Genesis of formation water in the northern sedimentary basin of South China Sea: Clues from hydrochemistry and stable isotopes (D, ^{18}O, ^{37}Cl and ^{81}Br)

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ABSTRACT

Formation water is an important fluid in sedimentary basins, hydrogeochemical characteristics of which has important instructions to oil and gas generation and preservation. The South China Sea (SCS) oilfield is a large oil field in China, but research on origin and evolution of formation waters in SCS oilfield has been poorly documented. In this study, major ions, as well as δ^2H, δ^{18}O, δ^{37}Cl and δ^{81}Br in formation waters of two basins (BBWB and ZJKB) of SCS were analyzed to fill the gap. The results showed that the chemical types of formation waters in both basins are Cl–Na. The relationship between Br vs major ions and ^{2}H/^{18}O compositions showed the origin of formation water are mainly ancient seawater. The formation waters are enriched in Ca and Sr, and depleted of Na and Mg compared with seawater mainly owing to albitization of plagioclase, whereas the dolomitization is minor. Comparing to the BBWB, the formation waters in ZJKB were more enriched in ^{2}H and ^{81}Br, and more depleted in ^{37}Cl. The formation waters in ZJKB were stored in a relatively more closed environment and might have been affected more by evaporation, whereas those in BBWB might experience more influence from halite dissolution by ancient precipitation through open fracture structures.

1. Introduction

Formation water (or called oilfield water), produced with crude oil or natural gas in reservoirs, is an important geofluid in sedimentary basins (Kharaka and Hanor, 2004). Understanding the origin and chemical evolution of this fluid has important implications for diagenetic history assessment and reservoir yield management (Hanor and McIntosh, 2007; Bagheri et al., 2014a). The possible origins of formation waters in sedimentary basins include meteoric water, seawater and endogenous water (generally volumetrically minor), and mixture of the waters above (Zhou et al., 1997). The possible processes controlling the salinity of formation waters include evaporative concentration, dissolution of salt minerals and membrane filtration of fine-grained sedimentary rocks, etc. (Kharaka and Hanor, 2004). In addition, water-rock interaction, such as dolomitization of calcite, albitization of plagioclase and ion exchange, are probably important processes responsible for modifying the original chemical and isotopic compositions of formation waters (Carpenter, 1978; Kharaka and Carothers, 1986; Davisson and Criss, 1996; Griffith et al., 2011; Bagheri et al., 2014a).

The geochemical and isotopic signatures of formation waters can provide valuable information on the origin and evolution of them, and further indicating significance to the formation, transport, accumulation and seal of hydrocarbon. Commonly, it is favorable to compare Br versus different ions between seawater evaporation trajectory and formation water to delineate enrichment or depletion of ions and provide the information about dissolution-precipitation of minerals (Stueber and Walter, 1991; Wilson and Long, 1993). δ^2H and δ^{18}O have been proven extremely useful for water sources and mixing (Clayton et al., 1966; Kharaka and Carothers, 1986), and undergo changes during evaporation (Holser, 1979), water-rock interaction, etc.

Chlorine stable isotope can be used to determine the source of salinity, water mixing and water-rock interaction. Some physical processes including salt precipitation (Eggenkamp et al., 1995; Luo et al., 2012, 2014), diffusion (Desaulniers et al., 1986; Eggenkamp and Coleman, 2009), ion filtration (Phillips and Bentley, 1987; Godon et al., 2004; Li et al., 2012) and anion exchange (Musashi et al., 2004, 2007) would result in the change of Cl isotope ratios. The research on geochemical behavior and application of Br stable isotope is still in its early stage, and only a few reports exist on this topic. Since Eggenkamp and Coleman (2000) first reported bromine stable isotopic compositions in
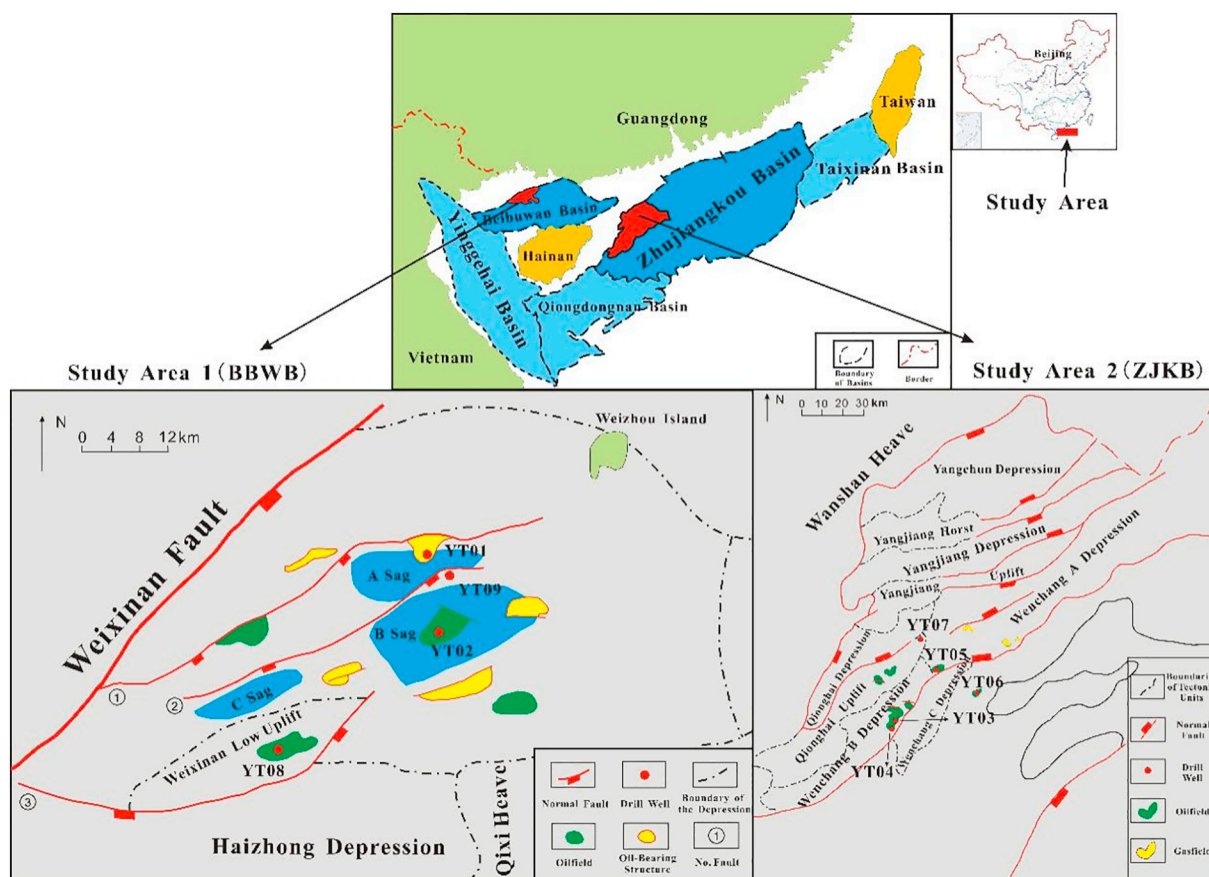
Fig. 1. The locations of all sampling sites where the numbers of water samples were labeled.

natural waters, bromine isotopic compositions of various waters have been researched (Shouakar-Stash et al., 2007a, 2007b; Frape et al., 2007; Stotler et al., 2010; Boschetti et al., 2011; Gwynne et al., 2013; Bagheri et al., 2014b; Chen et al., 2014; Du et al., 2016). The existing overall variation of bromine isotope is up to 4.85‰ (from −1.5‰ to +3.35‰) in hydrosphere, which showed the potential of using Br stable isotope to determine source and evolution of natural waters. Bromine isotopic fractionation could be observed in various geochemical processes, such as diffusion (Eggenkamp and Coleman, 2009), mixing (Shouakar-Stash et al., 2007a), precipitation and dissolution of salt minerals (Eggenkamp et al., 2011), ion filtration (Phillips and Bentley, 1987), water-rock interaction (Stotler et al., 2010), etc. However, bromine isotopic fractionation effect for most of these processes in geological environment are still poorly understood, requiring further investigation and examination.

The sedimentary basins in the north of South China Sea (SCS) are important areas for hydrocarbon enrichment and production in off-shore regions of China, with estimated oil reserves of $11 * 10^8 \, m^3$ (Mi, 2018). Owing to complex geological condition and limited accessibility, investigations on origin and evolution of the formation water in the northern sedimentary basins of SCS has been poorly documented. Only a few studies on formation water in Yinggehai Basin were reported in Chinese literature (Deng and Chen, 1994; Wang et al., 2010).

In present study, hydrochemistry, H and O stable isotopes, as well as Cl and Br stable isotopes were jointly applied to provide insight into the genesis of formation waters in Beibuwan Basin (BBWB) and Zhujiangkou Basin (ZJKB), two representative basins in the north of SCS. The results from this study could assist in guiding hydrocarbon production and exploration in the northern sedimentary basin of SCS.

2. Geological and Hydrogeological Framework

BBWB is a Cenozoic sedimentary basin with the area of 40,000 km^2, which was formed from the continental margin in the north of SCS. The thickness of Cenozoic strata in BBWB is about 7000 m. The faults in BBWB are well-developed, which play an important role during the generation, transport and storage of oil, and the evolution of formation water. Weixinan Depression in the study area is located in the north of the central depression of BBWB. The shale and interbed sandstone in Liushaxiang Group of Neogene are the main source bed and normal reservoir, respectively. The sandstone and mudstone in Weizhou Group of Neogene are the good reservoir and localized caprock, respectively.

ZJKB is one of the largest sedimentary basins in the north of SCS with an area of 150,000 km^2, which extends from west to northeast. Cenozoic strata are widely distributed in the basins with general thickness ranging from 8000 m to 10,000 m, of which clastic rocks are the dominant. The depositional environment of ZJKB transformed gradually from lacustrine facies at bottom to semi-closed and open marine at top. Semi-closed marine sedimentary system has important significance to the oil and gas generation. Zhusan Depression in the study area is located in the west of ZJKB. The mudstone and sandstone in Zhujiang and Zhuhai Group of Palaeogene and Neogene in Zhusan Depression are the primary source bed and reservoir rock, respectively.

3. Sampling and Analytical Methods

Nine formation water samples were collected in marine drilling platform in the north of SCS in January 2013. Among them, four were collected in BBWB and five were collected in ZJKB. The locations of all formation water samples are shown on Fig. 1. All the sample bottles used in the field were pre-cleaned with distilled water in the laboratory

Table 1
Chemical and isotopic compositions of the water samples.

Location	Sample Number	Stratigraphic Unit	Chemical type	TDS	K$^+$	Na$^+$	Ca^{2+}	Mg^{2+}	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$	Br$^-$	I$^-$	Sr^{2+}	δ^{2}H	δ^{18}O	δ^{37}Cl	δ^{81}Br
				g/L	mg/L										‰			
BBWB	YT01	Weizhou Group	Na-Cl	39.50	298.2	11,420	1572.0	252.8	25,506	96	233.0	100.717	1.324	40.209	−34.43	+0.14	+0.24	+0.33
BBWB	YT02	Jiaowei Group	Na-Cl	25.61	304.4	7070	1117.5	148.3	15,739	878	315.5	61.700	0.496	28.054	−24.94	−0.02	−0.08	+0.10
ZJKB	YT03	Zhujiang Group	Na-Cl	31.74	951.0	8985	454.9	170.1	19,444	446	1177.2	81.485	3.135	33.845	−13.06	+0.51	−0.30	+0.48
ZJKB	YT04	Zhuhai Group	Na-Cl	27.27	459.4	8320	508.0	79.0	16,785	336	682.0	63.251	1.495	38.803	−15.40	+0.42	−0.99	+1.46
ZJKB	YT05	Zhujiang Group	Na-Cl	31.05	389.8	9530	535.5	103.3	19,657	144	289.7	74.887	3.436	42.769	−10.52	+0.90	−1.33	+0.89
ZJKB	YT06	Zhujiang Group	Na-Cl	31.99	842.0	9730	294.2	34.0	18,646	153	3161.3	75.754	2.289	2.179	−5.80	+0.15	−0.53	+0.18
ZJKB	YT07	Zhujiang Group	Na-Cl	32.64	344.9	9845	707.5	119.1	20,756	312	224.5	77.798	2.303	43.894	−9.90	+0.51	−0.58	+0.31
BBWB	YT08	Weizhou Group	Na-Cl	25.54	301.1	7225	810.0	419.3	14,924	1248	194.2	63.319	0.309	10.062	−19.94	−0.86	+0.04	+0.17
BBWB	YT09	Weizhou Group	Na-Cl	32.98	339.7	9030	1566.5	221.2	21,092	182	306.4	84.483	4.668	61.167	−25.20	−0.10	−0.36	+0.22
	SW*		Na-Cl	35.20	399.0	10,760	412.0	1294.0	19,350	2712	45	67	0.06	8.1				

SW*: Modern seawater from Hanor (1988).

and rinsed with extracted water at least three times before samples were taken. Each water sample was divided into four portions, which were retained for anion, cation, ^{2}H and ^{18}O, ^{37}Cl and ^{81}Br analysis, respectively. All the water samples were filtered immediately using 0.45 μm membrane filters for analysis of cations and anions. Samples for cation analysis were preserved in acid-washed polyethylene bottles and acidified to pH < 2 with concentrated HNO$_3$. Alkalinity was determined by titration within 24 h of sampling.

The chemical compositions were determined by IC (Metrohm AG, 761COMPACTIC) and ICP-AES (Thermo Electric Com., IRIS Intrepid II XSP) for routine anions and cations, respectively with the detection limits of 0.01 mg/L and 0.001 mg/L in the experimental center of School of Environmental Studies, China University of Geosciences. The concentrations of some trace ions (Br$^-$, I$^-$, Sr^{2+}) were determined by ICP-MS with the detection limit of 0.01 μg/L in National Research Center for Geoanalysis, Chinese Academy of Geological Sciences. The accuracy and precision of all water samples meet the quality requirements, with an ionic balance less than or approximately 10% was chosen owing to the high dilution ratio (100) for measurement.

The hydrogen and oxygen stable isotopes were determined via H$_2$ and CO$_2$, and performed by zinc reduction and CO$_2$-H$_2$O equilibrium, respectively, which took Viena Standard Mean Ocean Water (V-SMOW) as the standard material, with the precision of ± 1‰ and ± 0.1‰, in CNNC Beijing Research Institute of Uranium Geology. The measurements for Cl and Br stable isotopes were carried out via CH$_3$Cl and CH$_3$Br by IRMS (Isotope Ratio Mass Spectrometry) coupled with a GasBench II device (Thermo Scientific, Bremen, Germany) (Liu et al., 2013; Du et al., 2013), in State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences. Chlorine and Bromine stable isotopic analysis took SMOC (Standard Mean Ocean Chloride) and SMOB (Standard Mean Ocean Bromide) as the standard materials with the analytical precisions better than ± 0.08‰ and ± 0.06‰, respectively.

4. Results

The chemical and isotopic compositions of the sampled water are shown in Table 1. Total dissolved solids (TDS) of the studied samples range from 25.54 to 39.50 g/L in BBWB, and 27.27 to 32.64 g/L in ZJKB, which are both close to the value of standard modern seawater (35.20 g/L). The chemical types of all water samples are Cl−Na, in which (Na$^+$ + K$^+$) and Cl$^-$ are more enriched, and Ca^{2+}, Mg^{2+} and SO$_4^{2-}$ are more depleted than those in seawater. Comparing to formation waters in ZJKB, formation waters in BBWB are closer to seawater on Piper Diagram (Fig. 2a). Brine Differentiation Plot (BDP) was used to discriminate between seawater-derived waters and waters from evaporite dissolution (Hounslow, 1995). Waters from evaporite dissolution are clustered towards the center of the plot, i.e., Ca / (Ca + SO$_4$) = Na / (Na + Cl) ≈ 0.5, whereas seawater-derived waters have Ca / (Ca + SO$_4$) ≈ 1 and Na / (Na + Cl) ≤ 0.46 (Boschetti, 2011; Boschetti et al., 2016). In Fig. 2b seawater has Na / (Na + Cl) = 0.27 and Ca / (Ca + SO$_4$) = 0.46, while the formation waters have 0.40 ≤ Na/(Na + Cl) ≤ 0.45 and 0.61 ≤ Ca/(Ca + SO$_4$) ≤ 0.98, indicating that the formation waters are seawater-derived.

The ^{2}H and ^{18}O compositions for all water samples range between −34.43‰ and −5.80‰, and from −0.86‰ to +0.90‰, respectively. The hydrogen isotopes of all studied samples are more depleted than SMOW (Standard Mean Ocean Water), and the δ^{2}H values of formation water samples in BBWB (−34.43‰ to −19.94‰) are generally lower than those in ZJKB (−15.40‰ to −5.80‰). The δ^{18}O values of formation waters between two sedimentary basins are approximate, which are both close to that of SMOW.

The chlorine stable isotopic compositions of all water samples vary from −1.33‰ to +0.24‰, for which the δ^{37}Cl values of formation waters in BBWB (−0.36‰ to +0.24‰) were generally higher than those in ZJKB (−1.33‰ to −0.30‰). The δ^{81}Br values of formation
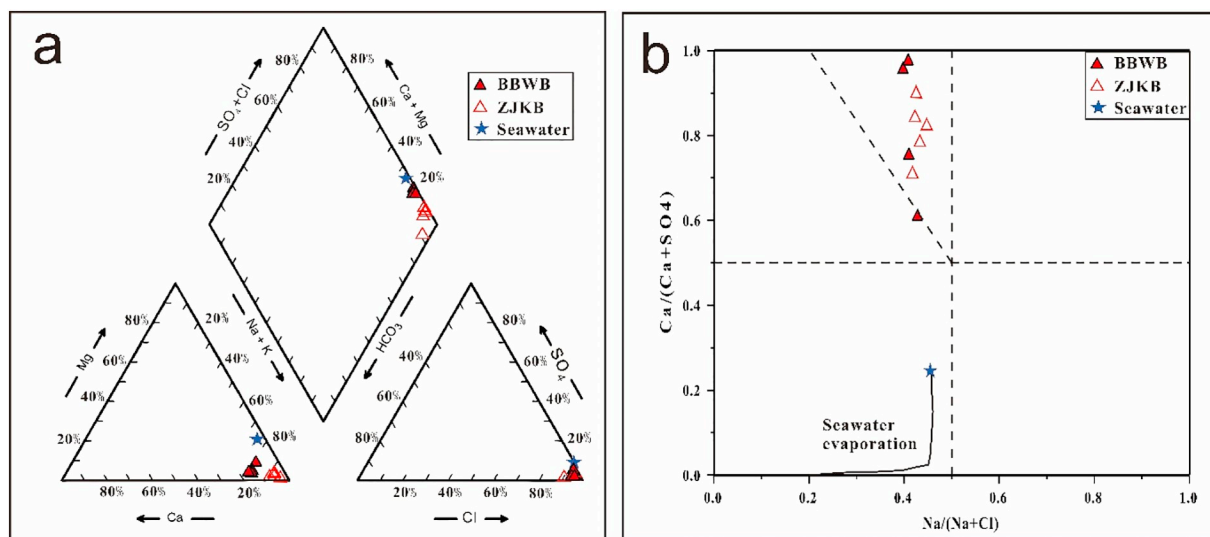
Fig. 2. The Piper Diagram (a) and brine differentiation plot (BDP) (b) for all water samples.

waters range between +0.10‰ and +1.46‰, which are all positive relative to SMOW, and fall within existing $\delta^{81}Br$ range of natural waters (−1.5‰ to +3.35‰). In contrast to Cl stable isotope, formation waters in BBWB exhibit depleted $\delta^{81}Br$ variation (+0.10‰ to +0.33‰) comparing to formation waters in ZJKB (+0.18‰ to +1.46‰).

5. Discussions

Classical hydrogeochemical approaches and isotopic methods were used to determine the origin of water and the source of salinity as follows.

5.1. Classical hydrogeochemical approaches

5.1.1. Characteristic coefficients

The ratios including $\gamma Na^+/\gamma Cl^-$, $100 \times (\gamma SO_4^{2-}/\gamma Cl^-)$, $\gamma Cl^-/\gamma Mg^{2+}$, $\gamma Ca^{2+}/\gamma Mg^{2+}$ and wBr^-/wI^-, which are closely related to genesis of formation water, were applied in analyzing the genesis of studied water samples (Table 2). In groundwater, these coefficients can keep relatively stable, the $\gamma Na^+/\gamma Cl^-$ of all formation waters vary from 0.66 to 0.81, lower than that of modern seawater, which suggests the depletion of sodium. $100 \times (\gamma SO_4^{2-}/\gamma Cl^-)$ of formation waters range between 0.28 and 6.18, indicating that sulfate was exhausted during formation water evolution, probably due to desulphidation. The $\gamma Cl^-/\gamma Mg^{2+}$ of formation waters range between 12.03 and 185.38, with an average of 59.26, much higher than that of normal $\gamma Cl^-/\gamma Mg^{2+}$ coefficient (5.13), which might result from Mg-Ca exchange. $\gamma Ca^{2+}/\gamma Mg^{2+}$ of formation waters range between 1.16 and 5.19, which indicates that

formation waters had been influenced by metamorphism. Commonly, wBr^-/wI^- of the seawater is about 1300. Those of the formation waters range between 18.10 and 204.92, far less than that of normal seawater, indicating that the formation waters might originate from the marine ooze water. Based on the analysis above, the formation waters in both basins might originate from seawater and experienced later water-rock interactions.

5.1.2. Br vs other ions

Br is usually applied to explain the origin of formation water because it usually occurs in solution and nearly does not participate in diagenetic reactions with other minerals. During seawater evaporation, the concentration of bromide in the residual brine increases until the precipitation of potash (Zherebtsova and Volkova, 1966). Seawater evaporation trajectory (SET) is extensively used to analyze the origin of salinity in the sedimentary basins (Carpenter, 1978; Bottomley et al., 1999; Kharaka and Hanor, 2004; Cartwright et al., 2006), thus providing the information of the dissolution and precipitation of minerals, and the source and evolution of formation waters (Stueber and Walter, 1991). The concentrations of Ca^{2+}, Mg^{2+}, Na^+ and Sr^{2+} are also significantly controlled by water-rock interaction. The relationships between Cl and Br, Ca and Br, Mg and Br, Na and Br, Sr and Br for formation waters in our study area coupled with those in North China Plain (NCP) and Siberian Platform, Russia are shown on Fig. 3.

On the relationship between Cl and Br (Fig. 3a), formation waters from NCP located on the upper left of SET may be interpreted as a mixture of seawater and meteoric water (Chen et al., 2014). The samples in the Siberian Platform which are located on the top right of the

Table 2
The results of characteristic coefficients for the studied formation waters (where γ is the meq/L and w is the mg/L).

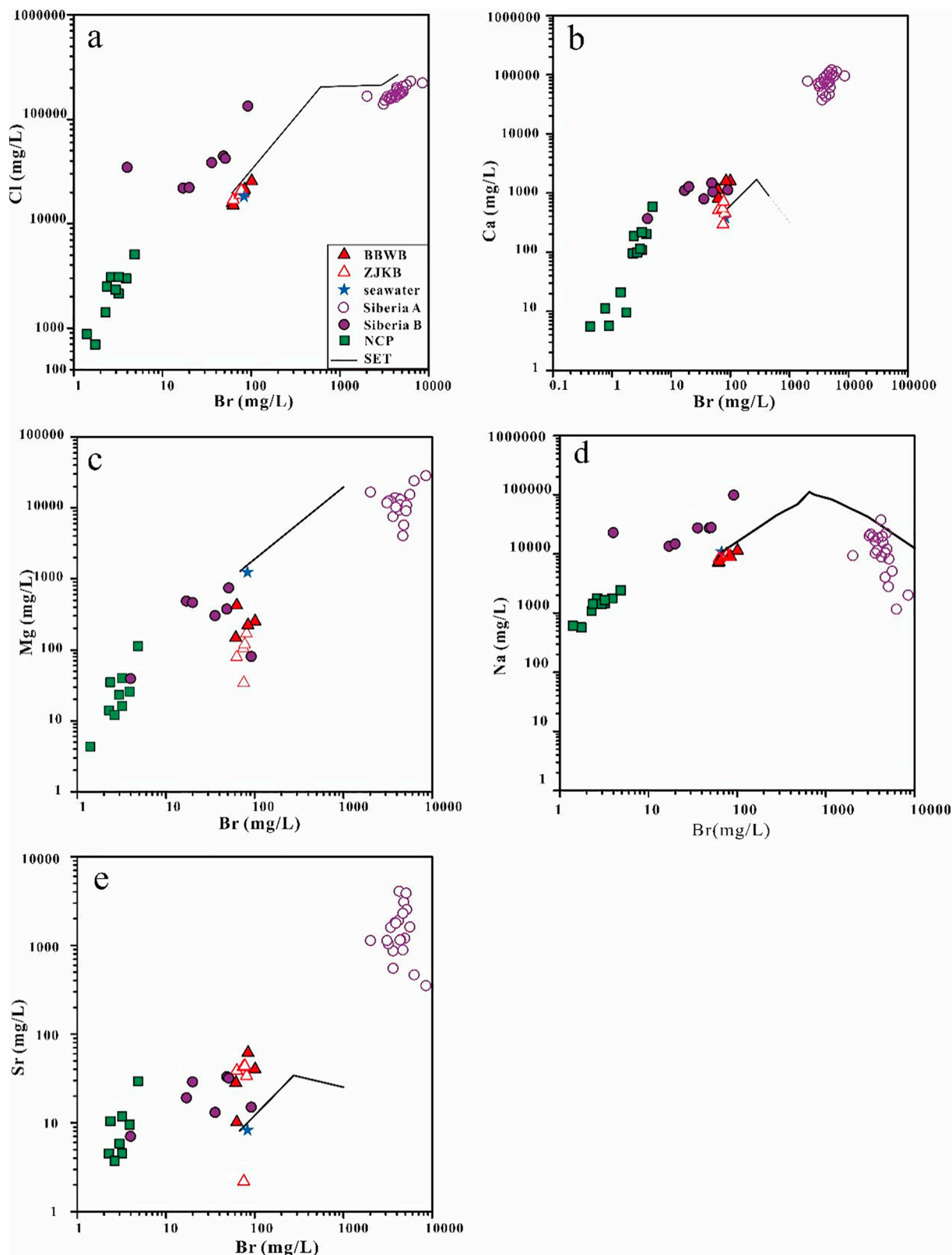| Sample number	$\gamma Na^+/\gamma Cl^-$	$100 \times (\gamma SO_4^{2-}/\gamma Cl^-)$	$\gamma Cl^-/\gamma Mg^{2+}$	$\gamma Ca^{2+}/\gamma Mg^{2+}$	wBr^-/wI^-
YT01	0.69	0.28	34.11	3.73	76.07
YT02	0.69	4.13	35.87	4.52	124.40
YT03	0.71	1.70	38.64	1.60	25.99
YT04	0.77	1.48	71.82	3.86	42.31
YT05	0.75	0.54	64.32	3.11	21.79
YT06	0.81	0.61	185.38	5.19	33.09
YT07	0.73	1.11	58.91	3.56	33.78
YT08	0.75	6.18	12.03	1.16	204.92
YT09	0.66	0.64	32.23	4.25	18.10
SW*	0.86	10.37	5.05	0.19	1116.67

Fig. 3. The concentration relationships of bromide versus major ions(Cl, Ca, Mg, Sr and Na)where the evaporation line of seawater is from the results given by Shouakar-Stash (2008). (Siberia A: the Ca-Cl brine which is the residual of an evaporated paleoseawater in the Siberian Platform, Russia; Siberia B: the Na-Cl brine that is derived mainly from halite dissolution in the Siberian Platform, Russia; NCP: the formation water that is derived from meteoric water in the NCP, China).

SET (Siberia A) are probably derived from seawater and experienced long time evaporation; and those plotted above the SET (Siberia B) are derived mainly from halite dissolution (Shouakar-Stash et al., 2007a).

The formation water samples of BBWB and ZJKB are located near seawater and on the SET, illustrating that the formation waters in both basins have the same origin, i.e., seawater. Fig. 3b and c shows that the
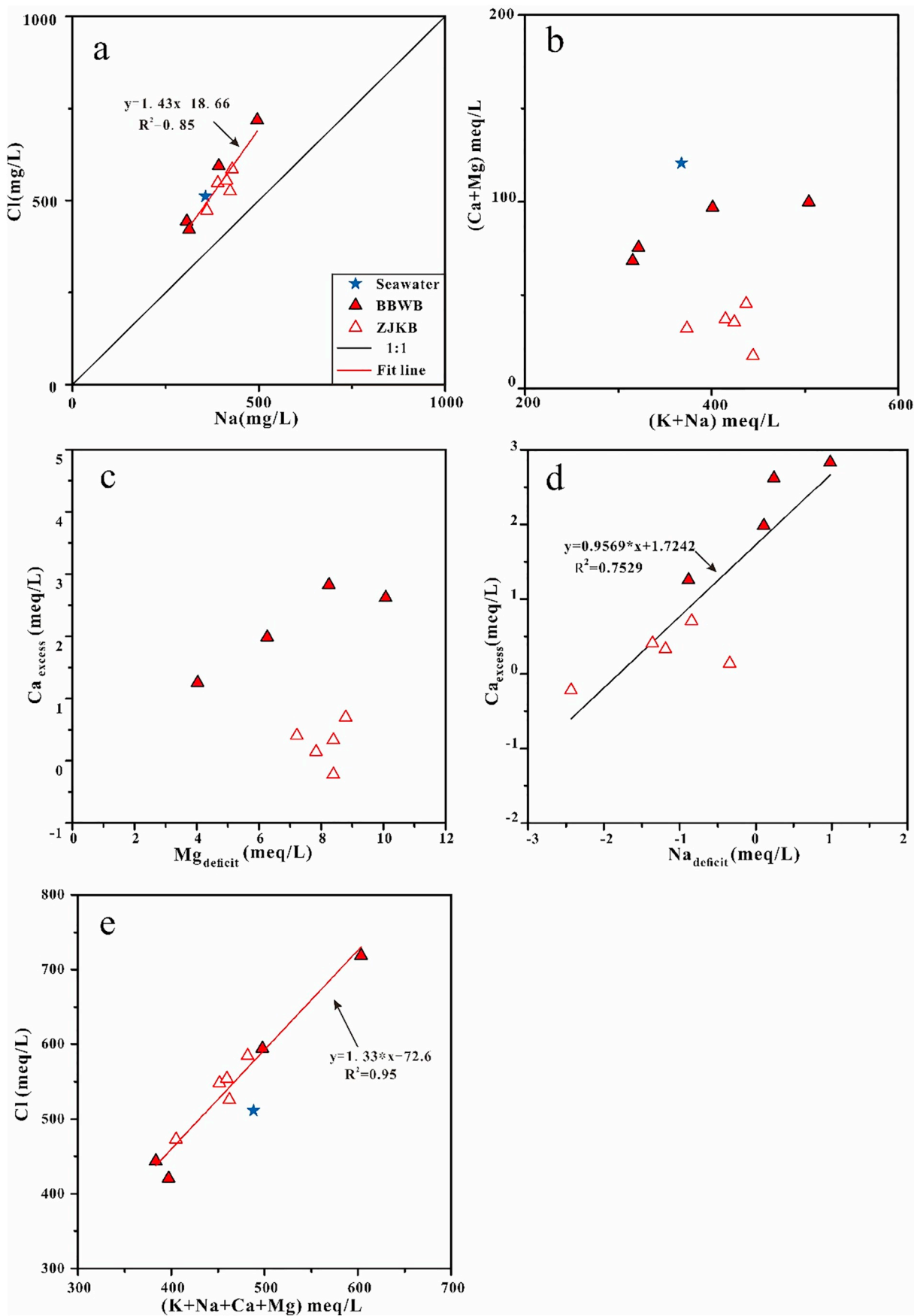
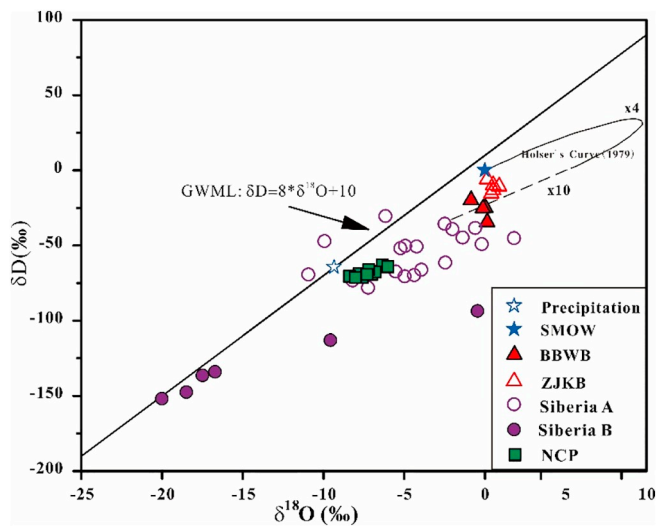**Fig. 4.** Relationships of some typical chemical parameters of formation water samples.

Fig. 5. Stable isotopic composition (δ^2H and $\delta^{18}O$) of water samples, shown relative to the Global Meteoric Water Line (GMWL) and Standard Mean Ocean Water (SMOW).

formation water in both basins are enriched in Ca and depleted in Mg. The enrichment of Ca^{2+} and depletion of Mg^{2+} in formation water is generally attributed to dolomitization of calcite, in which Ca^{2+} content will increase and Mg^{2+} will be reduced: $2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+}$. In addition, Ca^{2+} enrichment in formation water may be also attributed to cation exchange, which can be supported by the depletion of Na^+ in formation water (Fig. 3d). Fig. 3e shows that most samples in study area are more enriched in Sr^{2+} comparing to seawater. In our study area, surrounding rock is mainly siliceous rock containing much plagioclase, so dissolution of plagioclase is probably the main source of Sr^{2+} in formation water. In addition, Sr^{2+} enrichment in formation water may be also attributed to dolomitization of calcite.

5.1.3. Other relationships

The Cl/Na ratio of water in which salinity mainly originates from the dissolution of halite is about 1. However, formation water samples in the study area plot along the line with the slope of 1.43 (Fig. 4a). This suggests that the salinity was not only affected by halite dissolution, but also some other geochemical processes responsible for the deviation from the 1:1 line. The possible processes include: (1) cation exchange or other water-rock interactions which decrease the concentration of Na, (2) dissolution of other Cl-bearing minerals which increase the concentration of Cl. Cation exchange would remove K and Na and increase the concentration of Ca and Mg (Davisson and Criss, 1996; Martel et al., 2001; Bagheri et al., 2014a; Liu et al., 2016). The little correlation between Na + K and Ca + Mg (Fig. 4b) indicates that this process could not be the main process for the depletion in Na^+.

Dolomitization of calcite and albitization of plagioclase would decrease the concentration of Mg and Na, respectively, and both increase Ca concentration. The relationship among excess Ca, deficit Na and deficit Mg concentrations are calculated using the following equations (Davisson and Criss, 1996; Bagheri et al., 2014b):
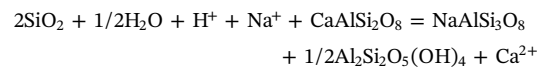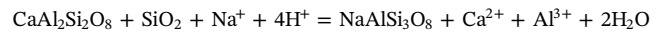
$$Ca_{excess} = [Ca_{meas} - (Ca/Cl)_{SW} * Cl_{meas}] * 2/40.08$$

$$Na_{deficit} = [((Na/Cl)_{SW} * Cl_{meas}) - Na_{meas}] * 1/22.99$$

$$Mg_{deficit} = [((Mg/Cl)_{SW} * Cl_{meas}) - Mg_{meas}] * 2/24.3$$

where ion concentrations of seawater (SW) and water samples (meas) are in mg/L, and Ca_{excess}, $Na_{deficit}$ and $Mg_{deficit}$ are in meq/L, respectively. The diagram of $Ca_{excess} - Na_{deficit}$ can be used to indicate the processes of albitization, while the $Ca_{excess} - Mg_{deficit}$ diagram can be used to indicate the processes of dolomitization (Boles, 1982; Davisson

and Criss, 1996; Martel et al., 2001; Bagheri et al., 2014b). If the formation waters were altered by dolomitization, linear relationship between Ca_{excess} and $Mg_{deficit}$ would be expected, which is not the case in Fig. 4c, indicating that dolomitization of calcite may be not the main reason for the enrichment of Ca. Fig. 4d shows that Ca_{excess} and $Na_{deficit}$ are well correlated for the formation waters, the slope of which indicates a net cation exchange ratio of 2 Na for 1 Ca, suggesting that Ca-rich formation waters had been modified through albitization of plagioclase. The possible exchange processes are the following (Merino, 1975; Boles, 1982; Davisson and Criss, 1996; Martel et al., 2001):

$$CaAl_2Si_2O_8 + SiO_2 + Na^+ + 4H^+ = NaAlSi_3O_8 + Ca^{2+} + Al^{3+} + 2H_2O$$

$$2SiO_2 + 1/2H_2O + H^+ + Na^+ + CaAlSi_2O_8 = NaAlSi_3O_8 + 1/2Al_2Si_2O_5(OH)_4 + Ca^{2+}$$

In addition, the formation water samples were plotted on a fitting line with the slope of 1.33 ($R^2 = 0.95$) in the diagram of (Na + K + Ca + Mg) versus Cl (Fig. 4e). This indicates that the salinity in formation waters were from the dissolution of halite or other Cl-bearing minerals (Liu et al., 2016).

5.2. Stable isotopes

5.2.1. δ^2H and $\delta^{18}O$ signatures

The δ^2H values were plotted against $\delta^{18}O$ values on Fig. 5, along with the global meteoric water line (GMWL) and seawater evaporation trajectory line (SET). During the evaporation process, both ^2H and ^{18}O of seawater are enriched. Once seawater is at an evaporation degree of four times, the situation would be started with a reversal trend (Holser, 1979). The salinity of the water samples are close to the seawater, which indicates that the samples have not passed the halite saturation stage that occurs at TDS > 150 g/L (Sharp, 2007; Boschetti, 2011; Boschetti et al., 2016).

The hydrogen and oxygen isotope compositions of formation samples ranged between −34.43‰ and −5.8‰, from −0.86‰ to +0.90‰, respectively. Among them, the hydrogen and oxygen isotopic composition of water samples in BBWB ranged from −34.43‰ to −19.94‰, and between −0.86‰ and +0.14‰, respectively. The hydrogen and oxygen isotopic composition of ZJKB ranged from −15.40‰ to −5.80‰, and between +0.15‰ to +0.90‰, respectively. The Group A samples of Siberian Platform from Shouakar-Stash et al. (2007a) plotted further down the estimated curve of Holser (1979) for concentrating seawater 10 times by evaporation, supporting evaporation as the major evolution from the original water. The Group B samples which derived from halite dissolution were deviated from the GMWL (Shouakar-Stash et al., 2007a). The formation waters of NCP deviated to the lower right of the GMWL and the origin of the formation waters were meteoric water, and the enrichment in ^2H and ^{18}O was explained by evaporation (Chen et al., 2014). The TDS of formation waters in our study area were much lower than those of the Group A samples, suggesting that the hydrogen and oxygen isotope compositions of formation water samples could not be the result of intensive evaporation. The water-rock interaction only cause a positive $\delta^{18}O$ shift, while low δ^2H and $\delta^{18}O$ values may be resulted from mixing with meteoric water. The hydrogen and oxygen isotope compositions of meteoric water of the study area are −65.2‰ and −9.47‰ (Liu et al., 2008). The $\delta^{18}O$ values of formation waters were close to seawater, whereas the δ^2H values of those were lower comparing to seawater. It was likely that water-rock interaction and mixing with meteoric water have occurred.

According to the geological history of the study area, both basins experienced tectonic processes since late Oligocene, producing large amounts of fractures, which made it possible that ancient atmospheric precipitation recharged formation water aquifers. Compared with the BBWB, the samples in the ZJKB were more enriched in ^2H, lending support that the sedimentary environment of ZJKB was more closed and
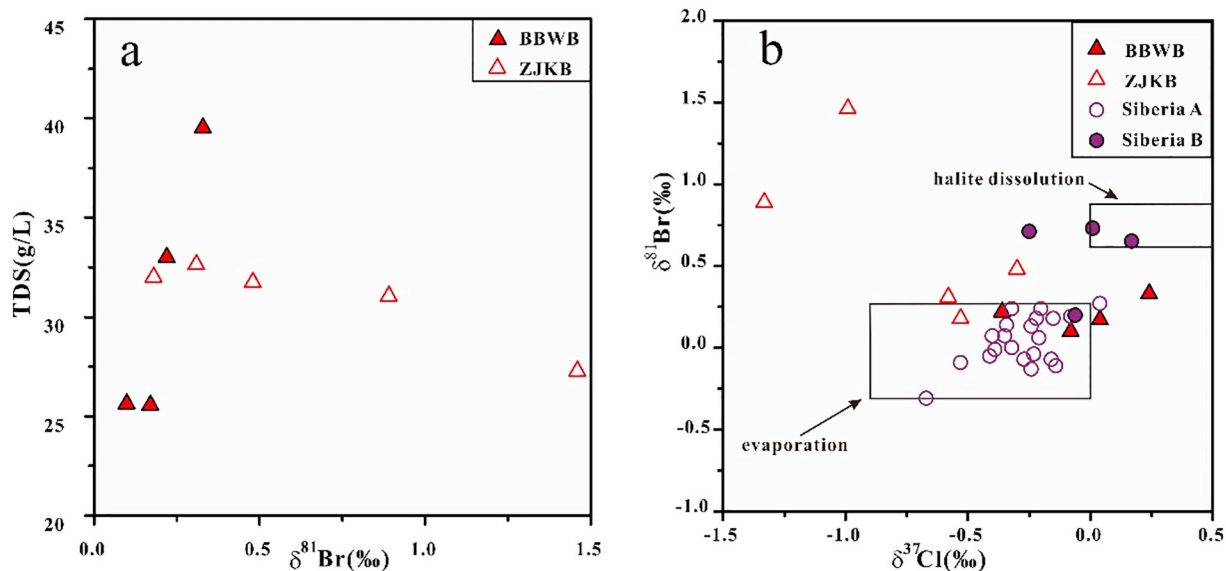
Fig. 6. a Relationship of TDS and $\delta^{81}Br$ for the samples in the study area.
b Relationship of $\delta^{37}Cl$ and $\delta^{81}Br$ for the different kind of samples.
(The $\delta^{37}Cl$ values of evaporated seawater and halite dissolution were from Eggenkamp et al. (1995), Eastoe et al. (1999) and Bagheri et al. (2014a). The $\delta^{81}Br$ values in formation waters that originated from evaporated seawater and the dissolution of halite were from Eggenkamp and Coleman (2000), Shouakar-Stash et al. (2007a), Shouakar-Stash (2008), Stotler et al. (2010), Boschetti et al. (2011b) and Bagheri et al. (2014a).)

the meteoric water had a less influence on ZJKB.

5.2.2. $\delta^{37}Cl$ and $\delta^{81}Br$ signatures

The $\delta^{37}Cl$ values and the relationship between $\delta^{37}Cl$ and Cl^- concentrations can be used to determine the source of salinity. Generally, $\delta^{37}Cl$ values of most natural material vary from -2.00 to $+2.00‰$ (Eggenkamp et al., 1995; Volpe et al., 1998; Eastoe et al., 1999; Bagheri et al., 2014a; Liu et al., 2016). There are various $\delta^{37}Cl$ values owing to different sources: $\delta^{37}Cl$ values are from $-0.9‰$ to $0‰$ for evaporated seawater and from $0‰$ to $+0.5‰$ for water affected by halite dissolution (Eggenkamp et al., 1995; Eastoe et al., 1999; Bagheri et al., 2014a). Only a few studies have been carried out on $\delta^{81}Br$ variations in formation waters. The $\delta^{81}Br$ values in formation waters that originated from evaporated seawater and the dissolution of halite, ranged from $-0.31‰$ to $+0.27‰$ and $+0.62‰$ to $+0.88‰$ (Eggenkamp and Coleman, 2000; Shouakar-Stash et al., 2007a; Shouakar-Stash, 2008; Stotler et al., 2010; Boschetti et al., 2011; Bagheri et al., 2014a), respectively.

The $\delta^{37}Cl$ values fall between $-1.33‰$ and $+0.24‰$ (variation of 1.57‰) and $\delta^{81}Br$ values are between $+0.1‰$ and $+1.46‰$ (variation of 1.45‰). The TDS versus $\delta^{81}Br$ values were shown on Fig. 6a. It is clear that the water samples in both two basins of our study had different Br isotopic characteristics from those in the Siberian Platform. The negative correlation between TDS and $\delta^{81}Br$ values was significant for the formation waters of ZJKB, while water samples in BBWB showed a significant positive relationships between TDS and $\delta^{81}Br$ values.

It can be seen that the water samples in BBWB and ZJKB show the negative correlation between $\delta^{37}Cl$ and $\delta^{81}Br$. The $\delta^{37}Cl$ of BBWB is higher than those of formation waters in ZJKB, but the $\delta^{81}Br$ show the opposite characteristics. The samples were divided and classified according to their $\delta^{37}Cl$ and $\delta^{81}Br$ signature. In terms of origin, halite dissolution produces much higher $\delta^{37}Cl$ and $\delta^{81}Br$ values than those found in present seawater and evaporate formation waters (Fig. 6b). The samples of BBWB have a trend approaching to the area for halite dissolution, indicating more influence from halite dissolution. Compared with the samples in BBWB, the samples of ZJKB are more enriched in $\delta^{81}Br$ and depleted in $\delta^{37}Cl$. This may suggests that the sedimentary environment of ZJKB is more closed and the formation waters had experienced more degree of evaporation.

6. Conclusions

Based on hydrogeochemistry and stable isotopes (D, ^{18}O, ^{37}Cl and ^{81}Br), accompanied with geological background, origin and evolution of formation waters from two basins in SCS were discussed. There are some similarities for the genesis of formation waters between BBWB and ZJKB. The TDS of formation waters in both basins are close to the value of standard modern seawater (35.20 g/L) and the chemical types are both Na-Cl. Formation waters in two basins both mainly originated from marine ooze water. The composition of original formation water had been modified by later water-rock interactions, such as albitization of plagioclase, desulphidation, etc.

Comparing to the BBWB, the samples in ZJKB were more enriched in ^2H and ^{81}Br, and more depleted in ^{37}Cl. The formation waters in ZJKB were stored in a more closed environment and might have been affected more by evaporation, whereas those in BBWB might experience more influence from halite dissolution by ancient precipitation through open fracture structures.

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