Origin and Geochemical Evolution of Formation Water in the Dameigou Shale Gas Reservoir in Northern Qaidam Basin

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Received: 10 July 2019
Accepted: 3 November 2019

Abstract

The origin and geochemical evolution of formation water trapped in continental shale of the Dameigou Formation in the Northern Qaidam Basin have been investigated for selecting unique signatures of formation water compared with shallow groundwater and conventional oilfield brines (COB). The formation water, which is trapped in a closed shale with no halite and sylvite in it, has a higher Cl/Br ratio (1183.43) than that of seawater (657.89). Furthermore, δ2H (−67‰) and δ18O (−8.1‰) values of the formation water lies near the local evaporation line. These suggest that the formation water originated from evaporated rainwater. The temperature (>120°C) of the Dameigou Formation and the vitrinite reflectance values (1.0-1.3%) of the shale indicate that thermochemical sulfate reduction (TSR) was responsible for the depletion of SO4 in the formation water. The increased CO2 concentration and Mg/Ca ratio in formation water leading by TSR caused kaolinization of plagioclase feldspar and dolomitization, respectively. The formation water depletion in Ca and HCO3 was caused mainly by calcitization. The Na/Ba ion exchange and dissolution of continental borate occurring in the shale-formation water system were vital to the geochemistry of trace elements in formation water. All these geochemical processes have given the formation water distinctive δ34S-H2S (25.9‰), 87Sr/86Sr ratio (0.713842), Ba/Ca ratio (2.60×10−2) and δ11B (1.1‰) signatures compared with COB in shallow groundwater.

Keywords: geochemical process, groundwater monitoring, continental shale, formation water, HFFF indicator

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Introduction

Shale gas has great resource potential \((31 \times 10^{12} \text{ m}^3)\) in China. Development of shale gas was made possible by the successful application of horizontal drilling and high-volume hydraulic fracturing (HVHF) as Chinese gas demand surged, with natural gas consumption increasing by over 15\% \((31 \times 10^9 \text{ m}^3)\) from 2016 to 2017 [1]. It is estimated that nearly 700 new wells from three major shale gas plays (Fuling, Changning-Weyuan and Zhaotong) will come online between 2018 and 2020 [2].

Although the success of unconventional gas development has radically changed the energy portfolio of China, the United States, and other countries, environmental concerns regarding the contamination of groundwater by hydraulic fracturing flowback fluids (HFFF) have arisen [3-5] due to the HFFF produced by HVHF containing a large amount of heavy metals and organic matter at toxic concentrations that pose risks to human health [6-9]. A robust methodology focused on hydrochemical and isotopic characteristics of HFFF has been researched in many studies for precise identification of HFFF spills [10-11]. Previous studies [12-13] on the Marcellus Shale reveal that HFFF is enriched in Na and Cl composition with high total dissolved solids (TDS) and high Br/Cl ratios relative to modern seawater that reflect different degrees of seawater evaporation. Warner et al. stated that diagnostic elemental and isotopic signatures \((\text{Br}/\text{Cl}>0.001, \delta^{11} \text{B} = 25 – 31\%o)\) are useful for characterizing HFFF and distinguishing sources of HFFF in the groundwater in most cases [12]. Chapman et al. suggested that strontium isotopic ratios of Marcellus Shale HFFF define a relatively narrow set of values \((^{87}\text{Sr}/^ {86}\text{Sr} = 0.710148 – 0.712119)\) closed to that of seawater and can be used to sensitively differentiate between Marcellus HFFF and other potential sources of contamination into groundwater or surface water [14]. It should be noted from these previous studies that the formation water trapped in marine shale that originated from seawater dominates the hydrochemical and isotopic compositions of HFFF as a result of mixing during fracturing and flowback processes.

A lot of shale gas reservoirs in China such as the Qaidam, Tarim, and Ordos Basins were deposited in continental environments [3]. Thus, the origin of formation water in these shales could be unlike that in most marine shale in the United States [10]. Consequently, the continental shale formation water may have distinctive hydrochemical and isotopic characteristics compared with marine shale formation water after geochemical evolution in geologic history. This issue highlights the need to improve our understanding of the origin and evolution of formation water for selecting distinguishing indicators of HFFF produced from continental shale formations.

Northwest China is an important production base of conventional oil and gas [15]. As well as HFFF, brines produced from conventional oil and gas wells are a potential source of contamination for shallow groundwater [16-17]. For forensic identification of contamination and subsequent groundwater remediation, it is necessary to distinguish between different sources of pollution in groundwater. Therefore, the aim of the present study is to identify the unique hydrochemical and isotopic signatures of formation water that could be taken as HFFF indicators, thus distinguishing it from conventional oil-field brines (COB) in groundwater.

![Fig. 1. Sampling locations of the formation water and shallow groundwater in this study are plotted on the topographic map of the research area; formation water of the Dameigou Shale (black circle) was collected from CY1 well; shallow groundwater occurring in the Upper Pleistocene strata was collected from springs (yellow triangles).](image-url)
The Dameigou Formation constitutes the most favorable reservoir for shale gas exploitation through the Qaidam Basin [18-19]. The indicators obtained from this study may be applied widely in the Qaidam Basin to identify HFFF in shallow groundwater at large scales within continental shale gas plays. Additionally, the results of this study are significant in risk assessment of drinking groundwater in shale gas plays located in arid and semi-arid areas of northwest China.

Research Area

The Chai Ye1 (CY1) well is the first continental shale gas exploration well and is located in Yuqia sag of the northern Qaidam Basin (Fig. 1). The Dameigou Shale, also referred to as the Dameigou Formation, is a Middle Jurassic-age, microfissure-developed, organic-rich and hydrocarbon producing shale that occurs in the subsurface beneath much of the Qaidam Basin [20].

The most promising shale gas intervals (2003-2045 m), which belonged to the 7th member of the Dameigou Formation, were comprised of grey-black shale and carbonaceous shale. A synthesized columnar section of these shale gas intervals in the CY1 well is shown in Fig. 2. These shale intervals are rich in brittle silicate minerals (quartz and feldspar) and clay minerals (kaolinite, illite, andreatitte and chlorite), and poor in carbonate minerals (siderite), with average contents of 42.6%, 52.8% and 4.5%, respectively (Fig. 2) [21]. The organic matters in these shales are high in vitrinite-reflectance (Ro = 1.0 – 1.3%) and are dominated by type II kerogen with a total organic carbon (TOC) content of between 0.3% and 7.6% [21]. In addition, micropores are developed in these shales. Pores in organic matters are mainly circular, ranging in size from 1 to ~20μm [21]. The main pore of the mineral skeleton are dissolution pores in grains and intergranular micropore, ranging in size from 1 to ~10μm [21].

Phreatic pore water in the Upper Pleistocene strata, which is the most easily polluted by HFFF, drains as multiple springs along the Naoer River at the south of the CY1 well.

Materials and Methods

Sample Collection and Treatment

In this study, two categories of water samples were collected: (1) a sample of formation water from most promising shale gas intervals was collected from CY1 well before hydraulic fracturing in August 2014; (2) samples from two spring discharged from the Upper Pleistocene, located at 1 km and 2 km northwest of CY1 well, were collected before hydraulic fracturing in July 2014 (Fig. 1). Formation water was collected, before fracturing, from perforated holes made into the shale formation (2008.0-2012.3 m, 2026.1-2027.9 m, and 2034.8-2037.1 m) using deep penetrating charges.

Samples were filtered through a 0.45 μm nylon filter into precleaned HDPE bottles with no head space. Samples for trace element (e.g., Sr, B) were acidified to pH 2 with ultrapure HNO₃. Samples for H₂S were precipitated to cadmium sulfide by saturated cadmium...
acetate at the sampling site. All samples were kept on ice while in the field and refrigerated in the lab at 4°C until the analyses were completed.

**Analytical Method**

The HCO₃ concentration was calculated by acid-base titration. Major anions, except HCO₃⁻, were determined by high-resolution ion chromatography (Thermo Scientific Dionex ICS-4000; precision, ±1%), and major cations and minor elements were analyzed by an inductively coupled plasma optical emission spectrometer (PerkinElmer Optima 8300; precision, ±1%).

The δD and δ¹⁸O were analyzed by a Picarro L2130-i Analyzer (precision, ±0.025/±0.1‰ for δ¹⁸O/δD). δ³⁴S in H₂S were determined by isotope ratio mass spectrometer (IRMS Finnigan-MAT 253). The mass spectrometric uncertainty (1σ) on individual δ³⁴S measurements is better than 0.05%. The ⁸⁷Sr/⁸⁶Sr and δ¹¹B were analyzed by thermal ionization mass spectrometry (IsotopX Phoenix X62) and inductively coupled plasma mass spectrometry (PerkinElmer ELAN DCR-e), respectively. The average ⁸⁷Sr/⁸⁶Sr ratio of NIST SRM 987 and the average ¹¹B/¹⁰B ratio of NIST SRM 951 over the period of these analyses is 0.710244±0.000015 (n = 30) and 4.0436±0.0016 (n = 25), respectively.

**Evaporation Modeling**

Simulation of evaporation is accomplished by removing water from the chemical system. Water can be specified as an irreversible reactant with a negative reaction coefficient in PHREEQC (Version 3, USGS, Reston, USA). In this study, the REACTION data block is used to simulate concentrations of rain water sampled from the study area by 5 fold, 10 fold, 25 fold, 50 fold, 100 fold, 200 fold, 300 fold, and 367 fold (by removing approximately 80.0%, 90.0%, 96.0%, 98.0%, 99.0%, 99.5%, 99.6% and 99.7% of the water) until the simulated Br concentration matched the measured Br concentration of the formation water. The Gibbs free energy increments (ΔG) for water-rock reactions are little influenced by pressure, but are influenced by temperature. Thus, the temperature of the shale formation during sedimentary history from the previous study was used in this evaporation modeling [22].

The chemical indices of rain water modeled in this modeling are Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻, SO₄²⁻, Br⁻, and pH.

**Results**

Hydrochemical and isotopic compositions of formation water from CY1 well along with shallow groundwater from the Quaternary Upper Pleistocene aquifer are shown in Table 1. The data of major ions in the formation water of the Dameigou Shale (Table 1) showed a distinct characteristic from that in shallow groundwater in the study area and COB reported from a previous study [23]. The formation water has a medium level of TDS (11.50 g/L), and is distinguished by Cl, HCO₃ and Na in the dissolved ions (Fig. 3), while the shallow groundwater has a low level of TDS (<300.00 g/L) and is controlled by Cl, SO₄, Na and Mg in the dissolved ions; the COB has a high level of TDS (>300.00 g/L) and is characterized by Cl and Na in the dissolved ions (Fig. 3).

| Sample | Na  | K   | Ca  | Mg  | Cl  | SO₄ | HCO₃ | Br   | TDS   |
|--------|-----|-----|-----|-----|-----|-----|------|------|-------|
| FW     | 4284| 376 | 65  | 61  | 5844| 24  | 2387 | 11.00| 11496 |
| SG1    | 1796| 58.1| 224 | 329 | 2017| 2052| 370  | 0.52 | 6791  |
| SG2    | 1531| 50.6| 221 | 377 | 1949| 2199| 341  | 0.43 | 6500  |

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Formation water and shallow groundwaters have similar deuterium and oxygen isotopic compositions with δ²H ranging from −51‰ to −58‰ and δ¹⁸O ranging from −8.7‰ to −5.1‰. In comparison to formation water, salt lakes contained more heavily isotopic compositions with δ²H ranging from −15.0‰ to 10.0‰ and δ¹⁸O ranging from 2.0‰ to 4.2‰ [23]. The ⁸⁷Sr/⁸⁶Sr ratio of formation water (0.713842) is higher than that of shallow groundwater (0.712140-0.712273) and COB (0.711210-0.711937). Similarly, the δ³⁴S of H₂S in formation water (25.9‰) is also higher than that in
shallow groundwater (6.2-8.6‰). On the contrary, the $\delta^{11}B$ value of formation water (1.1‰) is much lower than that of shallow groundwater (24.4-26.1‰) and COB (12.3-31.1‰).

Discussion

Origin of the Dameigou Formation Water

The ratio of Cl versus Br is an ideal parameter for identifying the origin of solutes, mixing and dilution of brines, and various water-rock interactions without diagenetic alterations [24]. The Cl/Br molar ratio (1183.43) and Cl concentration (164.62 mM) of formation water is lower than that of salt lakes, respectively, (3082.65-28427.89, 2121.97-5336.90 mM) in the northern Qaidam Basin, including Qinghai Lake [23] (Fig. 4a). Furthermore, the $\delta^2H$ (−67‰) and $\delta^{18}O$ (−8.1‰) values of formation water are much lower than those of salt lakes (Fig. 4b). These reflect that the possibility of formation water recharged by salt lake water through deep fault can be excluded.

The Cl/Br of formation water is higher than that of seawater (657.89). Conversely, the Cl concentration of formation water (164.62 mM) is lower than that of seawater (535.21 mM) (Fig. 4a). These indicate that the source of formation water may be ancient seawater, which is further modified by dilution and halite dissolution resulting in increased Cl/Br and decreased Cl concentration as shown in Fig. 4a. However, the low $SO_4/(Cl+SO_4)$ moral ratio (3.078×10⁻³) reflects that the formation water trapped in the continental shale of the Dameigou Formation was in a closed environment [25].

In addition, the Dameigou Formation contains no halite or sylvite (Fig. 2). Thus, the possibility of formation water originating from ancient seawater can be ruled out.

The low permeability of shale (<0.05×10⁻³ μm²) [21] and closed environment indicate that the formation water was trapped in the shale when the shale formation was deposited. A previous study reported that the Dameigou Formation was deposited in a semi-deep lake environment [20]. In addition, the formation water is plotted close to the local evaporation line (LEL) [26] in the $\delta^2H$–$\delta^{18}O$ plot (Fig. 4b). This suggests that the formation water is supposed to have originated from evaporated ancient lake water, which was mainly recharged by rainwater in the Middle Jurassic period.
Natural crystalline bromide minerals are very rare in sedimentary strata [27]. Thus, bromine occurrence in rock-forming minerals is most commonly associated with substitutions of Cl for Br in chlorine-rich minerals such as halite, sodalite and eudialyte because of the similar ionic radii of the two ions (Cl: 181 pm, Br: 196 pm) [28]. However, no chlorine-rich minerals have been found in the Dameigou Formation. Furthermore, in the water-rock interactive system, bromide dose does not participate in the geochemical process as a conservative constituent. This suggests that the concentration of Br in formation water is only controlled by the origin of formation water and evaporation. Distinctive Br concentration (11.00 mg/L) in formation water suggests a 367-fold evaporation of the rainwater (0.03 mg/L) beyond saturation stages of calcite, dolomite, and anhydrite (Table 2, Fig. 5).

The evaporation modeling of rainwater is established for the purpose of discussing the geochemical processes, not accounting for evaporation during the process of creating formation water, which would highly affect the hydrogeochemical compositions. The PHREEQC simulations show that the simulated (5520.3 mg/L) and measured (5844.1 mg/L) concentrations of Cl are almost consistent with the relative error less than 5%, which supports the evaporation-fold calculation using Br in the no Cl-bearing Dameigou Formation. The significant depletion of SO₄, Ca, Mg, and HCO₃ and enrichment of Na and K of measured formation water in comparison to the 367-fold evaporated rain water are also shown in plots.

### Table 2. Comparison of major ion compositions in measured formation water and calculated formation water; the major ion compositions in calculated formation water are determined from evaporated rainwater (367-fold) and geochemical processes.

| Ions | Rain water (mg/L) | Evaporated rainwater (367-fold) (mM) | ∆C_{Cl} (mM) | ∆C_{Evaporation} (mM) | ∆C_{Calcitization} (mM) | Calculated FW (mM) | Measured FW (mM) |
|------|------------------|------------------------------------|--------------|------------------------|--------------------------|---------------------|------------------|
| Na   | 9.64             | 153.90                             | /            | 32.36                  | /                        | 186.26              | 186.26           |
| K    | 1.01             | 9.39                               | /            | 0.23                   | /                        | 9.62                | 9.62             |
| Ca   | 15.30            | 80.47                              | -26.13       | /                      | -27.14                   | 1.63                | 1.63             |
| Mg   | 3.76             | 29.69                              | /            | -27.14                 | /                        | 2.55                | 2.55             |
| Cl   | 15.02            | 155.50                             | /            | /                      | /                        | 155.50              | 164.62           |
| HCO₃ | 46.39            | 162.60                             | -32.59       | /                      | /                        | -159.68             | 35.52            |
| SO₄  | 14.96            | 26.38                              | -26.13       | /                      | /                        | 0.25                | 0.25             |

**Geochemical Evolution of Formation Water**

**Evaporation**

Natural crystalline bromide minerals are very rare in sedimentary strata [27]. Thus, bromine occurrence in rock-forming minerals is most commonly associated with substitutions of Cl for Br in chlorine-rich minerals such as halite, sodalite and eudialyte because of the similar ionic radii of the two ions (Cl:181 pm, Br: 196 pm) [28]. However, no chlorine-rich minerals have been found in the Dameigou Formation. Furthermore, in the water-rock interactive system, bromide dose does not participate in the geochemical process as a conservative constituent. This suggests that the concentration of Br in formation water is only controlled by the origin of formation water and evaporation. Distinctive Br concentration (11.00 mg/L) in formation water suggests a 367-fold evaporation of the rainwater (0.03 mg/L) beyond saturation stages of calcite, dolomite, and anhydrite (Table 2, Fig. 5).

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**Thermochemical Sulfate Reduction (TSR)**

The concentration of SO₄ in formation water is only 24 mg/L showing a significant depletion (∆SO₄ = 26.13 mM) (Fig. 5g). In addition, the evaporation modeling of rainwater show that anhydrite
was precipitated from liquid phase when the evaporation reached about 200-fold. However, the formation water (367-fold evaporated rainwater) is unsaturated for anhydrite and no anhydrites have been found in the shale formation. This suggests that the depleted SO4 in formation water were not transferred from liquid phase to solid phase by precipitation, but resulted from the in-situ sulfate reduction. Thermochemical sulfate reduction (TSR) and bacterial sulfate reduction (BSR) are the two main desulfidation processes and form similar products and by-products [29-30]. However, the two processes take place in two mutually exclusive thermal regimes, which is the most important factor governing the involved redox-reactions [31]. Previous studies reported that BSR and TSR occur in geological settings with temperatures of 0-80°C which correspond to vitrinite reflectance values of about 0.2-0.3% and 120-200°C, which correspond to vitrinite reflectance values of about 1.0-4.0%, respectively [31]. In addition, the closed system is considered as a specific limit to BSR, because the associated increase in H2S concentrations are toxic to sulfate-reducing bacteria [32]. Hence, the temperature (>120 °C) of the Dameigou Formation from 150 Ma to 120 Ma, the vitrinite reflectance values (1.0-1.3%) of shale, and the closed environment of the formation water indicate that TSR was the main desulphidation according to above discriminating criteria, and resulted in secondary calcite, CO2 and H2S as described in equation 1 [33-34].

The δ34S-H2S value formed by TSR is very close to that of sulfate in the formation. Thus, the δ34S-H2S value in formation water (25.9‰), which was highly altered by TSR, is distinguished from that in shallow groundwater (6.2–8.6‰). This suggests that δ34S-H2S can be a promising tracer of HFFF.

\[
2C + Ca^{2+} + SO_4^{2-} + H_2O \rightarrow CaCO_3 + H_2S + CO_2
\]

**Kaolinization and Illitization of Feldspar**

The formation water has Na and K concentrations of approximately 186.26 mM and 9.62 mM, which is an enrichment of 32.36 mM and 0.23 mM relative to 367-fold evaporated rainwater (153.90 mM and 9.39 mM), respectively. The Dameigou Formation contains neither halite nor sylvite, reflecting the fact that dissolution of plagioclase feldspar and K-feldspar by carbonic acid produced by TSR is a potential source of enriched Na and K in formation water. The mineral stability diagrams (Fig. 6) show that plagioclase feldspar is weathered to illite or kaolinite during most of the formation water’s hydrochemical evolution history. Conversely, K-feldspar dissolved incongruently only in the early stages of hydrochemical evolution (original rainwater to 5-fold evaporated rainwater). These results show that feldspar dissolution leads to the considerable enrichment of Na and slight enrichment of K in formation water. Yuan et al. reported that K in the fluid makes the Gibbs free energy change (ΔG) of feldspar illitization less than that of feldspar kaolinization [36]. Thus, from the perspective of thermodynamics, illite...
would be preferentially precipitated. However, the influence of the kinetic barrier of nucleation results in diagenetic illite by feldspar dissolution occurring in formations at temperatures above 120°C [37]. Shao et al. studied the thermal history of the Middle Jurassic strata in the northern Qaidam Basin using apatite fission track dating and found that the formation temperature dropped rapidly from 120°C since 100-120 Ma due to the rapid compressional uplift of the strata, then remained at between 30°C and 60°C [22]. In addition, the dissolution of K-feldspar only occurred in the early stages of hydrochemical evolution. If the illitization of plagioclase feldspar occurred during the entire hydrochemical evolution period, K in formation water should be depleted relative to 367-fold evaporated rainwater, which is inconsistent with the data. All of these factors suggest that kaolinization of plagioclase feldspar and K-feldspar (Equation 2 to 4) resulted in the enrichment of Na and K in formation water [38].

Feldspar is the principal Sr carrier in shale. Feldspar in the Dameigou Formation is characterized by a high $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.720) [3]. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in formation water is highly influenced by the type of host rock through water-rock interactions [39]. Thus, the high $^{87}\text{Sr}/^{86}\text{Sr}$ value of the formation water (0.713842) relative to rainwater (0.706-0.709), which is the source of the formation water, suggests that dissolution of feldspar dominates the Sr isotope characteristics of formation water. The conventional oil reservoirs are composed of limestone, which are characterized by low $^{87}\text{Sr}/^{86}\text{Sr}$ values (<0.709) [40]. The interaction between limestone and COB led to lowering $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.71121-0.71194) in the COB. Therefore, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, which is distinct from that of COB and shallow groundwater (0.712140-0.712273), can be a potential tracer of HFFF.

$$2\text{KAlSi}_3\text{O}_8 (\text{K-feldspar}) + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{Kaolinite}) + 4\text{SiO}_2 + 2\text{K}^+ + 2\text{HCO}_3^- \quad (2)$$

$$2\text{NaAlSi}_3\text{O}_8 (\text{Albite}) + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{Kaolinite}) + 4\text{SiO}_2 + 2\text{Na}^+ + 2\text{HCO}_3^- \quad (3)$$

$$\text{CaAl}_2\text{Si}_2\text{O}_8 (\text{Anorthite}) + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{Kaolinite}) + \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (4)$$

**Dolomitization and Calcitization**

The formation water has an Mg concentration of approximately 2.55 mM, which is a 27.14 mM depletion relative to 367-fold evaporated rainwater (29.69 mM) obtained by simulation. Dolomitization of carbonates is considered to be the main mechanism for Mg depletion, coupled with Ca enrichment (Equation 5), which is widely reported in many basins [41].

$$\text{CaCO}_3 + \text{Mg}^{2+} \rightarrow \text{CaMg} (\text{CO}_3)_{2} + \text{Ca}^{2+} \quad (5)$$

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} \quad (6)$$
Dissolution of Borate

The δ11B of the formation water (1.1‰) is much higher than that of rainwater (16.7‰) [45] (the source of the formation water), indicating that geochemical processes have depleted the δ11B in formation water, because evaporation cause little B isotope fractionation [46]. Nir et al. found that the δ11B value in the aqueous phase (pH=6.7) increased as a result of the preferential adsorption of $^{11}$B(OH)$_4^-$ on clay minerals in a closed water-rock interactive system [47]. Thus, preferential adsorption could not be the major factor affecting B isotope in formation water. Boron in the crust is present mainly in the form of borate. The δ11B values of borate minerals in non-marine strata range from −30.1‰ to 10.2‰, with an average of 4‰ [49] and the δ11B of formation water (1.1‰) from Dameigou Shale is similar to that of brines (−0‰) in non-marine strata [50]. This suggests that dissolution of borates is dominated by the B isotope during the geochemical evolution of formation water.

The COB, which is originated from rainwater the same as formation water, have higher δ11B values (12-31‰) than that of the formation water. Li et al. reported that COB recharged from rainwater and evolved by the geochemical processes such as leaching and adsorption with surrounding rock and mixing with mantle source of thermal water during hydrologic circulation through deep faults [51]. The δ11B value (12-31‰) of COB approximate the rainwater (16.7‰) indicates that the water-rock interaction and mixing did not considerably affect the δ11B value. The δ11B values of shallow groundwater (24-26‰) which were mainly modified by preferential adsorption after recharging from rainwater, are also distinguishable from formation water. Therefore, the δ11B of the formation water, which is controlled by a distinctive geochemical process, can be used as a tracer of HFFF.

Conclusions

(1) The hydrochemistry (SO$_4^{2-}$/Cl+SO$_4^{2-}$, and Br/Cl) and isotopic compositions (δ2H and δ18O) of the formation water, mineralogical composition of the shale, fossil records in the shale, and sedimentary environment of the shale suggest that the formation water originated from evaporated rainwater.

(2) The major geochemical processes that dominate evolution of the geochemistry of the formation water were TSR, kaolization of plagioclase feldspar, dolomitization, calcitization and borate dissolution, leading to significant enrichment in Na and considerable depletion in Ca, Mg, SO$_4^{2-}$ and HCO$_3$.

(3) The leading geochemical processes have given the formation water a distinctive Br/Cl, Ba/Ca, δ44S-H$_2$S, $^{87}$Sr/$^{86}$Sr and δ11B compared with COB in shallow groundwater. These diagnostic tracers can be used in forensic identification of HFFF release into shallow groundwater.

Acknowledgements

We gratefully acknowledge funding from the National Natural Science Foundation of China (Grant No. 41302192), the Natural Science Foundation of Hebei Province of China (Grant No. D2018504011), the Chinese Academy of Geological Sciences (Grant No. JYYWF20181101), and the Ministry of land and resources of the People’s Republic of China (Grant No. 201411052).

Conflict of Interest

The authors declare no conflict of interest.

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