# Sources and a proposal for comprehensive exploitation of lithium brine deposits in the Qaidam Basin on the northern Tibetan Plateau, China: Evidence from Li isotopes

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## ABSTRACT

A thorough understanding of the origin and distribution of lithium brine deposits is the foundation for lithium resource exploration, development and utilization. The lithium isotope system, a sensitive geochemical tracer, can be used to track a wide range of geological processes and sources. This study investigates major cations, [Li], and $\delta^7$Li of samples (brine lakes, intercrystalline brines, river waters, rain, hot spring waters, spring waters and rocks) from the Qaidam Basin on the northern Tibetan Plateau, China. [Li] values vary from less than 0.01 mg L$^{-1}$ to ~408.83 mg L$^{-1}$. There are significant differences in [Li] for different sample types. spring water (rain) < river samples < brine lakes < intercrystalline brines. The $\delta^7$Li values of samples display as significant variations as [Li], ranging from 4.33‰ to +40.66‰. There are also significant differences in $\delta^7$Li for different sample types. The $\delta^7$Li values of spring water and river waters are relatively low and the values are from 4.33‰ to 18.37‰. However, intercrystalline brines and saline lakes have the higher values, and the heaviest $\delta^7$Li (+40.66‰) occurs in Chaka Lake. The $\delta^7$Li values in brine lakes in the Qaidam Basin show obvious regional distributions, which are also consistent with the structural characteristics of the Qaidam Basin. The possible sources of lithium in the brine lakes of the Qaidam Basin result from multiple mixing of redissolved Li from earlier salt sediments, deep groundwater via fractures (oil field brines, hot springs, etc.), low-temperature weathering processes of Li-rich rock, and freshwater. The results suggest that $\delta^7$Li should be a powerful tracer to unravel the sources of Li and reconstruct its accumulation processes in brine lakes. This study provides important theoretical and practical guidance for the effective protection of precious lithium brine deposits and sustainable lithium resource exploration.

## 1. Introduction

Lithium has an atomic number of 3, and an atomic weight of 6.941. Lithium and its compounds are widely used in electronics, metallurgy, agriculture and the chemical, pharmaceutical, nuclear, aerospace and other industries, known as "industrial MSG", "aerospace alloy", "energy metal" and other well-known names because lithium has low weight, soft texture, large specific heat, high negative potential and other excellent properties (Grosjean et al., 2012; Vikström et al., 2013).

Lithium has attracted much attention in the 21st century as a new energy source and strategic resource. Its role becomes even more prominent with the development of lithium battery technology and its

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application in the field of controlled nuclear fusion. At present, international demand continues to grow at rates of 7% to 11% per year (Gil-Alana and Monge, 2019). It is predicted that lithium will become as important a strategic resource as oil is currently.

Lithium resources mainly occur in brine deposits and granitic pegmatite deposits, among which salt lake lithium resources account for 69% of global lithium reserves (Kesler et al., 2012; Christmann et al., 2015). China is rich in lithium brine resources, with lithium reserves ranking third in the world behind Bolivia and Chile, and accounting for about 30% of the world reserves. This lithium is mainly distributed on Qinghai-Tibet Plateau. Among these reserves, the lithium brine deposits in the Qaidam Basin are very rich, with large reserves, high grades, and great potential economic value. According to statistics, the lithium in the Qaidam Basin accounts for more than 80% of China's total lithium resource reserves, and 1/3 of the world's total salt lake reserves (Gao et al., 2011; Zhao, 2003). In the past decade, great attention has been paid to improve the technology for the extraction of lithium from the brine deposits of salt lakes because of the increasing market demand and lower production costs of recovering lithium carbonate from the brines (Zhao et al., 2013; Wang et al., 2018; Shi et al., 2019). Studies on the geology, geomorphology, origin and mode of formation of lithium brine deposits are scant. In recent years, several researchers have used [Li] to explain the source of lithium for some brine lakes in the Qaidam Basin (Zhan et al., 2010; Tan et al., 2012, 2018; Yu et al., 2013; Liang and Han, 2013, 2014). These preliminary studies have not only important reference value for the sustainable exploitation of lithium deposits but also positive significance for deepening the study of salt formation and metallogenic regularity in salt lakes in the Qaidam Basin. However, much work is needed to reveal the distribution and origin of lithium brine deposits. Such information includes the distribution of lithium in all salt lakes of the Qaidam Basin and dry playas and the lithium isotope characteristics of these brine lakes.

As one of the members of the "non-traditional stable isotope" family, lithium isotopes have become one of the most popular fields and frontiers of isotope geochemistry in recent years. Lithium has two stable isotopes, $^6Li$ and $^7Li$, which have abundances of 7.5% and 92.5% in nature, respectively. The two isotopes have large mass differences (approximately 16.7%), which leads to large isotope fractionation during various geological processes (Tang et al., 2007; Tomascak et al., 2016; Penniston-Dorland et al., 2017). Therefore, lithium isotopes are sensitive geochemical tracer that covers the interactions between fluids and minerals from the surface to the mantle (Misra and Froelich, 2012; Pogge von Strandmann et al., 2013; Meredith et al., 2013; Teng et al., 2017). Compared with lithium contents, lithium isotopes provide an important approach to clarify the genesis of deposits. Lithium isotopes can not only help solve the problem of the evolution of the ore-forming environment in space and time but also indicate the sources of ore-forming materials and the physical and chemical conditions of mineralization. Lithium isotopes were successfully used to constrain the origin of lithium-rich playas by Araoka et al. (2014) and Orberger et al. (2015).

In this study, brine salts, intercrystalline brines, river waters, rain, hot spring water, spring waters and rocks were collected. Major cations, [Li] and $\delta^7Li$ of samples were analyzed. The aims of this study were to constrain the sources and distribution of lithium brine deposits in the Qaidam Basin on the northern Tibetan Plateau, China, and to provide a scientific basis for studying the metallogenic regularity and mechanism of salt lake Li resources.

## 2. Geological setting and samples

The Qaidam Basin is one of the four major basins in China. It is a large intermontane basin located at the northeastern corner of the Tibetan Plateau (Tan et al., 2012). The Altun, Qilian and Kunlun Mountains bound the northwestern, northeastern and southern edges of the Qaidam Basin (Fan et al., 2018) (Fig. 1). The Qaidam Basin is one of

the regions in China with the largest distribution of salt lakes. There are more than 32 large and small lakes in the region. Except for Crook Lake, which is a freshwater lake, the rest are salt lakes. There are many intercrystalline brines in the playas. And these intercrystalline brines have become valuable salt resources.

Most of the rivers in the Qaidam Basin are intermittent, mainly formed by snowmelt from mountains and by precipitation. The mountains surrounding the basin are the birthplace of many rivers and the main source of groundwater recharge in the basin. The river network is unevenly distributed in the area. The water systems are developed, and the river network is relatively dense in the relatively rainy southeastern and northeastern section. Otherwise, rivers are sparse in the northwestern part of the basin and often run dry with few rains. The central part of the basin is a large area without runoff.

The brine salts, intercrystalline brines, river waters, rain, hot spring waters, spring waters and rocks were collected in the winter of 2015, and the places were plotted on Fig. 1. The solution samples were filtered in situ through 0.2 μm Whatman nylon filters. One filtered unacidified sample was collected for anion analysis, and one sample for cation analysis was collected into a polyethylene bottle precleaned with 6 M quartz distilled $HNO_3$ and acidified to pH < 2. Bottles were wrapped with a parafilm strip around the closure to prevent leakage. All samples were kept chilled until analysis.

## 3. Analytical methods

### 3.1. Major cations and Li concentration analyses of water samples

The Salt Lake water, the intercrystalline brine samples, river water and spring brine samples were diluted and analyzed for $Na^+$, $K^+$, $Li^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, and $Cl^-$ concentrations at the Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. All analyses for major ions in this study followed the procedures of the Qinghai Institute of Salt Lakes (Fan et al., 2018). The analytical precision for major cations and anions is better than ± 2%. The results are plotted in table 1.

### 3.2. Lithium chemical purification procedure

Chromatographic isolation of Li was carried out using AG50W-X8 cation exchange resin with 100–200 mesh size, packed into customized PDF microcolumns with an internal diameter of 6.4 mm and a column length of 25 cm. To achieve Li purification, the samples were passed through columns and were eluted with 20 mL of 0.5 M $HNO_3$, and Li was collected with 28 mL of 0.5 M $HNO_3$. The column chemistry procedure was conducted twice to ensure pure Li solution recovery and Na/Li in all of the samples was less than 5. The Li separation procedures were following the steps described by He et al. (2019).

### 3.3. Measurements of Li isotope ratios

Li isotope ratios were measured using the sample standard bracketing (SSB) method on a NEPTUNE Plus MC-ICP-MS at IEECAS. All samples were conducted at a similar Li concentration and the same procedure as standards (L-SVEC). 1% NaCl and 2% $HNO_3$ were used to wash introduction system. The operating parameters are provided in Table 2.

To obtain the average values and standard derivations (s.d.), each sample was performed triple measurements. Two in-house standards were determined repeatedly for a one-year period, with the $\delta^7Li$ = 8.3 ± 0.2‰ (2 s.d., n = 43) for IEECAS-Li, and $\delta^7Li$ = 12.2 ± 0.2‰ (2 s.d., n = 59) for SPEX-Li, respectively (Gou et al., 2019).
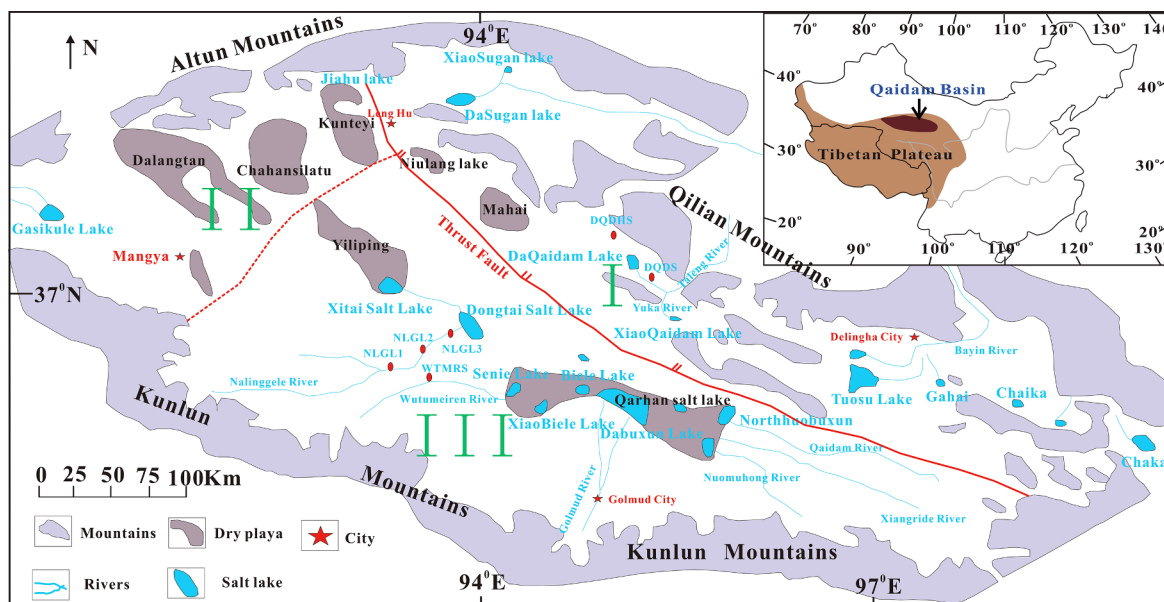
**Fig. 1.** Schematic map showing the brine lakes in Qaidam Basin (modified from Zhang et al., 1987; Fan et al., 2018).

## 4. Results

### 4.1. Lithium concentrations of salt lakes in the Qaidam Basin samples

The sample numbers, locations, and types and the $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, $Cl^-$, and $Li^+$ concentrations in samples are shown in Table 1. Among the samples collected in the Qaidam Basin, [Li] values vary from less than 0.01 mg $L^{-1}$ to ~408.83 mg $L^{-1}$. There are

significant differences in [Li] for different sample types. Spring water and rain samples have the lowest [Li] with less than 0.01 mg $L^{-1}$. River samples have relatively low [Li] from 0.04 mg $L^{-1}$ to 0.75 mg $L^{-1}$, which are within the range of the world's rivers. The [Li] of saline lakes are higher than those of river water, with the values varying from ~0.08 mg $L^{-1}$ to ~148.87 mg $L^{-1}$. Intercrystalline brines have the highest [Li] with values from ~9.18 mg $L^{-1}$ to ~408.83 mg $L^{-1}$.

**Table 1**
Chemical compositions of samples in the Qaidam Basin.

| Sample Nos. | Location | Sample type | $Cl^-$ | $SO_4^{2-}$ | $K^+$ | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Li^+$ mg $L^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| CK15-01 | Chaka lake | Surface brine | 180.82 | 17.72 | 3.73 | 87.72 | 0.27 | 18.86 | 8.40 |
| CKH15-01 | Chaika lake | Surface brine | 188.09 | 15.02 | 1.49 | 115.05 | 0.48 | 6.79 | 4.33 |
| GH15-01 | Gahai | Surface brine | 44.00 | 11.97 | 0.61 | 26.16 | 0.33 | 3.94 | 2.49 |
| TSH15-01 | Tuosu lake | Surface brine | 7.26 | 3.76 | 0.17 | 4.27 | 0.01 | 1.13 | 0.72 |
| DCD15-01 | DaQaiddam lake | Surface brine | 105.80 | 10.11 | 1.92 | 64.58 | 0.32 | 4.08 | 43.18 |
| DSG15-01 | DaSugan lake | Surface water | 8.00 | 8.16 | 0.43 | 5.91 | 0.04 | 1.54 | 1.16 |
| XSG15-01 | XiaoSugan lake | Surface water | 0.75 | 0.66 | 0.03 | 0.53 | 0.05 | 0.11 | 0.08 |
| GSKLL15-01 | Gasikule lake | Surface brine | 119.75 | 32.36 | 2.66 | 65.19 | 0.75 | 13.59 | 14.39 |
| XTL15-01 | Xitai Salt Lake | Surface brine | 8.72 | 1.61 | 0.28 | 5.05 | 0.15 | 0.56 | 8.72 |
| DBXL15-01 | Dabuxun lake | Surface brine | 214.08 | 5.80 | 5.41 | 32.80 | 0.89 | 55.28 | 148.87 |
| DCDY15-01 | DaQaiddam lake | Intercrystalline brine | 187.51 | 23.42 | 5.07 | 104.42 | 0.34 | 13.62 | 131.2 |
| NLA15-01 | Niulang Lake | Intercrystalline brine | 213.89 | 2.00 | 5.03 | 50.29 | 23.45 | 31.53 | 19.4 |
| JH15-01 | Jiahu lake | Intercrystalline brine | 219.44 | 7.64 | 10.65 | 34.22 | 0.69 | 55.45 | 9.18 |
| GYT15-04′ | Gasikule lake | Intercrystalline brine | 282.90 | 35.50 | 4.60 | 1.64 | 0.04 | 105.15 | 97.50 |
| DBX15-01 | Dabuxun lake | Intercrystalline brine | 259.58 | 0.78 | 15.97 | 11.74 | 8.31 | 73.04 | 84.50 |
| BLT15-01 | Biele lake | Intercrystalline brine | 250.59 | 5.00 | 21.12 | 14.46 | 0.60 | 72.62 | 129.54 |
| XBLT15-01 | XiaoBiele lake | Intercrystalline brine | 178.53 | 6.04 | 11.68 | 38.72 | 0.66 | 38.22 | 116.42 |
| SNH15-01 | Senie lake | Intercrystalline brine | 233.39 | 10.72 | 4.94 | 19.42 | 0.33 | 70.69 | 217.40 |
| YLP15-01 | Yiliping | Intercrystalline brine | 192.87 | 24.60 | 13.34 | 82.59 | 0.33 | 24.15 | 379 |
| XTW15-01 | Xitai Salt Lake | Intercrystalline brine | 193.82 | 19.02 | 11.76 | 70.16 | 0.36 | 30.04 | 408.83 |
| BYR | Bayin River | River water | 0.09 | 0.05 | 0.01 | 0.04 | 0.038 | 0.018 | 0.04 |
| YQH15-01 | Yuka River | River water | 0.10 | 0.04 | 0.01 | 0.05 | 0.04 | 0.02 | 0.04 |
| TLH15-01 | Taleng River | River water | 0.08 | 0.04 | 0.00 | 0.05 | 0.04 | 0.02 | 0.07 |
| NLGL1 | Nalinggele River (upper) | River water | 189 | 76.0 | 10.8 | 148 | 37.2 | 26.3 | 0.43 |
| NLGL2 | Nalinggele River (Middle) | River water | 175 | 61.2 | 13.6 | 145 | 32.6 | 23.3 | 0.62 |
| NLGL3 | Nalinggele River (lower) | River water | 191 | 90.3 | 10.7 | 153.7 | 32.1 | 27.2 | 0.56 |
| WTMR15-01 | Wutumeiren River | River water | 285 | 95.8 | 17.2 | 175 | 30.1 | 30.7 | 0.75 |
| GLM15-01 | Goldmud River | River water | 125 | 91.2 | 4.85 | 81.6 | 25.9 | 40.2 | 0.049 |
| DQDHS | DaQaiddam | hot spring water | 0.37 | 0.28 | 0.00 | 0.38 | 0.031 | 0.00 | 2.34 |
| DQDS | DaQaiddam | Spring water | | | | | | | < 0.01 |
| WTMRS | Wutumeiren | Spring water | | | | | | | < 0.01 |
| DCDR | DaQaiddam town | Rain | | | | | | | < 0.01 |

**Table 2**
Operating parameters for the Li isotope measurement on a Neptune-plus MC-ICP-MS.

| Parameters | Values |
|---|---|
| RF forward power (W) | 1200 |
| Ar cooling gas (L min$^{-1}$) | 15 |
| Ar auxiliary gas (L min$^{-1}$) | 0.76 |
| Ar sample gas (L min$^{-1}$) | 1.081 |
| Extraction voltage (V) | $-2000$ |
| Acceleration voltage (KV) | 10 |
| Detection system | L4, H4 Faraday cups |
| Nebulizer | Low-flow PFA microcentric (50 μL min$^{-1}$) |
| Focus Quad (V) | 0.5 |
| Dispersion (V) | 26.5 |
| Uptake time (s) | 60 |
| Integration time (s) | 4.195 |
| Measurement time (min) | 4 |
| Rinse time (min) | 4 |

*4.2. Lithium isotope compositions of salt lakes in the Qaidam Basin samples*

The $\delta^7Li$ values of samples in the Qaidam Basin display significant variation, ranging from 4.33‰ to $+40.66$‰ (Table 3). The $\delta^7Li$ values of spring water and river waters are relatively low, ranging from 4.33‰ to 18.37‰. However, intercrystalline brines and saline lakes have more positive values, and the most positive $\delta^7Li$ ($+40.66$‰) occurs in Chaka Lake. The $\delta^7Li$ value of rain samples collected from DaQaiddam town is 29.13‰. The $\delta^7Li$ values of intercrystalline brines are all higher than those of the corresponding saline lakes, which indicates the contributions of river water and rainfall.

## 5. Discussion

### 5.1. Distribution characteristics of $\delta^7Li$ in the Qaidam Basin samples

The variations in $\delta^7Li$ in the Qaidam Basin are relatively large. This variability is related to the brine lakes having many material sources and undergoing complex geological processes. The $\delta^7Li$ values show obvious regional distribution characteristics. The brine lakes of Qaidam Basin can be divided into three zones according to [Li] and $\delta^7Li$ values, which are also consistent with the structural characteristics of the Qaidam Basin.

Zone I, the eastern and northeastern Qaidam Basin. This zone is bounded by the central thrust fault. The zone includes Chaka Lake, Chai Kai, Gahai Lake, Tuosu Lake, DaQaidam Lake, XiaoQaidam Lake, Mahai and Niulang Lake from the eastern part of the basin. The $\delta^7Li$ values in this region are heaviest ranging from 22.69 to 40.66‰, with an average of 30.28‰. The $\delta^7Li$ values are slightly lower in Tuosu Lake, DaQaidam Lake and XiaoQaidam Lake, varying from 22.69‰ to 25.58‰.

These brine lakes are mainly distributed in the front of the Qilian Mountains. Their recharge water originates mainly as melting snow and rainwater from the Qilian Mountains. The $\delta^7Li$ value of rainwater collected at DaQaidam town is 29.13‰, which indicates that some of the lithium in the rain may have come from the ocean. The $\delta^7Li$ values of the Bayin River and the Yuka River may represent the $\delta^7Li$ values of river water. The $\delta^7Li$ values in these two rivers are 13.34‰ and 14.36‰, respectively. They are both lower than that of the rain, possibly due to dissolving rocks with low $\delta^7Li$.

Zone II, the western Qaidam Basin. The $\delta^7Li$ values in this area are also high, ranging from 24.43‰ to 32.58‰, with an average of 29.42‰. The higher $\delta^7Li$ in this area may be mainly due to the following two reasons. First, the area has strong evaporation. The light

**Table 3**
$\delta^7Li$ of samples in the Qaidam Basin.

| Sample No. | Location | Sample type | Li$^+$ (mg L$^{-1}$) | $\delta^7Li \pm 2SD$ (‰) | Li/Cl ($\times 10^{-3}$) | Zone |
|---|---|---|---|---|---|---|
| CK15-01 | Chaka lake | Surface brine | 8.40 | 40.66 ± 0.04 | 46.46 | I |
| CKH15-01 | Chaika lake | Surface brine | 4.33 | 34.77 ± 0.03 | 23.02 | |
| GH15-01 | Gahai | Surface brine | 2.49 | 31.03 ± 0.03 | 56.59 | |
| TSH15-01 | Tuosu lake | Surface brine | 0.72 | 25.58 ± 0.07 | 99.17 | |
| DCD15-01 | DaQaiddam lake | Surface brine | 43.18 | 22.69 ± 0.05 | 408.13 | |
| DCDY15-01 | DaQaiddam lake | Intercrystalline brine | 131.2 | 24.12 ± 0.09 | 699.70 | |
| NLA15-01 | Niulang Lake | Intercrystalline brine | 19.4 | 33.09 ± 0.30 | 90.70 | |
| DSG15-01 | DaSugan lake | Surface water | 1.16 | 27.77 ± 0.04 | 145.00 | |
| XSG15-01 | XiaoSugan lake | Surface water | 0.08 | 24.43 ± 0.60 | 106.67 | |
| JH15-01 | Jiahu lake | Intercrystalline brine | 9.18 | 30.98 ± 0.04 | 41.83 | |
| GSKL15-01 | Gasikule lake | Surface brine | 14.39 | 31.35 ± 0.01 | 120.17 | II |
| GYT15-04′ | Gasikule lake | Intercrystalline brine | 97.50 | 32.58 ± 0.09 | 344.64 | |
| DBXL15-01 | Dabuxun lake | Surface brine | 148.87 | 16.07 ± 0.07 | 695.39 | III |
| DBX15-01 | Dabuxun lake | Intercrystalline brine | 84.50 | 21.22 ± 0.04 | 325.53 | |
| BLT15-01 | Biele lake | Intercrystalline brine | 129.54 | 18.31 ± 0.05 | 516.94 | |
| XBLT15-01 | XiaoBiele lake | Intercrystalline brine | 116.42 | 15.13 ± 0.14 | 652.10 | |
| SNH15-01 | Senie lake | Intercrystalline brine | 217.40 | 15.25 ± 0.03 | 931.49 | |
| YLP15-01 | Yiliping | Intercrystalline brine | 379 | 11.93 ± 0.01 | 1965.05 | |
| XTL15-01 | Xitai Salt Lake | Surface brine | 8.72 | 9.21 ± 0.09 | 1000.00 | |
| XTW15-01 | Xitai Salt Lake | Intercrystalline brine | 408.83 | 11.48 ± 0.07 | 2109.33 | |
| BYR | Bayin River | River water | 0.04 | 13.34 ± 0.03 | | |
| YQH15-01 | Yuka River | River water | 0.04 | 14.36 ± 0.02 | | |
| TLH15-01 | Taleng River | River water | 0.07 | 10.92 ± 0.04 | | |
| NLGL1 | Nalinggele River (upper) | River water | 0.43 | 11.34 ± 0.03 | | |
| NLGL2 | Nalinggele River (Middle) | River water | 0.62 | 14.48 ± 0.04 | | |
| NLGL3 | Nalinggele River (lower) | River water | 0.56 | 16.46 ± 0.01 | | |
| WTMR15-01 | Wutumeiren River | River water | 0.75 | 15.37 ± 0.02 | | |
| GLM15-01 | Goldmud River | River water | 0.01 | 18.37 ± 0.03 | | |
| DQDHS | DaQaiddam | hot spring water | 2.34 | 4.33 ± 0.03 | | |
| DQDS | DaQaiddam | Spring water | < 0.01 | 10.81 ± 0.03 | | |
| WTMRS | Wutumeiren | Spring water | < 0.01 | 9.36 ± 0.03 | | |
| DCDR | DaQaiddam town | Rain | < 0.01 | 29.13 ± 0.04 | | |
| NLGLR | Nalenggele | Rock | 27.2 (mg kg$^{-1}$) | 6.26 ± 0.03 | | |
| WTMR | Wutumeiren | Rock | 28.2 (mg kg$^{-1}$) | 4.98 ± 0.03 | | |

lithium isotope ($^6$Li) is carried away with salts or sediments during the precipitation of salt in the brines, making the $\delta^7$Li of brines heavier. Second, the groundwater sources yield heavier $\delta^7$Li. The supply of river water in the region is not very plentiful, and the main source of recharge is groundwater. The area is rich in buried oil, so the groundwater is related to oil and is considered mostly oilfield water.

Zone III, the central sag of the Qaidam Basin. There are many brine lakes in this region, and the salt resources are extremely rich. These brine lakes are located in the lowest area of the basin. They are modern salt lakes formed on the basis of ancient lakes and retain part of the residual brines of the ancient lakes. The $\delta^7$Li values range from 9.21‰ to 21.21‰, with an average of 14.82‰, which is much lower than the $\delta^7$Li values (30.28‰ and 29.42‰) of brine lakes in the other two areas of the Qaidam Basin. This area is also rich in recharge water from the Kunlun Mountains. Generally, the brine lakes have large areas, deep water levels, and high Li/Cl ratios (Table 3). The southern margin of the zone is the Kunlun Mountains, where rainfall, snow and ice melt water are injected into the salt lakes through the Qaidam River, the Nuomuhong River, the Golmud River, the Wutumeiren River and the Nalinggele River.

## 5.2. The sources of lithium brine deposits in the Qaidam Basin

The Qaidam Basin is rich in elements such as K, Mg, B and Li. These elements are mainly distributed in the intercrystalline brines and surface brine waters. The possible sources of lithium in the Qaidam Basin may be as follows: 1) redissolution of Li from Tertiary salt sediments; 2) weathering and leaching from Li-rich parent rocks; 3) freshwater; and 4) deep groundwater via fractures (oil field brines, hot springs, etc.). These different sources of Li are brought into the brines by external evaporation. The intercrystalline lithium brine deposits form in the enriched intercrystalline brine.

### 5.2.1. Redissolution of Li from earlier salt sediments

The world's lithium-rich brine lakes are mainly distributed in plateau areas because the early formations of salt-bearing sediments have been exposed to the surface as the result of tectonic uplift and squeezed to the near surface. Lithium is leached and easily removed from Tertiary salt sediments due to their weak weathering resistance (Zhang et al., 1987; Risacher et al., 2003).

The $\delta^7$Li values of brine lakes in zone I are the heaviest and range from 22.69 to 40.66‰. These $\delta^7$Li values are close to those of seawater. The [Li] and $\delta^7$Li values are 0.18 ppm and 31.0 ± 0.5‰, respectively (Millot et al., 2004; Tomascak, 2004). Lithium is isotopically homogeneous in the open ocean reservoir because of the long residence time of lithium in the ocean (~1.2 Ma) (Tomascak, 2004; Misra and Froelich, 2012). The $\delta^7$Li value of seawater has ranged from +22 to +31‰ during the past 60 Ma (Misra and Froelich, 2012). The $\delta^7$Li values in Zone I are very high and fall within the range of seawater. However, the $\delta^{11}$B values of brine lakes indicate a nonmarine origin. Taken together, these results indicate that the lithium originates from earlier continental salt sediments. Leaching and weathering experiments on the combined samples of salt-bearing rock series in the western basin support our results (Zhang et al., 1987). Their results show that the anion migration order of the salt-bearing rock series is the same as the natural water ion content sequences ($Cl^- > SO_4^{2-} > HCO_3^- + CO_3^{2-}$) (except for atmospheric precipitation) within the basin, which proves the influence of salt mineral redissolution on the regional water chemistry of the Cenozoic salt-bearing strata in the Qaidam Basin. Salt crust redissolution has been found in other lakes, such as Lake Minchin on the Altiplano Plateau in Bolivia (Fornari et al., 2001; Risacher and Fritz, 2000), Chilean salars (Risacher et al., 2003), and the Salar de Atacama (Rissmann et al., 2015).

The brines in some brine lakes are the result of mixing brines from other current salt lakes and groundwater. Most of these recycled salts are transported by recycled brine (Risacher and Fritz, 2009; Rissmann et al., 2015). In the modern lithium-rich salt lakes of the world, the amounts of weathered matter inputs are much lower than the amounts of recycled salt (Risacher et al., 2003), which shows the importance of recycling brine.

### 5.2.2. From deep groundwater via fractures (oil field brines, geothermal water, etc.)

Deep groundwater is extremely important for the migration of lithium in lithium-rich salt lakes. When groundwater is transported in salt-bearing rock systems, lithium in the original salt minerals is dissolved to form a more lithium-rich intercrystalline brine. In addition, groundwater circulates deeply and then is heated by magma, finally reaching the surface in hot springs. In this process, much lithium leached from the surrounding rocks caused by water-rock reactions is brought to the salt lakes. Most lithium-rich salt lakes are located in deep fault zones of subduction-collision environments. Deep hydrothermal and shallow geothermal water reacts with the rocks through water-rock reactions, and elements such as lithium, potassium and boron are dissolved. Filtered and rising with deep fluids and the circulation of shallow groundwater, elements such as lithium are gradually enriched. Finally, lithium and other minerals are supplied to salt lakes in the form of volcanic jets and hot springs. This process is the main source of lithium resources in the lithium-rich salt lakes (Garrett, 2004).

The $\delta^7$Li values of brine lakes in zone III are lowest in the Qaidam Basin, with an average of 14.82‰. Li from deep groundwater to hot spring water has low $\delta^7$Li values (Table 3). The Nalinggele River and Wutumeiren River are enriched in Li, but the adjacent rivers (Golmud River, Nuomuhong River, etc.) have very low Li although they are affected by chemical weathering of similar types of rock. The [Li] values of the Nalinggele River and Wutumeiren River are 0.43 mg L$^{-1}$ and 0.75 mg L$^{-1}$, respectively, which are 50–100 times those of the Golmud River. The source of the Nalinggele River and Wutumeiren River is the Hongshui River, which is located in an active tectonic zone in the Kunlun Mountains and Altun Mountains (Tan et al., 2012; Yu et al., 2013). Deep geothermal water migrates upward, and discharges from high-temperature water-rock interactions produce a lithium-enriched hydrothermal solution with low $\delta^7$Li, which becomes an important source of Li inputs into these two rivers. Many lithium-enriched salt lakes have a source of deep groundwater (Zhan et al., 2010; Risacher et al., 2011; Godfrey et al., 2013; Araoka et al., 2014). The $\delta^7$Li values of deep groundwater are very low. One hot spring water (geothermal spring) from DaQaiddam has a value of 4.33‰. The $\delta^7$Li results for brines in the Salar del Hombre Muerto, central Andes, vary from +3‰ to +9‰, which also has significant contributions from geothermal springs.

### 5.2.3. Low-temperature weathering processes of Li-rich rocks

The world's lithium-rich lakes are located in active subduction-collision orogenic belts, which causes remelting of crustal rocks. Acidic or alkaline magma is formed during the remelting process of these rocks. Lithium-rich magmatic rocks form during the crystallization of the magma since lithium is a lithophile element (Zhang et al., 1987; Zheng, 2001; Risacher and Fritz, 2009; Araoka et al., 2014). The lithium in these surrounding rocks is activated and enters lithium-rich salt lakes along with fluids such as surface water. The chemical composition and isotopic characteristics of the fluid are changed in these processes (Boschetti et al., 2007).

The rocks in the Kunlun Mountains have higher [Li] than the crustal Clarke value (Zhang et al., 1987; Zhan et al., 2010). The elevation of the East Kunlun Mountains area is high (average 3000 m or more), which inevitably accelerates the weathering and leaching of rocks. Widely distributed granite and granitic gneiss in this area are weathered and leached through snow, ice melt, rainwater and other surface waters. Large amounts of lithium-containing material migrate into the river and enter the basin. The $\delta^7$Li values in the Nalinggele River gradually

change from 11.34‰ to 16.46‰ from upstream to downstream, and the lithium content gradually increases from 0.43 mg $L^{-1}$ to 0.53 mg $L^{-1}$. Moreover, the two rock samples have lower $\delta^7 Li$ values of only 4.98‰ and 6.26‰. These results indicate that the river water dissolves lithium from the surrounding rocks, which might cause the $\delta^7 Li$ values in the river to gradually decrease.

### 5.2.4. From freshwater

Atmospheric precipitation leaches weathered lithium-rich rock, activates lithium in the rock, and transports it into the lake, which is an important source of salt lake fluid.

The [Li] increases from 0.43 mg $L^{-1}$ to 0.53 in the Nalinggele River from the upper reach to the lower reach. Our results agree with those of previous studies (Tang et al., 2016). The [Li] decreases slightly from the middle reach (0.65 mg $L^{-1}$) to the lower reach (0.53 mg $L^{-1}$) due to the supply from other tributary rivers (Table 2). The [Li] increases from 11.34‰ to 16.46‰ in the Nalinggele River from upstream to downstream. These results indicate that atmospheric precipitation and surface water transport lithium to brine lakes. The results from the ratios of Cl /Br and other isotopes ($^{18}O$, $^2H$, $^{11}B$) indicate that the current lake brine originates from a mixture of brine and atmospheric precipitation (Risacher et al., 2003; Wei et al., 2014).

In conclusion, for lithium-rich salt lakes, lithium enrichment is the result of multiple mixing of Li from the above several sources. Among them, groundwater (geothermal spring) is the main source of fluids in lithium-rich salt lakes and plays a major role in the dissolution and migration of lithium. These fluids not only dissolve the salt deposits that formed earlier but also react with the surrounding rocks to produce water-rock reactions that leach the lithium out of the rocks.

### 5.3. A proposal for comprehensive utilization and large-scale exploitation of brine deposits (Li and K) in the Qaidam Basin

The Wutumeiren River and Nalinggele River on the northern slope of the eastern Kunlun Mountains in the Qaidam Basin, China, have very high concentrations of lithium. Correspondingly, the salt lakes fed by these rivers show unusual enrichments in lithium and have become an important economic resource. The total annual amount of Li input into salt lakes by these two rivers is more than 700 T, which is calculated based on our and previous results. Therefore, large amounts of lithium resources in the Qaidam Basin have accumulated over at least the last several thousand years and are mainly distributed in Beile beach, Xitai and Dongtai, accounting for 80% of the total lithium resources in China (Tan et al., 2012; Yu et al., 2013). However, potassium is mainly distributed in Qarhan Salt Lake, which hosts one of the largest potash operations in China. In recent years, the annual production of potash fertilizer has been close to $500 \times 10^4$ T and uses large amounts of lithium-enriched brine from Beile beach. Much lithium-rich brine might be waste in the production of potash under the current production model. Therefore, effectively avoiding the loss of lithium in the process of producing potash is a very important task for the future. At present, in addition to solving the key technical problems of lithium extraction as soon as possible, it is necessary to immediately transform the potassium fertilizer production mode to produce a combination of potassium and lithium from the brine.

### 6. Conclusions

[Li] and $\delta^7 Li$ data from the brine salts in the Qaidam Basin on the northern Tibetan Plateau, China, are presented. The [Li] and $\delta^7 Li$ variations throughout the brine lakes can be linked to the sources of lithium brine deposits and the structural characteristics of the Qaidam Basin. Our main conclusions are as follows:

1) There are significant differences in [Li] for different sample types: spring water (rain) < river samples < brine lakes <

intercrystalline brines. [Li] varies from less than 0.01 mg $L^{-1}$ to ~408 mg $L^{-1}$.

2) The $\delta^7 Li$ values of samples display significant variations, ranging from 4.33‰ to +40.66‰. There are also significant differences in $\delta^7 Li$ for different sample types. The $\delta^7 Li$ values of spring water and river waters are relatively low, ranging from 4.33‰ to 18.37‰. However, intercrystalline brines and saline lakes have more positive values, and the most positive $\delta^7 Li$ (+40.66‰) occurs in Chaka Lake.

3) The $\delta^7 Li$ values of brine lakes in the Qaidam Basin show obvious regional distributions that are also consistent with the structural characteristics of the Qaidam Basin.

4) Weathering and leaching of Li from Tertiary salt deposits, weathering and leaching from Li-rich parent rock, freshwater, deep groundwater via fractures (oil field brines, hot springs, etc.), and recycled brine are possible sources of lithium in the brine lakes of the Qaidam Basin.

### Declaration of Competing Interest

The authors declared that they have no conflicts of interest to this work.

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.oregeorev.2019.103277.

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