 to −7.8‰, respectively (Huang et al., 2010). δD and δ18O values of the intercept (−50‰ and −7.5‰, respectively) are slightly heavier than the composition of modern meteoric water in the Tarim Basin (Fig. 8). Tarim plate was located at lower latitude during the Silurian (10–20°N) than afterward with present-day location at 35°N (Fang and Shen, 2001), and paleo-meteoric water during the period are expected to have heavier δD and δ18O values. Thus the intercept with the heavier δD and δ18O values is likely to represent isotopic composition of paleo-meteoric water during the Silurian as initially proposed (Cai et al., 2001b). Thus the paleo-meteoric water probably mixed with the Ordovician formation water during the Silurian.

Water samples deviate far from the mixing line are considered to have been affected by water-rock interactions or hydrogen isotope exchange with TSR–H2S, or both. Oxygen and hydrogen isotopic compositions of formation water are essentially conservative at ambient temperatures. Water-rock interactions may perturb the oxygen and hydrogen isotopic composition at elevated temperatures (Gat, 1996). They could cause a positive shift in δ18O values and keep δD values of basin brine unchanged, depicted by right radiating arrow (Fig. 8), because oxygen is much more involved than hydrogen in carbonates (Chen et al., 2013; Clayton et al., 1966). Heavier δD and δ18O values of O1–2y formation water may have resulted from both seawater evaporation and water-rock interactions. Lighter δD and δ18O values of O3l formation water may have resulted from the mixing with paleo-meteoric water to greater degree. Hydrogen isotope exchange between water and TSR–H2S is represented by ZG6 with low δD value of −44.1‰ and high TAs concentration of 147.20 μg/g. This could cause a negative shift of δD values without changing δ18O values, depicted by downward radiating arrow.
5.4. Water mixing indicated by Sr concentrations and $^{87}$Sr/$^{86}$Sr

Strontium has three origins: (1) mantle derived strontium with $^{87}$Sr/$^{86}$Sr value of 0.703; (2) terrigenous strontium with $^{87}$Sr/$^{86}$Sr value of 0.720; (3) Ordivician marine carbonates derived strontium with $^{87}$Sr/$^{86}$Sr value of 0.708 (Veizer, 1989; Jia et al., 2001). Strontium shows higher contents in carbonate rocks than in siliciclastic rocks. In contrast, carbonate rocks have $^{87}$Sr/$^{86}$Sr ratios lower than siliciclastic rocks due to the higher content of Rb in carbonate rocks. The relationship between $^{87}$Sr/$^{86}$Sr and 1000/Sr is thus commonly utilized to trace the origin of formation water. Both O$_1$-O$_2$ and O$_3$ formation waters show higher $^{87}$Sr/$^{86}$Sr ratios (0.70937-0.71031 and 0.70958-0.71305, respectively) than Ordivician limestone and coeval Ordivician seawater (0.7078-0.7090, Jiang et al., 2001; Huang et al., 2006; Chen et al., 2008), and thus they must have obtained radiogenic $^{87}$Sr from siliciclastic rocks (up to more than 0.75; Cai et al., 2001b).

Line 1 in Figs. 9 and 10 indicates mixing of high $^{87}$Sr/$^{86}$Sr, low TDS and Sr fluid (EM1) with Ordivician formation water. EM1 can be meteoric water or shale-derived water. Both have obtained $^{87}$Sr from siliciclastic rocks, and thus are characterized by low TDS and high $^{87}$Sr/$^{86}$Sr ratios. Meteoric water and/or shale-derived water have mixed with formation water from the O$_3$ as indicated by O$_3$ water samples lying on line 1 (Figs. 9 and 10).

Mixing with meteoric water is indicated by low temperature of fluid inclusions (50–60 °C) in calcite and quartz (Cai et al., 2008; Jia et al., 2015; Jiang et al., 2015a) and the relationship between $^{81}$O and $^{18}$O values (Fig. 8). O$_1$ formation water from well TZY2-5H, located in the east, shows $^{87}$Sr/$^{86}$Sr ratio of 0.7131, Sr concentration of 173 mg/L and TDS of 75 g/L (Figs. 1b, 9 and 10). O$_3$ formation water from TZ22-H2, located in the west, shows $^{87}$Sr/$^{86}$Sr ratio of 0.7016, Sr concentration of 244 mg/L and TDS of 107 g/L (Fig. 1b, Figs. 9 and 10). This indicates that O$_3$ water in the east of No.1 Fault-Slope Zone mixed with meteoric water to more degrees than in the west. Eastern Tazhong was uplifted to a greater degree than the west during the Late Ordivician to Silurian. During the Late Silurian, the O$_3$ strata were exposed and eroded in the southeast to west TZZ6-H9 (see locations in Fig. 1b) and Silurian siliciclastic rocks were eroded and weathered (Zhang, 2006; Chen, 2005). Therefore, meteoric water mixing is most likely to occur during the Late Silurian. This proposal is partially supported by the heavier $^{18}$O and $^{81}$O values of the paleo-meteoric water (intersection dot in Fig. 8) than modern meteoric water.

The other source of EM1 is shale-derived water from the Awati Sag. Mixing with this water is supported by the three lines of evidence, 1) a decreasing trend in $^{87}$Sr/$^{86}$Sr data from the west to the east is proposed to indicate that the shale-derived water from the Awati Sag was expelled and flowed into the strata in the northwestern Tazhong area (Cai et al., 2001b); 2) the bulk oil and its dibenzothiophenes from well ZG19 (Fig. 1b) nearby the Awati Sag shows similar $^{34}$S values to the Middle and Upper Ordivician kerogen, and thus the oil is considered to have been derived from the source rock of that age in Awati Sag (Cai et al., 2015a); and 3) O$_3$ formation water from well ZG162-H2 (Fig. 1b), has high $^{87}$Sr/$^{86}$Sr of 0.71075 and low TDS of 96 g/L. This water sample is less likely to have mixed with paleo-meteoric water because well ZG162-H2 was not located in paleo-highland but around subsidence center near the Awati Sag and well ZG19 (Fig. 1a and b). Thus, the ZG162-H2 water with high $^{87}$Sr/$^{86}$Sr and low TDS is most likely to have mixed with shale-derived water from the Awati Sag.

Line 2 in Figs. 9 and 10 represents mixing between high $^{87}$Sr/$^{86}$Sr, TDS and Sr fluid (EM2) and Ordivician formation water. EM2 may be hydrothermal fluid up-migrated from the Lower Cambrian and Ediacaran siliciclastic rocks, as suggested by Cai et al. (2008) and Jia et al. (2015). The hydrothermal fluid may have up-migrated and mixed with formation water along the cross points of faults near the No.10 Structural Belt to more degrees. This is supported by water samples from the area having higher $^{87}$Sr/$^{86}$Sr ratios and higher Sr and TDS concentrations, such as in wells ZG431, ZG432, ZG433C, ZG441, ZG45 and ZG511-2 (Figs. 1b, 9 and 10). Significantly, oils are mainly producing from the area, thus it may indicate that oil and hydrothermal fluid may have up-migrated along similar pathways.

5.5. Model of water flow and its relationship to oil migration

A mixing model for the Ordivician formation water is proposed based on above discussion (Fig. 11). During the Late Ordivician to Silurian, the eastside of Tazhong was uplifted to a greater degree due to tectonic compression. Sediments of the top Silurian siliciclastic rocks were removed during the Late Silurian. Paleo-meteoric water received $^{87}$Sr from the Silurian siliciclastic rocks infiltrated into O$_3$ carbonate reservoir at the eastside of No.1 Fault-Slope Zone, flowed westwards and subsequently mixed with O$_3$ diagenetically altered evaporated seawater.

Hydrothermal fluid, obtained $^{87}$Sr and high TDS from the Lower Cambrian and Ediacaran siliciclastic rocks, may have up-migrated during the Permian (Cai et al., 2008; Jia et al., 2015) along faults especially near the No.10 Structural Belt and mixed with O$_1$-O$_2$ diagenetically altered evaporated seawater. Significantly, oils are found where hydrothermal fluid were active near the No.10 Structural Belt, and are proposed to have up-migrated from Cambrian source rocks during the Late Silurian to Early Devonian, and re-migrated from previously accumulated oil pools during the Permian (Cai et al., 2009a and b; 2016). That is, oils may have similar migration pathways to the hydrothermal water. Thus, chemical and isotopic compositions of formation water may provide clues to oil migrating direction.

6. Conclusions

(1) Formation water was originated from evaporated seawater, and enriched in Ca and depleted in Mg, SO$_4$ and Na likely by dolomitization, albitization, anhydrite dissolution and thermoch- mical sulfate reduction (TSR).

(2) δD values of formation water were negatively shifted likely due to hydrogen isotope exchange between water and TSR-H$_2$S.

(3) O$_1$-O$_2$ formation water may have mixed with hydrothermal fluid during the Permian, while O$_3$ water mixed with paleo-meteoric water during the Late Silurian. Thus O$_1$-O$_2$ water show higher TDS, heavier δD and δ$^{34}$S and lower δ$^{18}$O and lower $^{87}$Sr/$^{86}$Sr than the O$_3$.

(4) Both hydrothermal fluid with high TDS and $^{87}$Sr/$^{86}$Sr and oils may have up-migrated along faults near No.10 Structural Belt, and thus formation water geochemical composition may supply clues to oil migration.

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