Stable chlorine isotopes in saline springs from the Nangqen basin, Qinghai–Tibet Plateau: Brine genesis and evolution

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Chlorine isotopes can be used to study the evolution of different fluids, sources and the causes of various related deposits. In this study, Cl concentrations and chlorine isotope ($\delta^{37}\text{Cl}$, IAEA ISL-354 NaCl standard) values were determined for brine samples from Nangqen basin, located on the southern boundary of the Qinghai–Tibet plateau to study the source and the processes of these saline springs. The results demonstrated that the saline springs are distributed around a fault or fault zone, with a high average salinity of 228.30 g/l and flow rates ranging from 1.7 to 0.01 l/s. Na^+ and Cl^- are the predominant cations and anions, respectively, accounting for more than 90% of the total. The $\delta^{37}\text{Cl}$ values range from -1.55‰ to $+0.97\text{‰}$, and the Cl/Br ratios are from 1739 to 175,260. Coupled with the previous H, O and B isotope compositions (δD , VSMOW2 standard, ranges from -100.91‰ to -132.98‰ , $\delta^{18}\text{O}$, VSMOW2 standard, from -12.88‰ to -16.05‰ and $\delta^{11}\text{B}$, NIST 951 standard, from $+3.55\text{‰}$ to $+29.59\text{‰}$), it can be interpreted that the saline springs are mainly the result of the dissolution of halite hosted in mudstone and volcanic country rocks.

Keywords. $\delta^{37}\text{Cl}$; brine genesis; saline springs; Nangqen basin.

1. Introduction

Nangqen basin is located in the area spanning from $96^{\circ}00'\text{--}97^{\circ}00'\text{E}$ and $32^{\circ}00'\text{--}32^{\circ}40'\text{N}$ and was formed between the Late Eocene and Early Oligocene era (Deng *et al.* 2000). The terrain of the Nangqen basin is very steep, causing a series of north–west–south–east fault zones. Many saline springs are exposed adjacent to the fault zones, and they are characterised by high salinities (salinity is greater than 150 g/l) and large distribution areas ($10,000\text{ km}^2$), which are most likely the result of

the dissolution of the salt occurring underground (Han *et al.* 2018). The study of the brine geochemistry can allow the geochemical information of the underground salt layer to be determined and help predict the salt formation and mineralisation. However, little work has been done to investigate the formation and geochemical processes of saline springs in this area. Therefore, stable chlorine isotopes are used here to indicate the source and evolution of brine.

Chlorine is an abundant element in the oceans, salt lakes and related geological systems, and it

is brought into the salt lake through various channels, providing important information regarding the evolution of brine. Chlorine is the abundant anion in many geofluids and one of the chief volatile constituents on Earth (Bureau *et al.* 2000; Bonifacie *et al.* 2008). ^{35}Cl and ^{37}Cl are two naturally occurring stable isotopes, with a relative mass difference of 5.7%, and the natural range in the variation in $\delta^{37}\text{Cl}$ is approximately 7‰ (Liu *et al.* 1998; Xu *et al.* 2008; Barnes and Sharp 2017). Based on the mass fractionation of the two stable chlorine isotopes ($^{35}\text{Cl} = 75.53\%$ and $^{37}\text{Cl} = 24.47\%$) in natural environments, the element can be used as a tracer in many geochemical processes (Luo *et al.* 2012). Due to the development of high-precision chlorine isotope determination methods, the research on chlorine isotope fractionation in nature has achieved many results and promoted an in-depth study of chlorine isotope tracing in geochemistry (Magenheim *et al.* 1994; Xiao *et al.* 1994; Eggenkamp and Schuiling 1995; Tan *et al.* 2005). Chlorine isotopes are currently used as tracers to allow the tracing of the sources and the evolution of seawater, salt lake brines, groundwater, surface river water, evaporative rocks and hydrothermal fluids (Eastoe and Gilbert 1992; Eggenkamp *et al.* 1995; Banks *et al.* 2000; Gleeson and Smith 2009; Nahnybida *et al.* 2009; Richard *et al.* 2011). $\delta^{37}\text{Cl}$ values have been consistently proximate to the marine water values (0‰), and range from 3.0‰ to 7.2‰ in mantle and crust (Sharp *et al.* 2007). On the other hand, large surface reservoirs (evaporites, brines and the oceans) have exhibited mean $\delta^{37}\text{Cl}$ values of 0.05‰ to $\pm 0.5\%$ (Eggenkamp *et al.* 1995; Godon *et al.* 2004; Eastoe *et al.* 2007). Brines from salt lakes may range from -2.05% to $+1.01\%$ or slightly higher (Liu *et al.* 1997; Luo *et al.* 2012).

During the formation and evolution of brine, the chlorine isotope composition can exhibit corresponding differences due to factors such as the source of the supplemental water and evaporation (Liu and Xiao 1996). Vengosh's study shows that ^{37}Cl tends to concentrate in precipitated salt, compared to the source fluid, in the process of brine evaporation and halite deposition (Vengosh *et al.* 1989; Eggenkamp *et al.* 1995; Xiao *et al.* 2000). This fractionation of chlorine isotopes observed in the evaporation process of brines is also seen in the study of the Qaidam basin and the Michigan basin (Kaufmann *et al.* 1993; Luo *et al.* 2012, 2015). A large number of evaporation experiments have shown that ^{37}Cl is enriched in salt deposits. As the

evaporation process continues, the amount of salt minerals gradually decreases, and the amount of ^{37}Cl in the brine is continuously depleted. In addition, the $\delta^{37}\text{Cl}$ value gradually decreases in solid minerals precipitated at various stages of brine evaporation (Vengosh *et al.* 1989; Liu and Xiao 1996; Rodríguez *et al.* 1997).

In this study, Cl concentrations and $\delta^{37}\text{Cl}$ values were determined for all brine samples from the Nangqen basin. The aims were to delineate the geochemical origins of saline springs of the Nangqen basin and study the evolution and sources of the saline springs.

2. Geology and tectonic setting

The Nangqen basin is located on the eastern Qinghai–Tibetan plateau, on the north-eastern edge of the Qiangtang–Changdu area between the Jinshajiang suture and the Nujiang suture. It is a Tertiary inland basin, formed by the collision of the Eurasian and Indian plates. The long-term uplift and denudation of the Mesozoic basement has also contributed to the formation of the basin (Deng *et al.* 2000; Qi *et al.* 2017). As shown in figure 1, the exposed surface layers are relatively limited to the Mesoproterozoic, Carboniferous, Permian, Triassic, Palaeogene, Neogene and Quaternary. In addition, a small area of Cretaceous volcanic rocks and Palaeogene volcanic rocks are also exposed in the north-eastern area. The boundary of the basin is controlled by the faults, and their directions are north-west and south-east. The western boundary is eroded, and it is surrounded by the complex deformation of the Carboniferous–Permian Marine carbonate rocks, while the source area of the basin sediments consists of carbonate rocks and (purple-red) clastic rocks of the Triassic–Jurassic age and show parallel or angular unconformity. The formation time of the basin is from the Late Eocene to the Early Oligocene, the folds are widespread and the red continental clastic rock formation contains evaporates and is accompanied by massive high-potassium rocks (mainly volcanic rocks). The volcanic rocks in the basin occur as narrow and strip-shaped or round, and the small-scale outcrops are only a few hundred metres long and tens of metres wide. Volcanic activity is characterised by early eruption and a late overflow eruption cycle. Early volcanoclastic rocks were mainly distributed in the eastern part of the basin. Late volcanic activity mainly consists of coarse surface rocks and

Figure 1. Geological sketch of Nangqen basin. (Modified after Deng *et al.* 2000).

Figure 2. Distribution of the saline springs in the Nangqen basin.

shallow intrusive rocks (Yang 1988; Jiang *et al.* 2006). Many rivers flow through the area, i.e., the Lancang river (Zhaqu), Ziqu, Jiqu and Baqu. Until now, seven saline springs have been located and utilised. The saline springs exposed are mainly located in the volcanic rocks of the Eocene series and in conglomerate and carbonate sandstones of the Miocene series (figure 2).

In the study area, a series of fractures, which are very important for the formation and development of the basin, can be found to the north-west and south-east, and the saline springs are exposed in the fault

zones. The imbalanced development and multiperiodic activity of these fractures are concluded to be conducive to the formation of a salt basin tectonic environment (Brian *et al.* 2000; Spurlin *et al.* 2015).

3. Samples and analytical methods

3.1 Sample collection

Through data collection and field investigation, we analysed the samples of seven saline springs in the Nangqen basin. All the samples were collected in

Table 1. *Sampling sites.*

Saline spring	Location	Rock type	Age
Dagai	N32°12'15.1" E96°26'09.4"	Sandstone + mudstone	Palaeogene
Riazhong	N32°15'58.8" E96°27'00.7"	Sandstone, gypsum + mudstone	
Niuriwa	N32°08'38.7" E96°28'28.2"	Sandstone, gypsum + mudstone	
Duolunduo	N32°04'48.5" E96°56'14.7"	Sandstone, volcanic rock + mudstone	
Baizha	N31°56'02.6" E96°36'07.9"	Sandstone + mudstone	
Ranmu	N32°26'43.1" E95°50'51.9"	Clay	
Gayang	N32°03'47.9" E95°39'41.1"	Sandstone + mudstone	

December 2016, and the sampling locations are shown in table 1.

3.2 Analytical methods

3.2.1 Chlorine isotope

Chlorine isotope sample processing and testing process: As the SO_4^{2-} and NO_3^- ions interfere significantly with chlorine isotope determination, we sequentially passed the aqueous solution through a Ba-type resin to remove the SO_4^{2-} ions and an Ag-type resin to remove the NO_3^- ions, followed by an H-type resin to remove all the cations and to convert the Cl^- ions to HCl . Finally, the solution was passed through a Cs-type resin to form Cs_2Cl^+ . We coated the formed Cs_2Cl^+ with a mass spectrometer metal tantalum tape. First, we vacuumed the tantalum tape used ($1.5 \text{ cm} \times 0.098 \text{ cm} \times 0.0025 \text{ cm}$) at 3 A for 1 h. Then, at the time of coating, $2.5 \mu\text{l}$ of graphite suspension was applied to the tape surface, followed by drying under a 1.2-A current and steaming to near dry under a 1.2-A current, and then, the processed sample was added.

Mass spectrometry: We used a Thermo Fisher Triton thermal ionisation mass spectrometer (TIMS), with the main features as follows: a 90° fan-shaped magnetic analyser with an effective radius of 81 cm. When the acceleration voltage is 10 kV, the mass range is 3–320 amu, which provides the most precise and accurate isotopic ratio for both positive and negative ions; resolution: ≥ 450 (10% peak and valley definition); sensitivity: ≥ 3 ion/100 μmol or 1/500; and abundance sensitivity: no filter ≤ 2 ppm, filter ≤ 10 ppb. The

machine is a multi-collector TIMS which includes a central cup and eight independently movable Faraday cups that enable the determination of 303 ($\text{Cs}_2^{37}\text{Cl}^+$)/301 ($\text{Cs}_2^{35}\text{Cl}^+$) ions in static double-accepting chlorine isotopes.

Determination of Cl isotopic composition:

We determined the chlorine isotopic composition using positive thermal ionisation mass spectrometry and graphite-based Cs_2Cl^+ ions (Xiao *et al.* 1998). After loading the sample into the mass spectrometer, we vacuumed the ion source to $2\text{--}3 \times 10^{-7}$ Mbar and started the measurement. During analysis, we used the static double receiver method to determine the mode of detection and obtained the $R_{303/301}$ value. In this experiment, the $^{37}\text{Cl}/^{35}\text{Cl}$ ratio was calculated based on Cs_2Cl^+ , and the sample $\delta^{37}\text{Cl}$ value was calculated as follows:

$$\begin{aligned} \delta^{37}\text{Cl} (\text{‰}) &= \left[\left(^{37}\text{Cl}/^{35}\text{Cl} \right)_{\text{sample}} / \left(^{37}\text{Cl}/^{35}\text{Cl} \right)_{\text{standard}} - 1 \right] \\ &\times 1000, \text{ Error} \leq 0.09\text{‰}, \end{aligned}$$

IAEA ISL-354 NaCl standard

$$= 0.319028 \pm 0.000058 (n = 12).$$

3.2.2 H-O and B isotopes

For δD and $\delta^{18}\text{O}$ isotopes, MAT253 (Thermo Fisher Scientific, USA) and a Flash HT-IRMS analysis system were used.

VSMOW2 was used as the H_2O standard with $\delta\text{D}_{\text{VSMOW}}/\text{‰} = 0 \pm 0.3$ and $\delta^{18}\text{O}_{\text{VSMOW}}/\text{‰} = 0 \pm 0.02$.

For $\delta^{11}\text{B}$ isotopes, a thermal ionisation mass spectrometer (Thermo Fisher Finnigan, Germany) were used. The B isotopic composition can be expressed as follows:

$$\delta^{11}\text{B}(\text{‰}) = \left[\left(\frac{{}^{11}\text{B}/{}^{10}\text{B}}{({}^{11}\text{B}/{}^{10}\text{B})_{\text{standard}}} - 1 \right) \times 1000, \right. \\ \left. ({}^{11}\text{B}/{}^{10}\text{B})_{\text{standard}} \text{ NIST 951} \right. \\ \left. = 4.05262 \pm 0.00077 (2\sigma = 0.02\%, n = 9). \right]$$

Test details were obtained from a previous work (Han *et al.* 2018).

4. Results

The results of the hydrochemical analysis and δD , $\delta^{18}\text{O}$, $\delta^{11}\text{B}$ values of all samples are shown in tables 2 and 3 (Han *et al.* 2018). The flow rates of the seven salt springs in this area are quite different, with the largest being 1.7 l/s and the smallest being 0.01 l/s. Moreover, the saline springs are distributed around the faults or fault zones. The salinity of the saline springs is very high, with an average value of 228.30 g/l. Na^+ and Cl^- are the predominant cations and anions, respectively, accounting for more than 90% of the total. The chlorine isotope values range from -1.55‰ to $+0.97\text{‰}$, which is a large variation and indicate that several factors are responsible. The Ca^{2+} and Mg^{2+} content values are both below 3 g/l, and the K^+ content is relatively lower, with a range from 0.08 to 0.36 g/l. SO_4^{2-} is second only to Cl^- in the anion content of the saline springs, with a wide range of variation from 2.97 to 29.41 g/l. The content of B in Duolunduo is relatively high, reaching a maximum of 200.56 mg/l and a minimum of 1.00 mg/l in Ranmu. The content of Li^+ in

Table 3. δD , $\delta^{18}\text{O}$ and $\delta^{11}\text{B}$ analysis of the saline springs, Nangqen basin.

Samples	$\delta^{11}\text{B}$ (‰)	δD (‰)	$\delta^{18}\text{O}$ (‰)	Cl/Br (mol/mol)	$\delta^{37}\text{Cl}$ (‰)
Dagai	4.85*	-127.39*	-14.52*	60,769	-0.6
Riazhong	12.7*	-128.28*	-14.68*	33,412	-1.07
Niuriwa	18.01*	-124.14*	-14.38*	91,252	-0.03
Duolunduo	3.55*	-100.91*	-12.88*	1739	-0.21
Baizha	12.96*	-132.98*	-16.00*	16,815	-1.18
Ranmu	29.59*	-128.36*	-16.05*	175,620	-0.87
Gayang	18.27*	-129.57*	-15.93*	93,823	0.04

*Cited from preliminary results (Han *et al.* 2018).

Riazhong is 27.17 mg/l and below 10.00 mg/l in the other saline springs, with the lowest value being 1.03 mg/l in the Ranmu saline springs.

5. Discussion

5.1 H, O and B isotopes

Metrics such as hydrogen–oxygen isotopes (H–O) and B isotopes of the saline springs in the Nangqen basin have been previously studied by our research group, as shown in figure 3. For the H and O isotopes, the data of all seven samples were near the global water line value, which indicated that the sources of the saline springs are atmospheric precipitation and infiltration. For $\delta^{11}\text{B}$, the $\delta^{11}\text{B}$ –B relationships were analysed and the results showed that the leaching from the surrounding rocks (marine carbonate rocks and volcanic rocks) are the main sources of the B isotopes in the saline springs. It is speculated that the saline springs in the Nangqen basin were leached from the underground salt layer during atmospheric precipitation or groundwater upwelling and then formed on the exposed surface (Han *et al.* 2018).

Table 2. Geochemical analysis of the saline springs, Nangqen basin, (cited from preliminary results, Han *et al.* 2018).

		Concentrations of major ions									
Samples	pH	TDS (g/l)	Na ⁺ (g/l)	Ca ²⁺ (g/l)	K ⁺ (g/l)	Mg ²⁺ (g/l)	Li ⁺ (10 ⁻³ g/l)	B (10 ⁻³ g/l)	Cl ⁻ (g/l)	SO ₄ ²⁻ (g/l)	Br ⁻ (10 ⁻³ g/l)
Dagai	7.52	165.75	62.07	1.13	0.08	0.21	1.84	3.56	96.12	5.38	3.09
Riazhong	7.02	316.58	117.29	1.01	0.31	1.99	20.93	12.19	180.96	13.32	6.26
Niuriwa	7.18	150.89	57.11	1.13	0.19	0.29	3.91	2.17	87.98	2.98	3.98
Duolunduo	7.75	292.75	107.02	0.37	0.11	0.21	9.68	200.56	154.97	29.10	19.13
Baizha	7.04	269.48	103.77	1.23	0.07	0.14	4.88	21.38	159.73	4.45	4.70
Ranmu	7.14	229.26	86.03	1.19	0.29	0.41	0.75	1.74	135.77	4.49	20.30
Gayang	7.22	150.28	55.93	1.70	0.09	0.35	2.24	2.07	86.29	5.52	5.25

Figure 3. Isotope analysis of H, O and B (cited from Han *et al.* 2018). The green and pink shaded areas are the regions with boron geochemical characteristics of crustal marine carbonate rocks and magmatic rocks, respectively (Hemming and Hanson 1992). Tibetan geothermal hot water data are from Lv *et al.* (2014).

Figure 4. Relationship between the Cl/Br molar ratios and $\delta^{37}Cl$.

5.2 Cl isotope tracer

The Cl isotope analysis of these saline springs carried out in the present study further elucidates their sources and evolution (figure 4).

Several workers have analysed the relationship between the chlorine isotopes of various geological settings and the molar ratios of chlorine and bromine (Cl/Br) (Fontes and Matray 1993; Eggenkamp *et al.* 1995; Eastoe *et al.* 1999). According to the study of Banks *et al.* (2000), the

dissolution–recrystallisation process of the halite does not cause a change in the Cl/Br ratio of the brine, and the $\delta^{37}Cl$ value is not affected (Banks *et al.* 2000). As a result, the value of $\delta^{37}Cl$ in brine can reflect the dissolved halite characteristics. Bodnar's study showed that the dissolved chloride ion concentration of the halite is up to $\sim 170,000$ ppm at a temperature of $100^\circ C$ and is 4000 ppm at a temperature of $25^\circ C$. Therefore, the halite dissolution characteristic value is 4000 (Bodnar 1994).

By comparison, the Cl/Br ratio of the brine in the Nangqen basin ranges from 1739 to 175,260. Excluding the Duolunduo saline spring value of 1739, the Cl/Br ratio in the other salt springs is much higher than the halite characteristic value of 4000, which is within the halite dissolution characteristic value range (Chi and Savard 1997; Banks *et al.* 2000; Grandia 2003). However, the chlorine isotope values of some brines obviously exceed the range of halite eigenvalues, with a range from -1.55‰ to $+0.97\text{‰}$, and this range of variation is far greater than the variation of Cl isotopes in seawater evaporation stages. This result also shows that the brines are non-marine sources. The brine isotope values show a greater range of variation due to the presence of multiple water bodies in the brines of continental origins (Risacher *et al.* 2003). The Cl/Br ratios from a river or groundwater are comparable to those from seawater, but if mixed with brine before evaporation, the initial Cl/Br of the evaporating solution will be very different from that of the seawater. The study by Liu *et al.* (1997) shows that the chlorine isotope in salt lake brines has a wide range of variation from -2.05‰ to $+1.01\text{‰}$. Therefore, due to the high variation characteristics of chlorine isotopes, it is not sufficient to justify the source of the brine or marine origin of the brine based on the characteristic values of the chlorine isotopes. However, the common characteristics of the Cl/Br ratios and the chlorine isotope characteristics indicate that the brine in this area belongs to a continental source. In addition, the Nangqen basin is in the collision zone of Eurasia and formed in the Mesozoic–Cenozoic era. This period is an era of very dry and hot climate in the history of the Earth, which is conducive to the formation of salt minerals. The underground strata of the basin are rich in salt (halite) and formed in the Cenozoic Eocene–Oligocene period (Horton *et al.* 2000; Du *et al.* 2011). The evidence from the chlorine isotope shows that the saline springs are mainly formed by the leaching of the underground halite layer, and consist of leached brine, which provides more forceful evidence for the formation and evolution of saline springs in the area.

5.3 Water–rock processes

During the process of halite leaching, the initial chlorine content of the brine is the same as that of the halite, but the Cl/Br ratio and chlorine isotope characteristic values of the brine will be affected by other factors during the long-term brine evolution process, especially with regard to the water–rock interactions. Considering the geochemical process of

Figure 5. The range of variation of $\delta^{37}\text{Cl}$ in different fluids and saline minerals. Data sources: Rain water (Koehler and Wassenaar 2010); shallow groundwater (Eastoe and Dettman 2016); deep groundwater (Eastoe and Dettman 2016); biotite (Eastoe and Guilbert 1992); hornblende (Eggenkamp and Schuiling 1995); halite (Eggenkamp and Schuiling 1995).

the saline spring formation and the distribution of rocks in the study area, characteristics of the Cl isotope of rainwater, ground water, biotite and hornblende are shown in figure 5 (Eastoe and Guilbert 1992; Eggenkamp and Schuiling 1995; Koehler and Wassenaar 2010; Eastoe and Dettman 2016). In combination with the hydrogeological conditions of the Nangqen basin, factors that may cause changes in the Cl/Br ratio and chlorine isotope characteristic values of brines will also be discussed.

During the dissolution of the halite, the dissolved fluids, whether atmospheric precipitation, groundwater or seawater, the chloride ion content in the dissolved brine is mainly controlled by the solubility of NaCl in the water, fluid temperature and flow rate. Rainwater is very abundant in the study area, and the chlorine isotope range of the rainwater varies from -3.5‰ to $+4.48\text{‰}$ (Koehler and Wassenaar 2010). Therefore, rain or groundwater is another factor that can cause changes in chlorine isotopes in the saline springs.

Sandstone, mudstone and volcanic rocks are widely distributed in the exposed strata in the Nangqen basin, while biotite and hornblende may contain several hundred to several thousand ppm of Cl in igneous and metamorphic rocks, which are the main chlorine-containing minerals in nature (Kaufmann *et al.* 1984). The biotite in the Nangqen basin is mainly found in mudstones and volcanic rocks that are widely distributed in this area. Therefore, the leaching of rocks may become another important source of saline springs. Because biotite and amphibole have a high range of Cl/Br ratios, they have a great influence on

the ratio of Cl/Br in the saline springs. Based on the published $\delta^{37}\text{Cl}$ compositions of biotite ($-0.26\text{‰} \sim +3.4\text{‰}$) and $\delta^{37}\text{Cl}$ ($+0.7\text{‰} \sim +7\text{‰}$) in hornblende, the water–rock interactions can cause a shift in the $\delta^{37}\text{Cl}$ values of the brine.

Based on the analysis of Cl/Br ratios and $\delta^{37}\text{Cl}$ compositions of saline springs in this area, the following conclusions are drawn: (i) the leaching of halite layers is the main source of salt materials; (ii) abundant chlorine enrichment in atmospheric precipitation will cause an increase in the range of chlorine isotope values; and (iii) the leaching of surrounding rocks (volcanic rocks, mudstones) will cause an increase in the chlorine/bromine ratio and a positive shift in the chlorine isotope value.

6. Conclusions

The [Cl] and $\delta^{37}\text{Cl}$ data from the saline springs of the Nangqen basin are presented here. Our main views are as follows:

- (1) The chlorine isotope values range from -1.55‰ to $+0.97\text{‰}$, and the Cl/Br ratios of the brine in the Nangqen basin range from 1739 to 175,260.
- (2) Evidence of $\delta^{37}\text{Cl}$ indicates that the saline springs in the study area have been leaching out of the underground halite layers, which is consistent with the results of the B isotopes and H–O isotopes. In addition, during the formation and evolution of the saline springs, the dissolution of mudstones and volcanic rocks are the main causes of chlorine isotopic variation.
- (3) On considering the various aspects, it is speculated that the saline springs in the Nangqen basin were leached from the underground salt layer during atmospheric precipitation or groundwater upwelling and then formed on the exposed surface. During the upwelling process, the leaching of bedrock (volcanic rock and carbonate) plays an important role in the supply of boron and chlorine.

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