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Zhen Nie
*Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing*

Lingzhong Bu
*Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing*

Mianping Zheng
*Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing*

Yongsheng Zhang
*Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing*

# Crystallization Path of Salts from Brine in Zabuye Salt Lake, Tibet, During Isothermal Evaporation

**Zhen Nie[1,2,3] , Lingzhong Bu[1,2,3], Mianping Zheng[1,2,3] & Yongsheng Zhang[1,2,3]**

[1]Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, China; [2]R & D Center for Saline Lakes and Epithermal Deposits, Chinese Academy of Geological Sciences, Beijing, China; [3]Key Laboratory of Saline Lake Resources and Environment, Ministry of Land and Resources, Beijing, China

Corresponding author:
Zhen Nie
Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China
E-mail: nieezhen518@163.com

## ABSTRACT

Zabuye Salt Lake in Tibet, China is a carbonate-type lake, rich in Li, B, K and other useful trace elements that are of great economic value. We studied the concentration behavior of these elements and the crystallization paths of salts in the brine at 25°C, based on an isothermal evaporation experiment. The crystallization sequence of the primary salts from the brine at 25°C is halite (NaCl) → aphthitalite ($3K_2SO_4 \cdot Na_2SO_4$) → zabuyelite ($Li_2CO_3$) → sylvite (KCl) → trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) and thermonatrite ($Na_2CO_3 \cdot H_2O$), in accordance with the metastable phase diagram of the $Na^+$, $K^+//Cl^-$, $CO_3^{2-}$, $SO_4^{2-}$-$H_2O$ quinary system at 25°C, except for sodium carbonate heptahydrate ($Na_2CO_3 \cdot 7H_2O$) which is replaced by trona and thermonatrite. In the experiment, zabuyelite ($Li_2CO_3$) was precipitated in the early stage because $Li_2CO_3$ was supersaturated in the brine at 25°C. Potassium was precipitated as aphthitalite in the intermediate stage and as sylvite in the late stage, while boron was concentrated in the early and intermediate stages and precipitated as borax ($Na_2B_4O_7 \cdot 10H_2O$) in the late stage.

## INTRODUCTION

Zabuye Salt Lake, a carbonate-type saline lake, is located in the interior of the Tibetan Plateau, China, ~1000 km west of Lhasa, capital of Tibet (Figure 1). The lake's brine is supersaturated with NaCl and other salts. Millions of metric tons of halite, potash, trona, and other minerals are deposited on the bottom of the lake (Zheng et al. 1988, 1989). The salt lake is of great economic value as a new type of large sedimentary deposit containing dominantly lithium and borate salts in addition to potash, halite, natron and Glauber's salt. The lake also contains cesium, rubidium and bromine (Zheng et al. 1989; Zheng 1999; Zhao et al. 2003). The level of the lake, which has been subject to historical variations, is currently (2008) at ~4422 m above sea level. At this level, the lake's area is approximately 247 km$^2$. The salinity varies from 36 to 44%, depending on periodical differences in water input and evaporation rate (Qi & Zheng 2007).

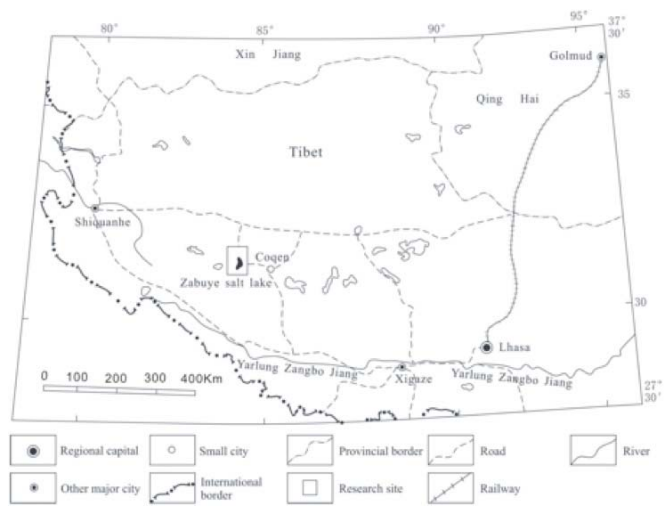


**Figure 1–** Location of Zabuye Salt Lake.

Zabuye Salt Lake was first recognized in 1961 to be a deposit of borax (Zheng et al. 1989). Since the 1980s, substantial scientific research has been performed in order to exploit and utilize its mineral resources (Yang et al. 1996; Nie & Zheng 2001). Here M. Zheng first found zabuyelite, a mineral of natural lithium carbonate (Zheng & Liu 1987). In 1990, the Research & Development Center for Saline Lakes and Epithermal Deposits at the Chinese Academy of Geological Sciences, established a long-term scientific observation station near Zabuye Salt Lake to monitor the physical-chemical data of the lake. This station is still in operation (Zhang et al. 2001; Nie et al. 2005).

Mineral exploitation in Zabuye Salt Lake is now conducted exclusively by a mining company, the Tibet Zabuye High-Tech Lithium Industry Company Ltd. This company has built a production plant and produced nearly 2000 metric tons of lithium carbonate per year since 2005 (Huang et al. 2008). Lithium carbonate is the company's only product; though lithium ranks only eighth in abundance in the lake, out of every 100 metric tons of minerals contained in the lake, only ~1.25 metric tons are lithium carbonate. Therefore, many tons of mineral salts have been stockpiled near the solar ponds during the process of extracting lithium carbonate from Zabuye Salt Lake. This stockpiled material may be harmful to the environment. This paper reports a

test designed to study the element concentration characteristics and mineral crystallization paths of Zabuye Salt Lake brine through an isothermal evaporation test at 25°C. This study will help us to devise ways to extract halite, potash, borax and lithium carbonate together, leading to an improved use of the total mineral resources of Zabuye Salt Lake and to enhance the protection of the environment.

## MATERIALS AND METHODS

A brine sample for the experiment was collected from Zabuye Salt Lake in October 2001. The temperature of the lake's brines generally ranges between -15°C in January to 25°C in late summer. The experiments with the brine were conducted at 25°C.

The main chemical composition of a Zabuye Salt Lake brine sample is shown in Table 1. Na and Cl ions account for to up to 80% of the total chemicals in the lake, while Na, Cl, K, $CO_3^{2-}$ and $SO_4^{2-}$ ions together make up 95% of the total. The quinary water-salt system $Na^+$, $K^+//CO_3^{2-}$, $SO_4^{2-}$, $Cl^-$-$H_2O$ can be used to explain the concentration and crystallization behavior of the various elements in brine (Fang et al. 1991). From the metastable phase diagram of the quinary water-salt system $Na^+$, $K^+$, $CO_3^{2-}$, $SO_4^{2-}$, $Cl^-$-$H_2O$ at 25°C (Figure 2) we may conclude that the sequence of mineral precipitation at 25°C is aphthitalite, $Na_2CO_3 \cdot 7H_2O$ and sylvite.

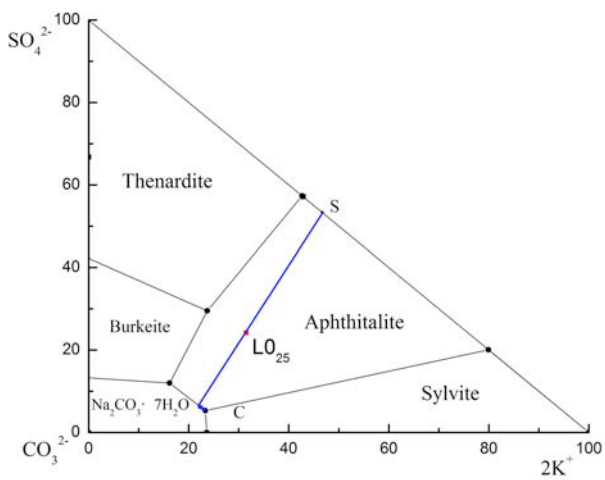


**Figure 2**–Metastable phase diagram and crystallization path of the quinary water-salt system $Na^+$, $K^+$, $CO_3^{2-}$, $SO_4^{2-}$, $Cl^-$-$H_2O$ (at 25°C). $L0_{25}$, the compositional point of the original brine for the experiment; S, the solid compositional point of Aphthitalite; C, the steady equilibrium point of the metastable phase diagram; Thenardite, $Na_2SO_4$; Burkeite, $Na_2CO_3 \cdot 2Na_2SO_4$.

For the isothermal evaporation experiment the brine was placed on a glass evaporating dish and the experiment was conducted in a temperature-controlled environment at 25±0.5°C, regulated by a mercury contact thermometer. An exhaust fan was used to supply a discontinuous air draft and an incandescent lamp was used as the heat source. Newly precipitated material was removed three times per day, chemically analyzed, and examined under the microscope to identify the precipitated minerals. The solid and liquid phases were separated when a new mineral was observed (Zhang et al. 2005; Zheng et al. 2007), and the relevant parameters of the solid and liquid phases were then determined, including complete chemical analysis of all the samples. The evaporation experiment was continued until the brine had dried up.

The following analytical methods were used (Analysis Group 1988): K, Li, and Na ions were quantified by atomic absorption spectrometry; Cl ion by silver nitrate volumetric analysis; the $SO_4$ ion was assayed gravimetrically as barium sulfate, and $B_2O_3$ and $CO_3$ ions were measured by mannitol volumetric analysis.

**Table 1**–The main chemical composition of Zabuye Salt Lake brines (g/l).

| Sample no. | $Na^+$ | $K^+$ | $Li^+$ | $Cl^-$ | $SO_4^{2-}$ | $B_2O_3$ | $CO_3^{2-}$ |
|---|---|---|---|---|---|---|---|
| $L0_{25}$ | 129.6 | 40.9 | 1.05 | 156.2 | 38.6 | 11.0 | 44.2 |

## RESULTS

In the course of the isothermal evaporation experiment we analyzed the chemical composition of brines and precipitated (solid phase) mineral salts. Table 2 shows the chemical composition of the liquid phases formed by isothermal evaporation of autumn brines at 25°C, while Table 3 presents the composition of the minerals (solid phase) precipitated during this process.

There are five solid-phase regions saturated with NaCl in the metastable phase diagram of the quinary water-salt system $Na^+$, $K^+//CO_3^{2-}$, $SO_4^{2-}$, $Cl^-$-$H_2O$ at 25°C; these are sylvite (KCl), aphthitalite ($3K_2SO_4 \cdot Na_2SO_4$), sodium carbonate heptahydrate ($Na_2CO_3 \cdot 7H_2O$), thenardite ($Na_2SO_4$), and burkeite ($2Na_2SO_4 \cdot Na_2CO_3$). The compositional point of the original brine for the experiment is located in the aphthitalite region. Because the brine is saturated with NaCl, halite is precipitated immediately after the isothermal evaporation experiment begins. Then, aphthitalite becomes saturated as the experiment proceeds. The liquid-phase compositional points basically move along the extension of the tie line of the original brine compositional point and the aphthitalite solid phase point. The precipitated salts are mainly halite and aphthitalite.

Then, $Li_2CO_3$ becomes saturated and zabuyelite is precipitated together with halite and aphthitalite. After that, KCl saturation is reached, and sylvite is precipitated. In the late stage of the experiment, trona and thermonatrite start to precipitate in large amounts. The sequence of mineral precipitation from the brine is thus halite → aphthitalite → zabuyelite → sylvite → trona and thermonatrite. The whole 25°C isothermal evaporation and salt precipitation path essentially coincides with the metastable phase diagram of the $Na^+$, $K^+//Cl^-$, $CO_3^{2-}$, $SO_4^{2-}$-$H_2O$ quinary system at 25°C (Figure 3).

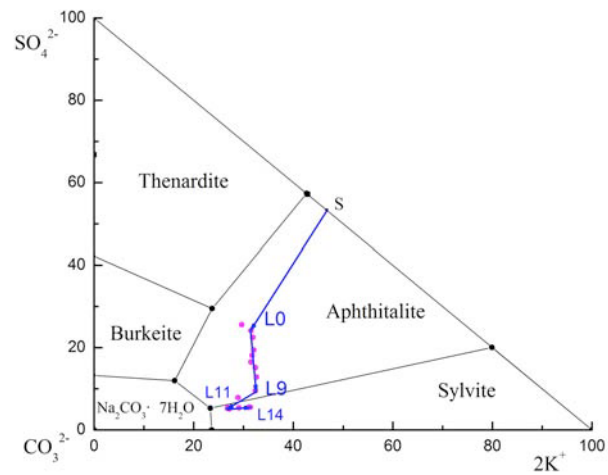


**Figure 3**–Crystallization path of autumn brine in Zabuye Salt Lake at 25°C.

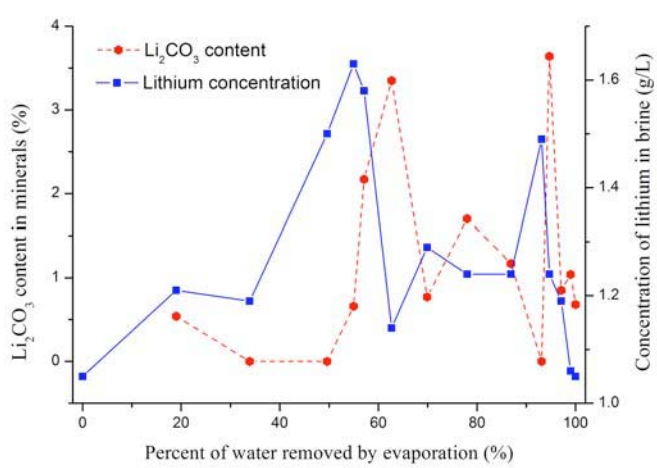


**Figure 4**–Content of lithium and its minerals during isothermal evaporation at 25°C. The relation of the weight percentages of minerals in the solid phase and ion concentration is shown as a function of the percentage of water removed by evaporation.

## DISCUSSION

The main ions in Zabuye Salt Lake brine are Na and Cl, which account for 80% of the brine chemical composition. NaCl in the brine is in a saturated state during evaporation at 25°C. Therefore, halite is precipitated throughout the entire isothermal evaporation process. In the early and middle stages of the experiment, halite was the dominant solid phase component. Only in the late stage did the amount of halite decrease.

The concentration and precipitation behavior of lithium in Zabuye Salt Lake brine at the 25°C temperature and its relation to the evaporation rate are shown in Figures 4. In the early stage of evaporation, lithium is concentrated in the brine. However, lithium attains saturation fast and a large amount is precipitated as lithium carbonate. The peak content of zabuyelite in the solid phase corresponds to the lowest lithium concentration in brine, exhibiting an inverse relation. Two main peaks of lithium precipitation were observed during the experiment, but overall, lithium precipitation is a continuous process that occurs throughout the experiment. During the experiment it was not easy to obtain a high-grade lithium salt through evaporation and separation.

During the early and middle stages of evaporation, potassium is mainly precipitated as aphthitalite. In the late stage it is precipitated as sylvite, accompanied by minor amounts of aphthitalite. In the whole evaporation process of the experiment, potash started to precipitate as soon as potassium became saturated in the brine. High-grade potash can be obtained from Zabuye Salt Lake brine through proper operation. The relation between the potassium mineral content in the solid phases and the evaporation rate is shown in Figure 5. The potassium concentration in the liquid phases went up progressively during the experiment.

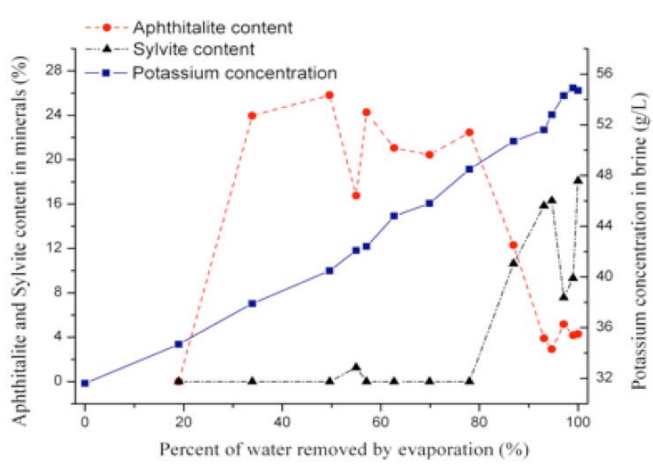


**Figure 5**–Content of potassium and its minerals during isothermal evaporation at 25°C.

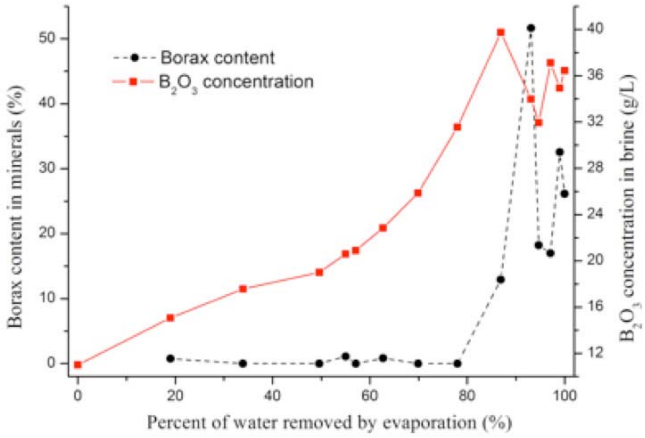


**Figure 6**–Content of boron and its minerals during isothermal evaporation at 25°C.

Boron becomes highly concentrated during evaporation (Figure 6). The concentration of boron in the liquid phases increased progressively with evaporation, especially in the late stage of the experiment. When the CWR (percent of water removed during evaporation) reached 85%, boron became saturated in the brine and borax began to precipitate. As a result, the boron concentration in the brine decreased. In the evaporation experiment, hardly any borax precipitated in the early stage of the experiment, and only when the CWR reached 90% was a large amount of boron precipitated as borax with a grade of almost 50%. Therefore, the bittern remaining in the intermediate and late stages of evaporation can be used to extract borax.

After performing the isothermal evaporation experiment at 25°C with the brine of Zabuye Salt Lake, we have drawn the following conclusions.

1. The crystallization path of salts from brine in Zabuye Salt Lake is in accordance with that of the metastable phase diagram of the $Na^+$, $K^+//Cl^-$, $CO_3^{2-}$, $SO_4^{2-}$-$H_2O$ quinary system at 25°C.

2. Trona and thermonatrite precipitate earlier in the experiment compared to the metastable phase diagram.

3. Lithium precipitation is a continuous process that occurred throughout the experiment. During the experiment it was difficult to obtain high-grade lithium salt.

4. Potash is precipitated as aphthitalite and sylvite. Aphthitalite is precipitated first, then, sylvite and aphthitalite precipitate together. High-grade potash can be obtained from Zabuye Salt Lake brine.

5. Boron is enriched in brine in the early and middle stage of the experiment and borax is precipitated in the late stage. The bittern remaining after evaporation can be used to extract borax.

**Table 2**–The chemical composition of the liquid phase formed by 25 °C-isothermal evaporation of autumn brines of Zabuye Salt Lake.

| Sample No. | CWR % | $Na^+$ g/l | $K^+$ g/l | $Li^+$ g/l | $Cl^-$ g/l | $SO_4^{2-}$ g/l | $B_2O_3$ g/l | $CO_3^{2-}$ g/l |
|---|---|---|---|---|---|---|---|---|
| L0 | 0.00 | 129.63 | 40.92 | 1.05 | 156.18 | 38.59 | 11.01 | 44.16 |
| L1 | 19.00 | 136.90 | 45.46 | 1.21 | 153.14 | 48.21 | 15.07 | 52.53 |
| L2 | 33.90 | 133.32 | 50.03 | 1.19 | 151.27 | 43.43 | 17.56 | 54.78 |
| L3 | 49.60 | 133.85 | 53.46 | 1.50 | 149.95 | 39.86 | 19.01 | 62.04 |
| L4 | 55.00 | 134.29 | 54.52 | 1.63 | 148.02 | 38.33 | 20.59 | 66.05 |
| L5 | 57.10 | 136.01 | 56.82 | 1.58 | 146.73 | 36.58 | 20.90 | 71.82 |
| L6 | 62.70 | 135.96 | 59.14 | 1.14 | 145.46 | 34.06 | 22.84 | 73.39 |
| L7 | 69.90 | 135.34 | 61.37 | 1.29 | 142.98 | 29.75 | 25.86 | 78.66 |
| L8 | 78.00 | 136.95 | 65.96 | 1.24 | 136.54 | 23.94 | 31.55 | 90.58 |
| L9 | 86.90 | 148.04 | 70.47 | 1.24 | 121.21 | 23.63 | 39.75 | 118.15 |
| L10 | 93.10 | 156.79 | 72.76 | 1.49 | 118.02 | 18.05 | 33.98 | 141.00 |
| L11 | 94.70 | 150.66 | 74.98 | 1.24 | 107.64 | 17.47 | 31.95 | 143.70 |
| L12 | 97.10 | 146.00 | 74.93 | 1.19 | 114.68 | 17.11 | 37.12 | 129.44 |
| L13 | 99.00 | 136.64 | 74.94 | 1.06 | 117.94 | 16.24 | 34.94 | 115.48 |
| L14 | 100.00 | 137.41 | 74.94 | 1.05 | 115.35 | 16.30 | 36.44 | 117.96 |

**Table 3**–Compositions of solid phases precipitated by 25 $^{o}$C-isothermal evaporation of autumn brines of Zabuye Salt Lake.

| Sample No. | CWR wt% | Zb wt% | Tr wt% | Th wt% | Bo wt% | Ap wt% | Sy wt% | H wt% |
|---|---|---|---|---|---|---|---|---|
| **S1** | 19.00 | 0.54 | 0.00 | 0.17 | 0.74 | 0.00 | 0.00 | 98.55 |
| **S2** | 33.90 | 0.00 | 7.35 | 0.00 | 0.00 | 23.97 | 0.00 | 68.68 |
| **S3** | 49.60 | 0.00 | 10.93 | 0.00 | 0.00 | 25.81 | 0.00 | 63.26 |
| **S4** | 55.00 | 0.66 | 0.81 | 0.00 | 1.09 | 16.76 | 1.27 | 79.41 |
| **S5** | 57.10 | 2.17 | 0.00 | 0.00 | 0.00 | 24.26 | 0.00 | 73.57 |
| **S6** | 62.70 | 3.35 | 4.78 | 0.00 | 0.82 | 21.06 | 0.00 | 69.98 |
| **S7** | 69.90 | 0.77 | 18.43 | 0.00 | 0.00 | 20.43 | 0.00 | 60.37 |
| **S8** | 78.00 | 1.70 | 5.42 | 0.25 | 0.00 | 22.45 | 0.00 | 70.19 |
| **S9** | 86.90 | 1.17 | 2.84 | 7.62 | 12.92 | 12.29 | 10.64 | 52.52 |
| **S10** | 93.10 | 0.00 | 0.00 | 15.26 | 51.64 | 3.90 | 15.84 | 13.35 |
| **S11** | 94.70 | 3.64 | 0.40 | 17.10 | 18.21 | 2.92 | 16.31 | 41.42 |
| **S12** | 97.10 | 0.85 | 0.00 | 65.43 | 17.00 | 5.17 | 7.58 | 3.96 |
| **S13** | 99.00 | 1.04 | 0.00 | 44.48 | 32.55 | 4.17 | 9.33 | 8.43 |
| **S14** | 100.00 | 0.68 | 0.00 | 37.47 | 26.13 | 4.28 | 18.09 | 13.36 |

## REFERENCES

Analysis Group, Qinghai Saline Lake Institute, Chinese Academy of Sciences. 1988. Analysis Methods of Brine and Salt (2nd edition). Science Press, Beijing (in Chinese).

Fang, C., Z. Niu, Z. Liu & J. Chen. 1991. Studies on the metastable phase diagram in the quinary system $Na^+$, $K^+$// $Cl^-$, $CO_3^{2-}$, $SO_4^{2-}$-$H_2O$ at 25$^o$. Acta Chimica Sinica 49: 1062–1070 (in Chinese with English abstract).

Huang, W., Z. Sun, X. Wang, Z. Nie & L. Bu. 2008. Progress in industrialization for lithium extraction from salt lake. Modern Chemical Industry 28 (2): 14–17 (in Chinese with English abstract).

Nie, Z. & M. Zheng. 2001. A study of the brine solarizing behavior in solar ponds of Zabuye Salt Lake. Acta Geoscientia Sinica 22: 271–275 (in Chinese with English abstract).

Nie, Z., Y. Zhang, L. Bu, W. Hang & M. Zheng. 2005. Experimental study on concentration of winter brines in Zabuye Salt Lake, Tibet. Geological Bulletin of China 24: 386–390 (in Chinese with English abstract).

Qi, W. & M. Zheng. 2007. Rates of evaporation from saline lakes on the Tibetan Plateau: an approach to measurements and calculations. Acta Geologica Sinica 81: 1727–1733 (in Chinese with English abstract).

Yang, J., Y. Zhang, W. Cheng & X. Jiang. 1996. 25$^o$ isothermal evaporating research in winter brine of Zabuye Salt Lake in Tibet. Sea & Lake Salt and Chemical Industry 25 (5): 21–24 (in Chinese with English abstract).

Zhang, Y., Z. Nie, L. Bu & M. Zheng. 2001. Composition evolving rule of the carbonate Li-rich brine under serial freezing temperature. Sea & Lake Salt and Chemical Industry 30 (1): 3–6 (in Chinese with English abstract).

Zhang,Y., M. Zheng, Z. Nie & L. Bu. 2005. 15$^o$-isothermal evaporation experiment on carbonate-type brine from Zabuye Salt Lake, Tibet, Southwestern China. Sea & Lake Salt and Chemical Industry 34 (4): 1–5 (in Chinese with English abstract).

Zhao, Y. 2003. Saline lake lithium resources of China and its exploitation. Mineral Deposits 22 (1): 99–106 (in Chinese with English abstract).

Zheng M. 1999. On salinology. Acta Geoscientia Sinica 20: 395–401 (in Chinese with English abstract).

Zheng, M. & W. Liu. 1987. A new Li mineral-Zabuyelite. Acta Mineralogica Sinica 7: 221–227 (in Chinese with English abstract).

Zheng, M., J. Xiang, X. Wei & W. Liu. 1989. Saline lakes of Tibet and Qinghai. Science and Technology Press, Beijing: 192–256 (in Chinese).

Zheng, M., Y. Deng, Z. Nie, L. Bu & S. Shi. 2007. 25$^o$-isothermal evaporation of autumn brines from the Zabuye Salt Lake, Tibet, China. Acta Geologica Sinica 81: 1742–1749 (in Chinese with English abstract).

Zheng, X., Y. Tang & T. Xu. 1988. Salt Lakes of Tibet. Science and Technology Press, Beijing (in Chinese).