

# Chemical and isotopic constrains on the origin of brine and saline groundwater in Hetao plain, Inner Mongolia

Jun Liu<sup>1</sup> · Zongyu Chen<sup>1</sup> · Lijuan Wang<sup>1</sup> · Yilong Zhang<sup>1</sup> · Zhenghong Li<sup>1</sup> · Jiaming Xu<sup>1</sup> · Yurong Peng<sup>1</sup>

Received: 21 January 2016 / Accepted: 3 April 2016 / Published online: 15 April 2016  
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**Abstract** The origin and evolution of brine and saline groundwater have always been a challenged work for geochemists and hydrogeologists. Chemical and isotopic data of brine and saline waters were used to trace the sources of salinity and therefore to understand the transport mechanisms of groundwater in Xishanzui, Inner Mongolia. Both Cl/Br (molar) versus Na/Br (molar) and Cl (meq/L) versus Na (meq/L) indicated that salinity was from halite dissolution or at least a significant impact by halite dissolution. The logarithmic plot of the concentration trends of Cl (mg/L) versus Br (mg/L) for the evaporation of seawater and the Qinghai Salt Lake showed that the terrestrial halite dissolution was the dominated contribution for the salinity of this brine. The stable isotope ratios of hydrogen and oxygen suggested that the origin of brine was from paleorecharge water which experienced mixing of modern water in shallow aquifer.  $\delta^{37}\text{Cl}$  values ranged from  $-0.02$  to  $3.43\text{‰}$  (SMOC), and reflecting mixing of different sources. The Cl isotopic compositions suggest that the dissolution of halite by paleometeoric water had a great contribution to the salinity of brine, and the contributions of the residual seawater and the dissolution of halite by the Yellow River water could be excluded.

**Keywords** Stable isotope · Ratios of chemical compositions · Source of salinity · Brine and saline water · Conceptual model · Water quality

Responsible editor: Kenneth Mei Yee Leung

✉ Zongyu Chen  
chenzy88@hotmail.com

<sup>1</sup> Laboratory of Groundwater Sciences and Engineering, Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang, Hebei, China

## Introduction

Groundwater salinization is one of the most conspicuous phenomena of water quality degradation, and it is more serious in arid and semiarid regions where groundwater is the main source for water supply in the local area (e.g., Ghassemi et al. 1995; Vengosh 2003; Carmelita et al. 2010; Al-Harbi et al. 2014; Yamanaka et al. 2014; Kwong et al. 2015). The increasing demands for water have created tremendous pressures on water resources that have resulted in lowering water level and increasing salinization. Concerns for the sustainable management of groundwater resources require sufficient knowledge on the distribution of fresh and saline groundwater and the processes affecting groundwater salinization (Langman 2008). However, the origin of water and solutes of brines in sedimentary basin remains a controversial aspect of sedimentary and hydrogeochemistry (Stueber and Walter 1991) due to the various sources of groundwater salinity such as natural saline groundwater; halite dissolution; seawater intrusion; oil and gas field brine; domestic, agricultural, and industrial effluents; and road salts (Park et al. 2005; Salem and El-horiny 2014). To successfully describe groundwater salinization processes, methods detailed characterization and identification of the source of salinity and the origin of waters is required (Kura et al. 2014; Bouzourra et al. 2015).

Chemical and isotopic compositions of different kinds of waters such as brine, lake water, river water, and spring water exposed in the surrounding salt sediments are good indicators for understanding the origin of brine and saline groundwater. For instance, Cl and Br ions can be applied as indicators of water sources and rock interactions because they are commonly considered to be conservative tracers (Carpenter 1978; Edmunds 1996; Stotler et al. 2010). Oxygen and hydrogen isotopic ratios can provide information regarding the source of water molecules and effects of water-rock interactions

(Moldovanyi et al. 1993; Grobe et al. 2000). The fundamental relationships between  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , and  $\delta^{18}\text{O}$  and salinity can be used to identify different salinization pathways (Gaye 2001). Chlorine stable isotopes are mainly used to define salinity sources, mixing of different waters, and water-rock interaction (Kaufmann 1984; Kaufmann et al. 1992; Eastoe and Guilbert 1992; Eggenkamp and Coleman 1998; Eastoe et al. 2001; Zhang et al. 2007; Bagheri et al. 2014). However, many geochemical processes, such as water-rock interaction, ion exchange, and mineral alteration, may influence the concentration of chemical compositions in the process in groundwater salinization. It is often ambiguous to differentiate the sources of salinity from major ion chemistry (Tellam and Lloyd 1986) without information from isotopes. Multiple isotope approach can provide unique information on sources of groundwater salinity (Gaye 2001). Previous studies suggested that the stable Cl isotope ratio together with other geochemical parameters was a useful tool to differentiate the sources of solute and to trace the transport mechanisms of solute (e.g., Eggenkamp 1994; Eastoe et al. 1999; Hendry et al. 2000; Godon et al. 2004; Zhang et al. 2007).

The terrestrial brine with total dissolved solid (TDS) up to 90 g/L was found at the depth of 5–50 m in Xishanzui area, Inner Mongolia. Some studies (Liu 2009; Yu et al. 2010; Xiao et al. 2012) on geochemistry suggested that brine originated from deep aquifer flowing upward through fractures. But, they did not give any discussions on the occurrence and genesis of brine in deep aquifer because of the absence of isotopic data. The results of geochemical modeling by PHREEQC (Liu 2009) suggested the salinity originated not only from halite dissolution, but also from other sources. Unluckily, the sources have not been well demonstrated yet. The origin of shallow brine is still an unanswered question. The main objectives of this study are to differentiate the sources of salinity and trace the origin and movement of brine by using Cl, H, and O stable isotopes and chemical data.

## Study area

### Regional geological and hydrogeological setting

The study area is located at the eastern part of Hetao plain, which lies in the western part of Inner Mongolia. The Hetao plain, covering a total area of 13,040 km<sup>2</sup> with total population about one million, is bounded by the Langshan Mountains in the north and the Yellow River in the south (Figs. 1 and 2). Geographically, the mean altitude of Hetao plain ranges from 1025 to 1040 m a.s.l., and the terrain is high in the SW and low in the NE. The plain consists of alluvial plain and alluvial-lacustrine plain. The alluvial fans occur in the piedmont plain and extend from the mountain front to the flat plain.

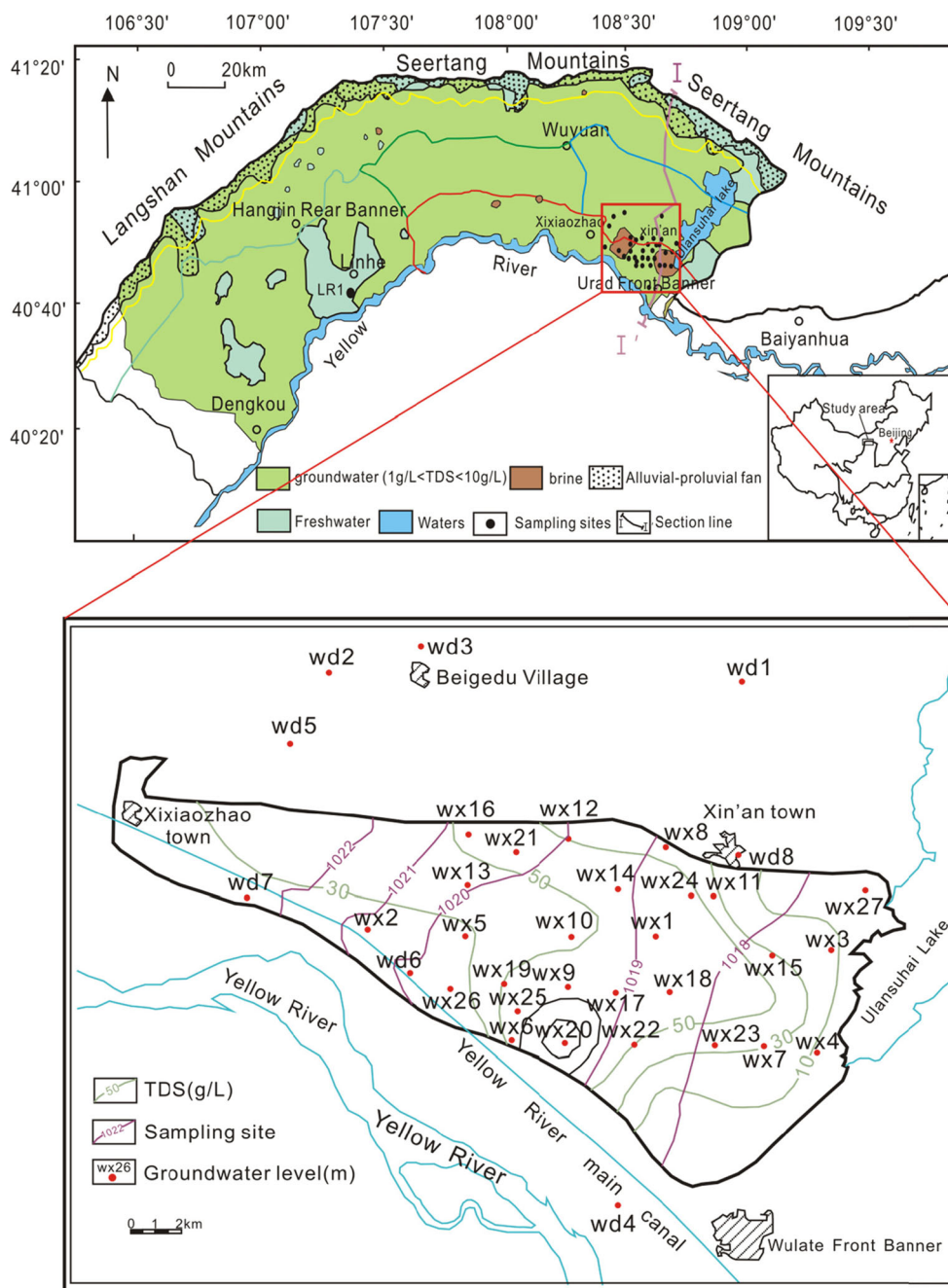
The shallow saline waters and brine deposits are located at alluvial-lacustrine plain in Xishanzui, which is surrounded by Yellow River to the south and Ulansuhai Lake to the east (Fig. 1). The climate is continental and semiarid, with a low annual mean precipitation of 130–220 mm and high evaporation of 2000–2500 mm (Zhu et al. 2015). Precipitation mainly concentrates in July and August, accounting for 56.3 % of the total rainfall (Tong et al. 2014). The annual mean temperature ranges from 5.6 to 7.8 °C, and the relative humidity is about 48.5 %. The Yellow River flows across the plain from west to east.

The Langshan Mountains are mainly composed of a metamorphic complex (slate, gneiss, and marble), generally of Jurassic to Cretaceous age, which is folded and fractured (Li and Li 1994). Hetao basin is also a Cenozoic rift basin which is controlled by series of faults (F1–F7) striking NE–SW and NW–SE (Fig. 2). The bedrock is Precambrian granitic gneiss overlying Cretaceous, Tertiary, and Quaternary formations. The overlying Tertiary formation is fluvio-lacustrine sediments. It consists of red sandstone and mudstone with scattered gypsum or evaporate. The Tertiary sediments often occur in the conditions with great amounts of salinity. The Quaternary formation is a thick lacustrine-fluvial deposit consisting of gravel, sand, and silt. The thickness ranges from 500 to 1500 m in the southeast and from 1000 to 2400 m in the northwest. Mirabilite deposits were found within the middle Pleistocene formation in the south of Baotou (Fig. 2).

There are three uplifts and depressions from west to east, which were successively named Langshan uplift, Linhe depression, Xishanzui uplifted, Baiyanhua depression, Baotou uplifted, and Huhe depression (Fig. 2). The Xishanzui uplifted zone (area of brine deposits) is bordered by faults in the north and south and extends about 100 km from west to east and 12 km from north to south, covering an area of 1200 km<sup>2</sup>. The depth to the bedrock is 1–2 km in the eastern and increases to 2–4 km toward the western part. The geological formations from Cretaceous, Tertiary, and Quaternary were overlain the bedrock (Fig. 3).

The regional aquifer system consists of Quaternary and Neogene aquifers (Fig. 3). The Quaternary aquifer system is composed of alluvial and lacustrine deposits and changes from a thick single layer with coarse deposits in the piedmont to a multi-layer confined aquifer system in the central plain. The single-layer aquifer consists of sandy gravel with pebble and coarse-medium sand with gravel. The thickness of the aquifer is about 50–80 m in the upper part of alluvial fan and 20–40 m in the distal fan. Groundwater changes from HCO<sub>3</sub>-Ca.Na (Ca.Mg) with the TDS of 0.5 g/L to HCO<sub>3</sub>.Cl-Na.Ca or Cl.HCO<sub>3</sub>-Na.Mg with the TDS of 3.0 g/L. The multi-layer aquifers in the alluvial lacustrine plain are mainly

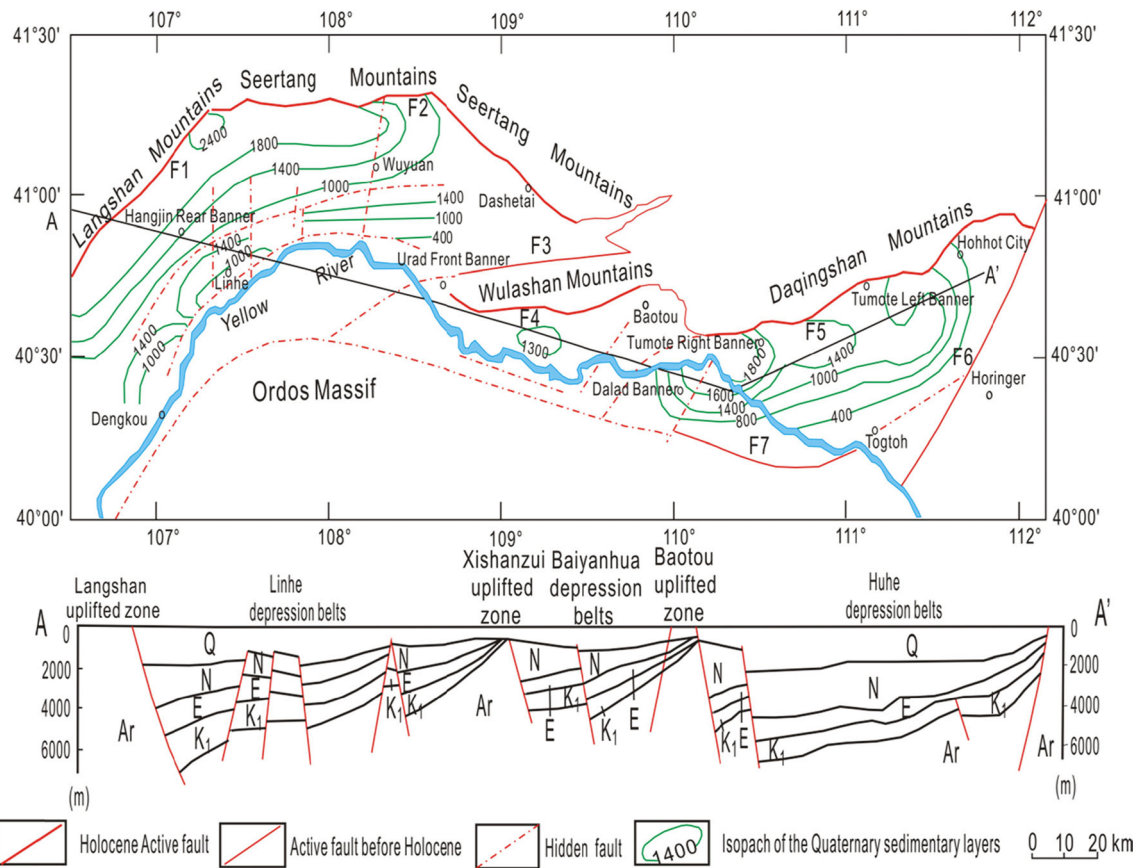
**Fig. 1** Study area and sampling sites



composed of medium-fine sand, fine sand, and silt-fine sand. Medium-coarse sand with gravel occasionally occurs in some areas. The depth to the roof of aquifer is less than 20 m. And, the floor of aquifer is 80~100 m in the eastern part, 150~300 m in the western part, 30~80 m in the southern part, and 100~200 m in the northern part. Accordingly, the thickness of aquifers increases from east (60–80 m) to west (150–240 m) and from south (20–60 m) to north (100–200 m). The water type is mainly Cl-Na with the TDS of 0.4~60.5 g/L. The maximum value of TDS was found in the south Xishanzui uplift zone where the area of the present study has brine deposits. The Neogene aquifer is mainly composed of fine

sandstone with a thickness up to 300 m. A well-penetrated aquifer produced geothermal water of Cl-Na type with the TDS of 47.0 g/L and the temperature of 57.0 °C.

The contributions of recharge to aquifers are successively as follows: the seepage of river and irrigation ditch, the infiltration of irrigation water from the Yellow River, the infiltration of local precipitation, and the lateral flows from mountain area. Naturally, groundwater flows from the piedmont to the lowland. And, the regional groundwater flows from the west to east and discharges into the Ulansuhai Lake. Groundwater for potable use in the rural areas is abstracted mainly from the shallow aquifer with depths less than 30 m (Deng et al. 2009).



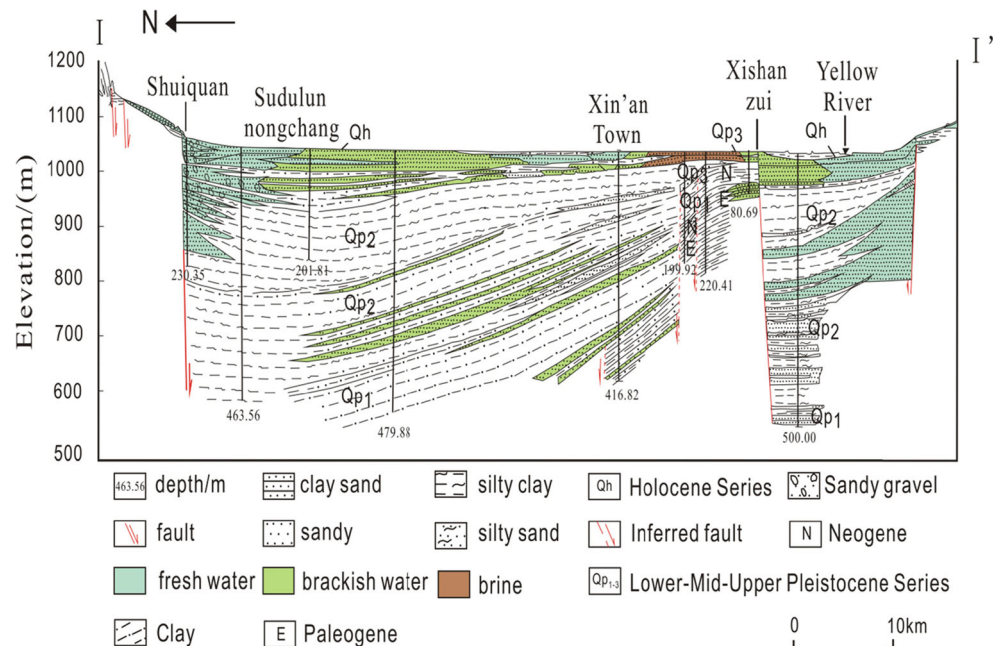
**Fig. 2** Geological cross section along the line A–A' of quaternary aquifers in Hetao basin (modified from Chen, 2002)

**Shallow saline waters and brine deposits in Xishanzui**

The shallow saline water and brine deposits occupy an area of 32 km long and 3–12 km wide, covering a total area of about

238.8 km<sup>2</sup>. It is surrounded by Yellow River to the south and Ulansuhai Lake to the east (Fig. 1). The aquifer contained saline water, and brine is the Upper Pleistocene formation which is mainly composed of medium to fine sand. The overlying

**Fig. 3** Hydrogeological section along the line I–I' in Hetao Basin





**Table 1** Chemical and isotopic compositions of groundwater samples in Xishanzui area

Sample no.	Well depth (m)	Length of filter (m)	K <sup>+</sup> (mg/L)	Na <sup>+</sup> (mg/L)	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)	Br <sup>-</sup> (mg/L)	pH	TDS (g/L)	D (‰)	<sup>18</sup> O (‰)	<sup>3</sup> H (TU)	<sup>37</sup> Cl (‰)	d-excess (‰)
wx1	36.80	12	19.90	5500.0	541.1	705.30	9573.4	2521.7	533.9	4.00	7.42	19.1	-65	-7.7	1.7	-0.02	-3.4
wx2	34.70	6	11.70	8800.0	470.9	760.00	12,764.5	3026.1	566.3	20.00	7.56	26.2	-66	-7.5	13.4	1.86	-6
wx3	24.95	9	10.20	6880.1	751.5	2006.40	13,119.1	5163.5	518.7	16.00	7.33	28.2	-73	-9.1	5	0.2	-0.2
wx4	21.00	18	59.80	7999.9	1493.0	948.50	16,664.8	1441.0	128.1	40.00	7.08	28.7	-82	-9.5	<1.0	0.64	-6
wx5	31.00	24	9.00	9400.1	831.7	845.10	17,444.8	1873.3	396.6	30.00	7.18	30.7	-71	-8.9	9	1.84	0.2
wx6	31.00	12	60.20	9921.1	571.1	820.80	18,083.1	2449.7	451.5	64.00	7.58	32.2	-71	-7.5	4.5	2.13	-11
wx7	28.42	12	59.80	11,080.1	2074.1	1872.60	23,047.1	2401.7	291.7	60.00	7.00	40.8	-68	-7.3	11.6	1.16	-9.6
wx8	42.00	9	59.80	13,400.1	481.0	1045.80	25,174.5	960.7	24.4	45.00	8.36	41.2	-56	-7.5	29	0.33	4
wx9	33.94	24	35.20	13,516.4	1202.4	1398.40	26,947.3	960.7	286.8	45.00	7.08	44.3	-68	-7.4	1	1.71	-8.8
wx10	35.59	12	39.90	14,099.9	1142.3	1617.30	25,883.6	1441.0	341.7	65.00	6.84	44.5	-67	-7.3	4	1.13	-8.6
wx11	34.04	24	30.10	12,300.0	731.5	2444.20	22,692.5	7445.1	414.9	28.00	7.34	45.9	-70	-8.4	17.5	0.54	-2.8
wx12	42.00	9	14.50	13,839.9	120.2	3331.80	28,365.6	3650.5	265.4	40.00	7.66	49.5	-74	-7.8	<1.0	1.91	-11.6
wx13	43.60	21	59.80	16,199.9	701.4	1520.00	29,074.7	2281.6	326.5	60.00	7.06	50.1	-69	-7.4	<1.0	2.78	-9.8
wx14	36.40	9	50.00	15,000.0	1272.5	1994.20	30,847.6	3242.2	295.9	40.00	7.02	52.6	-71	-7.9	5.1	0.54	-7.8
wx15	33.62	6	30.10	15,700.1	1553.1	2158.40	28,365.6	5043.5	219.7	40.00	7.05	53.0	-61	-7.4	<1.0	1.72	-1.8
wx16	40.00	12	109.90	17,600.1	1022.0	2784.60	32,975.0	2281.6	184.3	10.00	6.75	56.9	-75	-8.1	2.3	0.84	-10.2
wx17	24.00	12	50.00	19,900.1	1503.0	1246.40	35,457.0	2041.4	106.8	70.00	6.88	60.4	-67	-7.6	2.3	0.61	-6.2
wx18	32.04	21	30.10	17,500.1	2024.0	2261.80	36,166.1	3698.5	203.8	56.00	6.68	61.9	-67	-7.6	1.1	0.73	-6.2
wx19	34.04	12	89.90	21,900.1	1162.3	1696.30	40,775.6	840.6	389.3	70.00	6.64	66.8	-55	-6.2	11.6	1.65	-5.4
wx20	33.00	12	80.20	26,599.9	1523.0	3453.40	50,703.5	8165.6	277.6	80.00	6.80	90.8	-52	-5.5	11.8	2.96	-8
wx21	41.70	12	39.90	18,392.8	1052.1	2188.80	36,875.3	1801.2	271.5	56.00	-	60.6	-65	-7.9	<1.0	0.71	-1.8
wx22	31.50	9	19.90	6497.3	591.2	796.50	13,119.1	2041.4	475.9	4.00	7.37	21.8	-65	-8.1	16.3	1.01	-0.2
wx23	31.85	12	50.00	16,793.3	2615.2	2699.50	34,393.3	3194.2	262.4	-	6.80	60.0	-63	-6.3	2.1	1.12	-12.6
wx24	37.00	18	50.00	13,194.8	1042.1	2316.50	25,174.5	6844.7	311.2	40.00	7.60	48.9	-66	-7.7	6.1	3.43	-4.4
wx25	38.50	12	39.90	18,492.6	1392.8	2073.00	36,166.1	3242.2	268.5	56.00	7.09	61.7	-67	-7.8	1.6	0.02	-4.6
wx26	37.00	6	39.90	11,195.7	440.0	522.90	19,501.4	1320.9	598.0	64.00	7.24	33.3	-66	-7.5	2.1	1.11	-6
wx27	30.10	9	5.10	850.0	212.4	296.70	1152.4	1320.9	622.4	1.00	7.64	-	-57	-7.1	28.5	0.17	-0.2
wd1	7.00	-	4.65	122.4	92.88	42.18	133.8	59.27	498.2	0.20	-	0.7	-74	-9.8	1.5	-	4.4
wd2	12.00	-	2.62	80.81	97.86	68.25	102.2	155.6	472.2	0.05	-	0.8	-85	-9.9	12	-	-5.8
wd3	12.00	-	4.10	258.2	129.8	61.22	315.1	324.3	448.1	0.05	-	1.3	-78	-8.9	28.2	-	-6.8
wd4	12.00	-	4.48	444.0	83.49	33.70	564.6	128.1	392.1	0.30	-	1.5	-73	-10.5	4.2	-	11
wd5	15.00	-	2.66	289.4	118.3	87.36	269.4	460.2	518.8	0.26	-	1.5	-76	-9.5	34.9	-	0
wd6	18.00	-	3.56	454.6	66.96	49.32	529.6	232.7	437.4	0.85	-	1.6	-76	-9.3	39.5	-	-1.6
wd7	9.00	-	3.93	984.6	36.30	61.62	1180.0	282.4	654.4	2.15	-	2.9	-81	-10.3	2.6	-	1.4
wd8	16.00	-	15.12	588.7	235.6	161.30	1179.0	650.8	203.2	0.94	-	2.9	-74	-9.2	4.5	-	-0.4
LR1	-	-	63.33	14,154.0	1953.9	759.69	25,667.97	3662.44	78.1	71.40	7.48	47.3	-	-	-	-	-

Holocene formation with the thickness of 3~13 m consists of silt and clay. The thickness of aquifer increases from east (10~30 m) to west (60~75 m) and from south (10~30 m) to north (30~60 m). Groundwater flows slowly from the west to east (Fig. 1). And, the depth to water table is often less than 5 m. Groundwater is NaCl type with TDS >10.0 g/L, and the maximum value is found nearby the south Xishanzui uplifted zone. The area of TDS >50.0 g/L occurs in the middle part of the study area with a total area of 27.0 km<sup>2</sup> (Fig. 1).

**Methods**

Groundwater samples were collected for the measurement of chemistry and isotopes from pumping wells in August 2011 along the flow path. Sampling sites were also considered to cover the different area of TDS concentrations and different well depths. The sample sites were shown in Fig. 1. At least three borehole casing volumes of groundwater were extracted

before a water sample was taken. Samples for stable O, H, and Cl isotope analyses were collected in 50- and 250-mL glass bottles, respectively. Samples for tritium measurement (<sup>3</sup>H) were collected in 500-mL glass bottles. Samples for chemical analysis were filtered through a 0.45-μm filter paper and acidified to a pH value of less than 2 for cation analysis. Parameters such as temperature, pH, electrical conductance, and alkalinity were measured at the sampling sites. Sample measurements were performed at the Institute of Hydrogeology and Environmental Geology (IHEG), Chinese Academy of Geological Sciences. The measurements for the stable isotope ratio of oxygen and hydrogen were analyzed with a Finnigan MAT 253. The isotope compositions were reported in standard δ-notation represented as per mil deviation from the Vienna Standard Mean Ocean Water (V-SMOW) standard. The precision of the δ<sup>2</sup>H and δ<sup>18</sup>O values is ±1.0 and ±0.1 ‰, respectively. Tritium values were electrolytically enriched and measured using the liquid scintillation counting method (1220 Quantulus), and the results are

reported in tritium units (TU), with a typical error of  $\pm 0.5$  TU. Sample measurements for Cl isotope were performed at the Salt Lake Analytical and Test Department, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. The method used for Cl isotope analysis was first proposed by Xiao and Zhang (1992) and modified by Xiao et al. (1995). The water sample was run successively through Ba-form resin and H-form resin to remove sulfates and cation and then run through Cs-form resin to produce a solution of  $\text{Cs}_2\text{Cl}^+$ . The Cl isotope ratio was measured with  $\text{Cs}_2\text{Cl}^+$  ions on a thermal ionization mass spectrometer (Triton). The reference NaCl ISL354 was analyzed with each sample set and has a mean value with  $0.319078 \pm 0.000054\%$  ( $n=9, 2\sigma$ ).

## Results

### Water chemistry

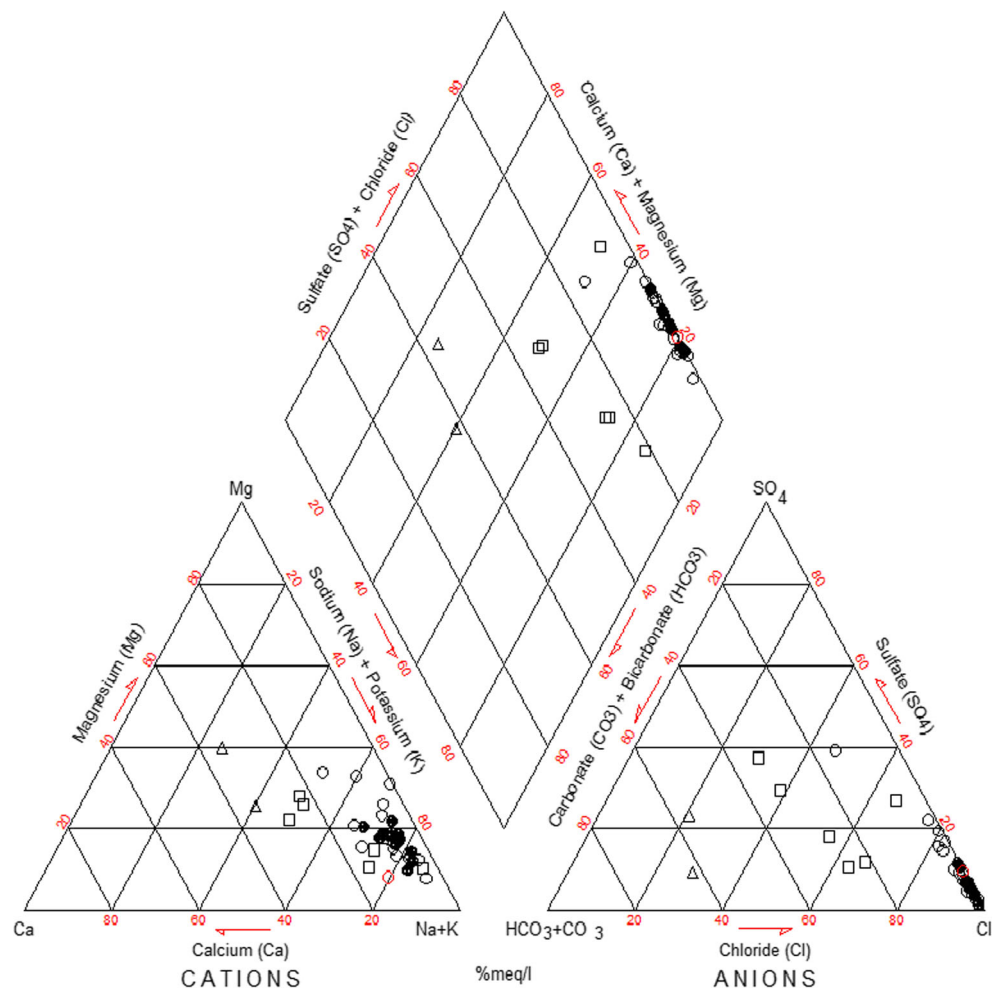
The chemical compositions of samples in the study area are given in Table 1. The samples can be divided into two groups:

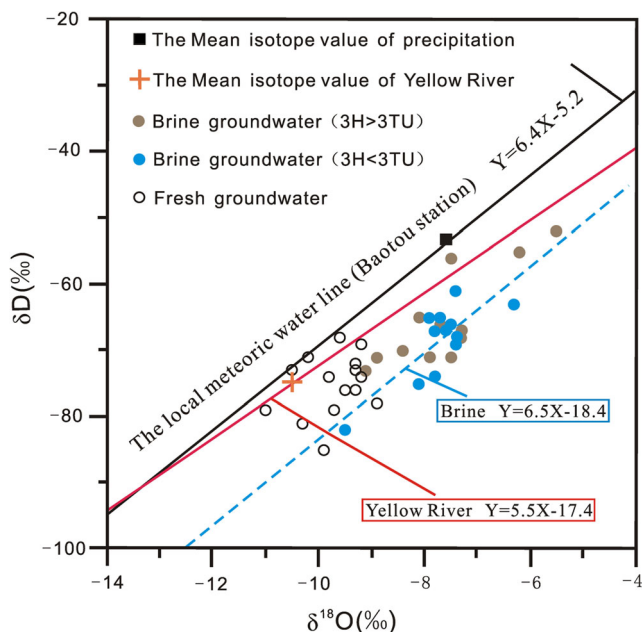
one group is fresh and brackish water, and the other is saline and brine water. TDS concentrations of two groups are 0.7–2.9 g/L with a mean value of 1.7 g/L for fresh and brackish group and 19.1–90.8 g/L with a mean value of 46.5 g/L for saline and brine group. The pH of the saline and brine water samples varies from 6.64 to 8.36. The dominated ions are  $\text{Na}^+$  (5500.00–26,599.90 mg/L) and  $\text{Cl}^-$  (9573.40–26,513.66 mg/L) in the saline and brine water and  $\text{Na}^+$  (80.81–984.6 mg/L) and  $\text{HCO}_3^-$  (203.20–654.40 mg/L) in the fresh and brackish water. The piper plot of the major ions shows that samples of saline and brine water ( $\circ$  and  $\bullet$ ) are predominantly Na-Cl-type water, and the samples of fresh and brackish water ( $\Delta$  and  $\square$ ) are mainly Na-Cl- $\text{HCO}_3$ -type water (Fig. 4).

### Hydrogen and oxygen isotope ratios of groundwater

The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of samples ranged from  $-82$  to  $-52\%$  and from  $-10.5$  to  $-5.5\%$ , respectively (Table 1). All groundwater samples lie to the right of the local meteoric water line in the plot of  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  (Fig. 5). Fresh groundwater samples are plotted at the left end of LMWL

**Fig. 4** Piper triangular diagrams of samples collected from Xishanzui area





**Fig. 5** Stable isotopic compositions of hydrogen and oxygen of brine and saline water samples in Xin’an town (notes: isotopic values (mean value  $-10.5$  and  $-78.4$ ‰) of Yellow River water were from ten samples from Toudaoguai in Tuoketuo, inner Mongolia (Gao et al., 2011); precipitation and its average value were from IAEA’s GNIP data in Baotou station)

within a narrow range of  $\delta^{18}\text{O}$  ( $\delta^2\text{H}$ ) values between  $-10.5$ ‰ ( $-85$ ‰) and  $-8.9$ ‰ ( $-73$ ‰). The mean value of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  ( $-9.7$  and  $-77$ ‰) for these samples was more negative than the mean value of precipitation in Baotou ( $-8.1$  and  $-57$ ‰), but close to the mean value of Yellow River water. This suggested that recharge from Yellow River has a significant contribution to the fresh groundwater. The samples of brine and saline waters are scattered along a fitted line  $\delta^2\text{H}=6.5\delta^{18}\text{O}-18.4$ . They had a wide range of  $\delta^{18}\text{O}$  ( $-7.6$ ‰  $< \delta^{18}\text{O} < -1.7$ ‰) and  $\delta\text{D}$  ( $-56$ ‰  $< \delta\text{D} < -41$ ‰) values, which was more negative than the mean value of precipitation in Baotou and less negative than the mean value of Yellow River water.

**Tritium contents of groundwater**

The tritium content of fresh groundwater samples (TDS  $< 3.0$  g/L) which were sampled from the wells with depth less than 20 m ranged from 2 up to 40 TU. The high tritium contents (28~40 TU) were found for the groundwaters (Nos. wd3, wd5, wd6) emerging along the NW boundary (Xixiaozhao) of brine and saline water area, while the low ( $< 5$  TU) tritium contents (Nos. wd1, wd4, wd7, wd8) were found for the groundwaters along the north boundary except wd8 which was located in the uplift zone of Xishanzui-Wulashan. The tritium content in brine and saline water samples (TDS  $> 19.0$  g/L), which were sampled from the depth of 20~44 m, ranged from  $< 1$  up to 29 TU. The high tritium

contents ( $> 5$  TU) were found in wells located at the southern part near the river, which was attributed to admixture of modern river water with high tritium content. The low ( $< 5$  TU) tritium contents were found for the groundwaters located far away from river.

**Chlorine isotope ratios of groundwater**

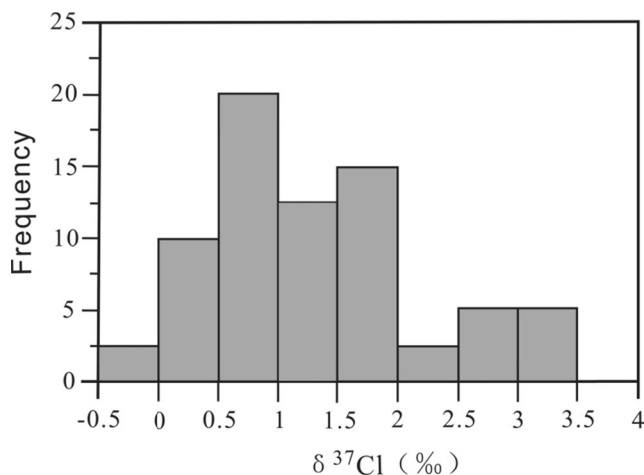
$\delta^{37}\text{Cl}$  values for brine and saline water samples range from  $-0.02$  to  $3.43$ ‰. Only sample (wx1) shows a negative value. Most samples fell in the range of  $0.00$ ~ $2.00$ ‰ with the high frequency range of  $0.50$ ~ $1.00$ ‰ (Fig. 6).

**Discussion**

**Sources of recharge to aquifer**

The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are good conservative tracers to identify the sources of recharge since they are part of the water molecule itself, which can reflect its history and origin before infiltration (Clark and Fritz 1997).

As Fig. 5 shown, all groundwater samples lie to the right of the local meteoric water line in the plot of  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$ . The delta values of fresh groundwater samples vary in a narrow range, and most of them fall on the left of local meteoric water line (except for very few samples). Their values are more negative than the average value of local precipitation and close to the mean value of the Yellow River water. These features show that the Yellow River water is the dominated source of recharge to fresh groundwater in the study area. Whereas  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of brine are apparently higher than those of fresh groundwater, indicating the different sources of recharge from the fresh groundwater, the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of



**Fig. 6** Frequency of chloride isotopic composition of saline groundwater samples

brine samples are lower than the mean value of local precipitation, but higher than the mean value of the Yellow River water. This indicates that the source of recharge to brine should not be the Yellow River water and local precipitation. The big range of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values (or the scatter of brine samples in Fig. 5) suggests that brine was recharged by multi-sources or mixed by different groundwater when brine moved in aquifers. The  $\delta^{18}\text{O}$  values of brine are less than the mean value of modern precipitation, indicating a cold recharge period. However, the brine samples which contain the considerable content of tritium fall near the line fitted by the data of samples of Yellow River. This fact suggests that these brine samples have been mixed with water from the Yellow River, whereas those samples free of tritium should not be affected by modern recharge.

### Sources of salinity

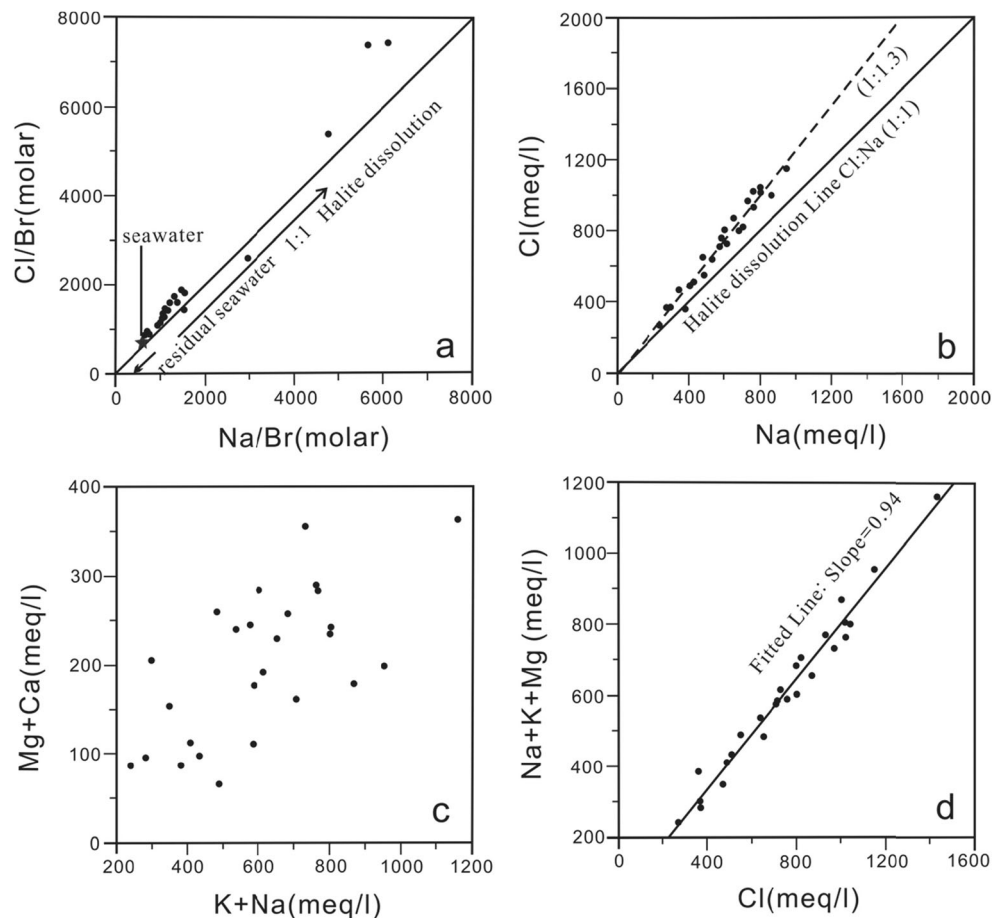
#### Indications from hydrogeochemical data

The ratios of chemical compositions are a useful tool for tracing the sources of salinity of brine and its evolution. The ratios of

Cl/Br (molar) and Na/Br (molar) are usually used to identify salinity source of brine. When seawater experienced evaporation and crystallization, Br is not easy to enter into the mineral lattice of halite and would concentrate in the remained seawater, which lead to a significant decrease of Na/Br (molar) and Cl/Br (molar) ratio in the residual seawater. In contrast, the brine, which formed from the re-dissolution of precipitated halite by fresh water, has much higher Na/Br (molar) and Cl/Br (molar) ratios than seawater. Walter et al (1993) proposed that the plot of Cl/Br-Na/Br can differentiate the sources of salinity. This diagram can be used to identify source of salt and determine dilution effect in depleted Br water (such as meteoric water) and halite dissolution. The plot of Cl/Br (molar) vs. Na/Br (molar) is shown in Fig. 7a. Seawater falls on the line of slope 1, and all brine samples plot along the line. The Na/Br and Cl/Br ratios are bigger than those of seawater except two samples. These suggest that the source of salt may predominantly originate from the dissolution of halite.

The ratio of Cl/Na (meq/L) can be used as an indicator for tracing sources of salinity of brine. Figure 7b presents the variation of Cl/Na (meq/L) ratio in the study area. Water whose salinity originates from the dissolution of halite would lie along a line with the slope of 1. However, brine samples in

**Fig. 7** Ratios of chemical compositions of saline and brine water in Xishanzui area. **a** Cl/Br (molar) versus Na/Br (molar), **b** Cl (meq/L) versus Na (meq/L), **c** Mg + Ca (meq/L) versus Na + K (meq/L), and **d** Na + K + Mg (meq/L) versus Cl (meq/L)



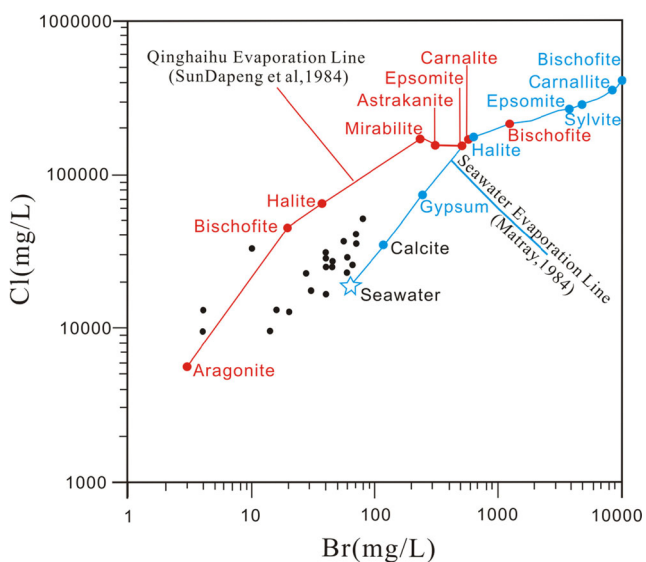


the study area plot along the line of 1:1.3 slightly shift to the high concentration of chloride. This suggests that the source of salt was dominated by the dissolution of halite, and some other geochemical processes should be responsible for the deviation from the 1:1 line. The possible processes involve with (1) cation exchange and adsorption, (2) mixture of Ca-Cl-type water, and (3) dissolution of other Cl-bearing minerals following the dissolution of halite, such as epsomite (KCl), carnallite (KMgCl<sub>3</sub>·6H<sub>2</sub>O), and bischofite (MgCl<sub>2</sub>·6H<sub>2</sub>O). Cation exchange and adsorption would remove K and Na from solution and increase concentration of Ca and Mg. The poor correlation between Na+K and Ca+Mg (Fig. 7c) indicates that this process could not be responsible for the elevated Cl/Na ratio in the brine. Mixing with Ca-Cl-type water would result in the elevation of Cl concentration in groundwater. However, the Ca-Cl-type water was not found in the study area, and therefore, this process should be excluded. The dissolution of Cl-bearing minerals would elevate the Cl concentration and give a Cl/(K+Na+Mg) ratio of about 1 in groundwater. The samples of brine were plotted on a fitted line of slope 0.94 in the diagram of K+Na+Mg vs. Cl (Fig. 7d). This indicates that the sources of salts of brine were from the dissolution of halite and other Cl-bearing minerals.

The ratio of Cl/Br (mg/L) is also used for tracing sources of salinity of brine. Bromine usually occurs in solution, and the Br-bearing minerals are rarely found in the nature. Zherebtsova and Volkova (1966) suggested that the bromine content would increase until the precipitation of potash salts (e.g., sylvite and carnallite) when the seawater evaporated. And, Li and Br would remain in the solution during the formation of potash deposition. Figure 8 illustrates the logarithmic relationship between Cl (mg/L) and Br (mg/L), in which the evaporation lines

of Qinghai Salt Lake and the sequence of mineral precipitation were from the experiment results given by Sun et al. (2002), and the evaporation line of seawater and the sequence of mineral precipitation are from the results given by Matray's study after 1984 (Stash 2008). The concentration of Br in brine samples is less than that in initial seawater and the residual seawater and plots above the evaporation line of seawater. Normally, the sources of salinity of brine could be from the residual seawater and dissolution of evaporites. Those samples with Cl concentrations less than those of initial seawater may indicate the dilution of fresh water if the salinity originated from the residual seawater. But, this inference was not true because the occurrence of residual seawater has been excluded in the above discussion.

The dissolution of evaporites by precipitation also could be the source of salinity. The Br concentration in marine evaporites, such as halite and sylvite, ranges from 68 to 260 ppm (Valyashko 1956; Holser 1979). The typical saturated concentration of bromine is 24–93 mg/L in salt water which originated from the dissolution of marine evaporates by precipitation and 90–150 mg/L in the salt water which originated from the dissolution of marine evaporates by seawater (Rittenhouse 1967). The Br concentration of brine samples in the study area varies from 4 to 80 mg/L, which is close to the range of halite dissolution by precipitation. Unluckily, no marine evaporites were found in the study area. In contrast, many terrestrial evaporites were found in the study area. Thus, the possible source of salinity is from the dissolution of terrestrial evaporites because the dissolution and recrystallization of halite would increase the Br concentration in water. In Fig. 8, three samples fall on the evaporation line of Qinghai Salt Lake and other samples deviate from and plot below the line; i.e., the Br concentration of most samples is higher than that of evaporated water in Qinghai Lake. This phenomenon suggests that solute may originate from the evaporation of salt lake or dissolution of terrestrial halite by precipitation. When the dissolution of halite is re-equilibrium with respect of brine, the Br will be moved into the liquid phase from the halite, resulting in elevated Br content in brine.



**Fig. 8** The logarithmic plot of the concentration trends of chloride versus bromide of brine

*Indications from chloride stable isotope*

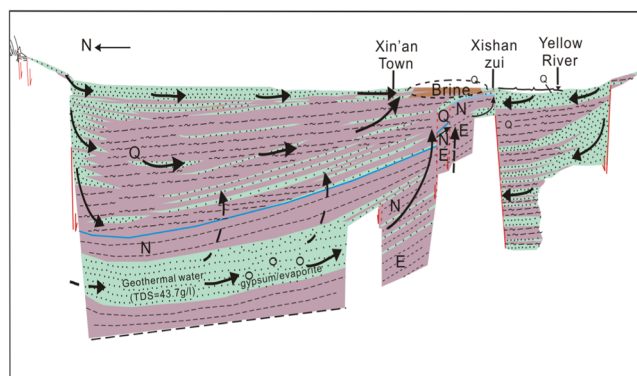
Kaufmann and Lon (1988) stated that the Cl isotopic composition, especially the relationship between  $\delta^{37}\text{Cl}$  and the Cl<sup>-</sup> concentrations, can be used to determine the sources of Cl<sup>-</sup> and mechanisms responsible for fractionation of Cl isotopes. Generally,  $\delta^{37}\text{Cl}$  values in natural material vary from -8.00~ to +8.00‰, and most of them vary from -2.00 to +2.00‰. There are various  $\delta^{37}\text{Cl}$  values for different sources:  $\delta^{37}\text{Cl}$  values are +0.42~+

2.53‰ for aerosol, +0.74~+2.85‰ for river water, -2.06~+1.01‰ for salt lake brine, -0.50~+0.69‰ for groundwater, and -0.60~+1.20‰ for halite.

$\delta^{37}\text{Cl}$  values of samples show a larger variation range, which suggests that the salinity is from multi-sources. The high-frequency samples give a  $\delta^{37}\text{Cl}$  range of 0.00~2.00‰, which overlaps with the range of halite. This fact indicates that the chloride of samples with  $\delta^{37}\text{Cl} < 1.00\text{‰}$  was predominately from the dissolution of halite. Those samples of  $\delta^{37}\text{Cl}$  values  $> 1.00\text{‰}$  (the maximum value up to 3.40‰) may indicate the mixing of different water body or the dissolution of different evaporites. The possible reason for  $^{37}\text{Cl}$  enrichment in some samples is the dissolution of terrestrial carnallite. Generally,  $^{37}\text{Cl}$  would preferentially move from the solution into the salt minerals during the salt crystallization and precipitation, which result in  $^{37}\text{Cl}$  depletion in solution and enrichment in salt deposits. For example, Vengosh et al. (1989) reported that a sample of carnallite collected from Chaidan basin in Qinghai, China, has a  $\delta^{37}\text{Cl}$  value  $24.70 \pm 2.90\text{‰}$ . On the contrary, the  $^{37}\text{Cl}$  will be enriched in solution as salt mineral dissolution. Thus, the leaching of evaporites by groundwater which may recharge from precipitation or surface water could be responsible for the high  $\delta^{37}\text{Cl}$  value of those samples. This contribution to the source of salinity has been differentiated by the chemical indicators and discussed in the section of sources of salinity.

### Conceptual model

Synthesizing the previous results inferred from multiple chemical and isotopic methods with the geologic structure and hydrogeological conditions, a conceptual model for the origin of saline and brine groundwater in shallow aquifer can be inferred (Fig. 9). For saline and brine water, faults can be considered as an effective channel for salt transport and the movement of saline and brine water.



**Fig. 9** Conceptual model for the origin of brine in shallow aquifers

The uplifting of basement plays an important role for the migration of brine in the deep aquifers which consists of red sandstone and mudstone with scattered gypsum or evaporite in the overlying Tertiary formation. Another possible channel is the aquitards (mainly composed of silty sand) between the shallow aquifer and deep aquifer due to the difference of water pressure, which makes the saline and brine water in shallow aquifers recharged by the saline and brine water in deep aquifers by leakage. The alternation of salt-enriched strata and the lakes in the basin results in elevated salinity groundwater under the influence of paleoclimate and sedimentary environment in the study area. So, the third possible origin is the salt accumulation from halite dissolution by precipitation or surface water followed by strong evaporation due to a closed basin and shallow groundwater table.

### Conclusion

Identifying the origin of saline and brine groundwater can provide a better understanding of groundwater salinization processes. Multiple chemical and isotopic methods have been used in this study to analyze the sources of water and salt of saline and brine water in Xishanzui area. Evidences from chloride isotope and hydrogen and oxygen stable isotope indicate that not only there is salt origin in this region but also it is multiple. Its source has no obvious relationship with the Yellow River, and it may originate from paleometeoric water but not from residual seawater. The ratio of Cl/Br presents that salinity mainly from salt lake evaporation or continental halite dissolved by precipitation. The ratios of Cl/Br (molar) and Na/Br (molar) indicate that the source of salinity is not from residual seawater but dissolved halite or has had a strong impact from halite dissolution. The ratio of Cl/Na (molar) shows that salinity originated from halite dissolution and there are other salts containing Cl<sup>-</sup> concentration dissolved during this processes. According to geological and hydrogeological conditions, fracture structure plays a significant controlling role in the formation and distribution of brine and salt transport and leakage of saline and brine water in deep aquifers through the intermediate aquitards may be another possible channel. In consideration of paleoclimatic condition and paleosedimentary environment in the study area, the salt accumulation from halite dissolution by precipitation or surface water may be another possible origin of saline and brine water in shallow aquifers.

**Acknowledgments** This work was financially supported by the National Natural Science Foundation of China (NSFC grant No. 41272252 and No. 41502250).

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