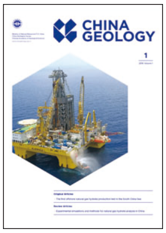
China Geology 1 (2018) 72−83

China Geology

Journal homepage: chinageology.cgs.cn



The tempo-spatial characteristics and forming mechanism of Lithium-rich brines in China

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ARTICLE INFO

Article history:
Received 19 January 2018
Received in revised form 3 March 2018
Accepted 11 March 2018
Available online 15 March 2018

Keywords:
Lithium
Brine
Saline lake
Brine formation
Tibetan plateau

ABSTRACT

With the technological development of exploitation and separation, the primary sources of lithium have gradually changed from ore to brine, which has become the main raw material, accounting for more than 80% of the total production. Resources of lithium-bearing brine are abundant in China. This paper has summarized the spatial and temporal distribution, characteristics, and formation mechanism of the lithium-rich brine in China, aiming to provide a comprehensive set of guidelines for future lithium exploitation from brines. Lithium-rich brines usually exist in modern saline lakes and deep underground sedimentary rocks as subsurface brines. The metallogenic epoch of China's lithium-rich brine spans from the Triassic to the Quaternary, and these brines exhibit obvious regional distribution characteristics. Modern lithium-rich saline lakes are predominately located in the Qinghai-Tibet Plateau. In comparison, the subsurface lithium-rich brines are mainly distributed in the sedimentary basins of Sichuan, Hubei, Jiangxi provinces and so on in south Block of China, and some are in the western part of the Qaidam Basin in Qinghai province in northwestern China. Lithium-rich saline lakes are belonging to chloride-enriched, sulfate-enriched, and carbonate-enriched, while the deep lithium-rich brines are mainly chloride-enriched in classification. On the whole, the value of Mg/Li in deep brine is generally lower than that of brine in saline lakes. The genesis of lithium-rich brines in China is not uniform, generally there are two processes, which are respectively suitable for salt lakes and deep brine.

1. Introduction

Lithium (Li), an energy metal of the 21st century, is widely applied in many industries, such as glass and ceramics (30%), lubricating grease (8%), and especially in rechargeable batteries (39%) (Jaskula BW, 2015). In recent years, with the rapid development of science and technology, especially the development of new energy vehicles, lithium and its compounds are becoming increasingly important. The role of lithium as a strategically influential element is becoming increasingly prominent (Fox-Davies Resources Specialist, 2013).

In nature, the occurrence state of lithium is divided into solid ore minerals and liquid brine. In the 1970s, the minerals, such as spodumene, lepidolite, and zinnwaldite, were the main sources of lithium product. With the technological development of exploitation and separation, the primary source of lithium has gradually changed from solid ore to brine, and brine has become the main raw material. The extraction technology of lithium from solid ore is complex, resulting in high energy consumption, high cost, and environmental pollution. However, extracting lithium from brine is relative simple, giving rise to low production costs, high resource utilization, and is comparatively environment-friendly. As a result it is difficult for, the extraction of lithium from solid ore to compete with the extraction of lithium from brine. Lithium production yield from brine is nearly four times greater than from minerals (Choubey et al., 2016). At present, the extraction of lithium from brine is becoming the main direction for lithium production in the world, resulting in the products of lithium from brine accounting for over 80% of the whole of lithium production (Nie Z et al., 2013).

Lithium-rich brines are abundant in China. The general in-

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doi:10.31035/cg2018009

dustrial standard for brine in China has been established (Manual for Mineral Industry Requirements, 2014). When concentration of Li^+ in brine reach up to 33 mg/L and 25 mg/L, it respectively meets the industrial requirements for separate mining and comprehensive utilization. In this paper, brine with Li^+ reaching 25 mg/L or above is defined as lithium-rich brine.

2. The Spatial and temporal distribution of lithium-rich brine deposits in China

In China, Li-rich brines can be divided into two types based on the reservoirs, i.e., the brine of salt lakes and underground brine. Underground lithium-rich brine is usually deeply buried, down to hundreds or thousands of meters, and this kind of brine is also called deep-buried underground brine. Lithium-rich brine is very abundant in China, and its spatial and temporal distribution has clear regional characteristics (Fig. 1). The lithium- rich brines of salt lakes are mainly concentrated in the Qaidam Basin and the northern part of Tibet on Tibetan Plateau. The deep-buried lithium-rich brines are mainly concentrated in the sedimentary basins of Sichuan basin in Sichuan Province, Jianghan Basin in Hubei Province, Jitai Basin in Jiangxi Province and other regions. The deep-buried oil field brines in western Qaidam Basin are also enriched in high-content lithium. In addition, the Lop Nur saline lake in the Tarim Basin contains some lithium in brine. After potassium extraction, the residual brine enriches lithium so that its concentration outweighs the industrial standard.

Lithium-rich brines in China are preserved in distinct reservoirs with varied ages ranging from the Triassic to the Quaternary (Zheng MP et al., 2012). Quaternary lithium-rich salt lakes, are mainly distributed in the Cenozoic basins within the Tibetan Plateau.Deep-buried underground lithium-rich brine was found in Triassic strata in the Sichuan Basin, Cretaceous redbeds in the Jitai Basin (Jiangxi 902 geological team, 2016), Paleogene strata in the Jianghan basin (Pan YD et al., 2011), and Neogene strata in the western Qaidam basin.

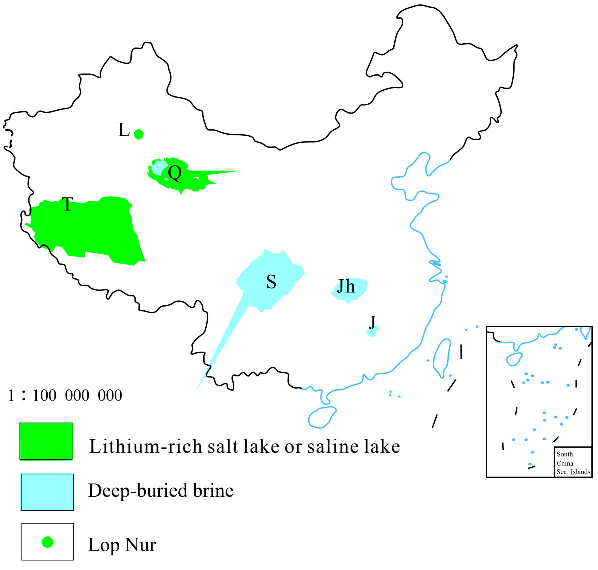

Fig. 1. The main distribution area of lithium-rich brines in China. Q-Qaidam basin, Qinghai Province; T:Tibetan saline lake zone, Xizang Province; L:Lop Nur saline lake, Xinjiang Province; S:Sichuan basin, Sichuan Province; Jh:Jianghan basin, Hubei Province; J:Jitai basin, Jiangxi Province.

In Qinghai and Tibet provinces, the lithium-rich brines are mainly preserved in salt lakes, such as the Qarhan Salt Lake, West Taijinar Salt Lake, East Taijinar Salt Lake, and the Zhabuye Salt Lake. These Li-rich brines are being exploited with recent rapid expansion.

3. Characteristics of lithium-rich brines in China

3.1. Lithium-rich brines in saline lakes

Lithium-rich brines in the Tibetan Plateau are mainly distributed in the Qaidam Basin, Tibet and Hoh Xil, and Lop Nur in the east end of the Tarim basin.

3.1.1. Lithium-rich brine in the Qaidam Basin

The Qaidam Basin has an area of 121000 km^2, and the elevation is around 3500-4500 m above sea level. Situated on the northeastern Tibetan Plateau, the giant basin is surrounded by the Qilian Mountains (Mts) to the northeast, the Altun Mts to the north, and the Kunlun Mts to the south. Along these mountains, tremendous strike thrust, and/or slip faults which cut through basal rocks, controlled the basinal evolution during the Cenozoic. Owing to the long-term tectonic activities of these faults, secondary faults, local uplifts, and depressions were formed within the basin, separating it into several sub-basins which evolved asynchronously, leading to a diverse subsidence and uplifting history. These tectonic activities have resulted in the migration of brines, causing their differences in depositional conditions in the sub-basins (Yuan JQ et al., 1981).

There are twenty seven saline lakes in the Qaidam basin, averaging a salinity of 332.4 g/L. The main ions in the brine are Na^+, Mg^{2+}, K^+, Ca^{2+} Cl^-, and SO_4^{2-} (Zhang, 1987). According to the characteristics of the basinal tectonic movement, salt minerals and the brine chemical properties, the Qaidam basin can be divided into three sub-regions (Fig. 2): (1) salt lake zone of the Mangya depression; (2) intense - depression salt lake zone in the Qaidam basin interior; (3) fault-block salt lake zone along the front of the Qilian Mountains.

The salt lake zone of the Mangya fault depression is located in the southwestern Qaidam basin, where lithium-rich brine is distributed throughout Gasikule Salt Lake. The salt minerals of Gasikule Salt Lake mainly include halite, sylvinite, carnallite, bischofite, gypsum, polyhalite. This lake is a Cenozoic-tectonic depression basin. The thickness of the Quaternary sediments in Gasikule Salt Lake is up to 500 m. In the middle of the early Pleistocene, gypsum deposition occurred. In the late early Pleistocene, halite began to deposit. The late Pleistocene - Holocene is dominated by halite deposition, and the thickness of the upper halite is up to 20 m (Ye CY et al., 2013).

The intense-depression salt lake zone is in the middle part

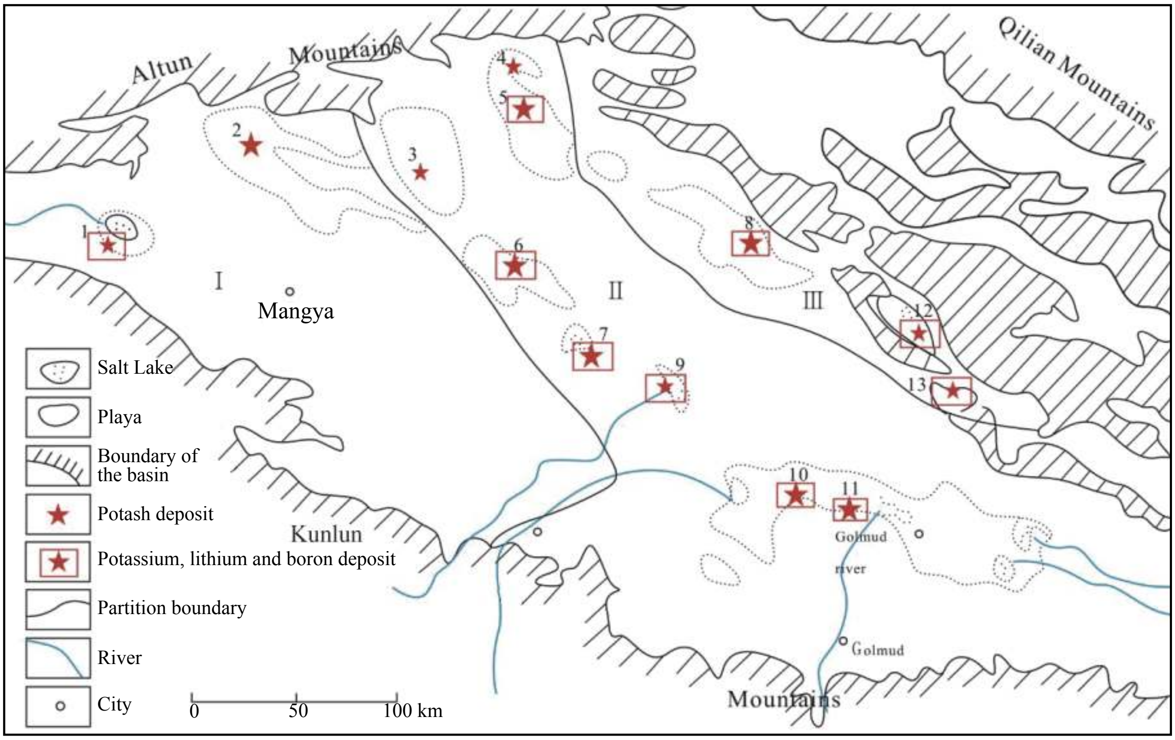

Fig. 2. The distribution of the salt-lake zones in the Qaidam Basin (modified from Liu et al., 2010) Salt lake zone of the Mangya depression: 1:Gasikule salt lake, 2:Dalangtan playa; Ⅱ Salt lake zone in the Qaidam basin interior: 3:Chahansilatu playa, 4:Jiahu saline lake, 5:Kunteyi playa, 6:Yiliping salt lake, 7:West Taijinar Salt Lake, 9:East Taijinar Salt Lake, 10, 11:Qarhan Salt Lake area; Ⅲ Salt lake zone in the front of the Qilian Mountain: 8:Mahai, 12:Da Qaidam salt lake, 13:Xiao Qaidam salt lake.

of the Qaidam Basin. There are many salt lakes in this zone. Lithium-rich salt lakes are Yiliping Salt Lake, Kunteyi Salt Lake, West Taijinar Salt Lake, East Taijinar Salt Lake, and Qarhan Salt Lake. In this zone, salt minerals are very abundant, and so are the potassium, magnesium and lithium resources. Halite is rich in Yiliping Salt Lake, Kunteyi Salt Lake, West Taijinar Salt Lake and East Taijinar Salt Lake, and sulfates such as mirabilite and gypsum are sandwiched within the halite layers. The area of Qarhan Salt Lake is up to 5800 km^2, its Quaternary sediments in this area reaching a thickness of 3100 m, and the thickness of salt mineral deposits is up to 70 m (Zhang PX, 1987). The Qarhan Salt Lake (Fig. 3) is divided into four zones, and from east to west these zones are respectively Huobuxun, Qarhan, Dabuxun and Bieletan, where five lithium-rich salt lakes are developed.

The salt lake zone in front of the Qilian Mountainis is located in the northeast of Qaidam Basin. Lithium-rich salt lakes are Mahai Salt Lake, Da Qaidam Salt lake, and Xiao Qaidam Salt Lake. Mahai Salt Lake is located in the northwest of this zone and its area is about 2000 km^2. Halite is the main mineral in this Lake, and the thickness of the halite deposit is usually 6-8 m (Zhang PX, 1987). However, in Da Qaidam Salt Lake and Xiao Qaidam Salt lake, Sulfate is the main mineral, and in addition there are a wide variety of borate minerals in these two lakes (Yang YZ, 2001).

The hydro-chemical characteristics of Lithium-rich salt lakes in Qaidam Basin are shown in Table 1. According to Valyashko's classification (Valyashko MG, 1965), salt lakes in the Qaidam Basin are divided into the chloride type (CL) and magnesium sulfate subtype (MS).

As shown in Table 1, the brines of the salt lakes are supersaturated with halite except for Da Qaidam Salt Lake. The average salinity is up to 354.629 g/L, and the average concentration of Li$^+$ is 198.12 mg/L. According to hydro-chemical classification, most of the salt lakes are MS type, and the content of lithium in MS type is higher than that in CL type. In Qarhan Salt Lake the value of Mg/Li is relatively high, which influences the extraction of lithium. The relationship between the content of Li$^+$ and Mg/Li value is shown in Fig. 4.

Generally, the content of Li$^+$ in these salt lakes has a significant inverse relationship with the value of Mg/Li (Fig. 4). When the content of Li$^+$ is low, the value of Mg/Li is high, and vice versa.

3.1.2. Lithium-rich brines of salt lakes in Tibet Plateau

Glacier deposits, mechanical weathering, freeze-thaw debris flows, chemical deposits and permafrost are distributed widely on the Tibetan Plateau. The salt lakes in Tibet are classified into four types, depositing carbonate, sulfate, borate and chloride, such as gypsum, mirabilite, borate and trona. (Zheng MP et al., 1989). There are a great deal of salt lakes in Tibet, with about thirty lithium-rich salt lakes. Due to being supplied by geothermal water or warm springs which are rich in K, Li elements, the brine of the lakes have enriched lithium after experiencing evaporation (Xuan ZQ, 1994). According to Valyashko's classification, lithium-rich salt lakes in

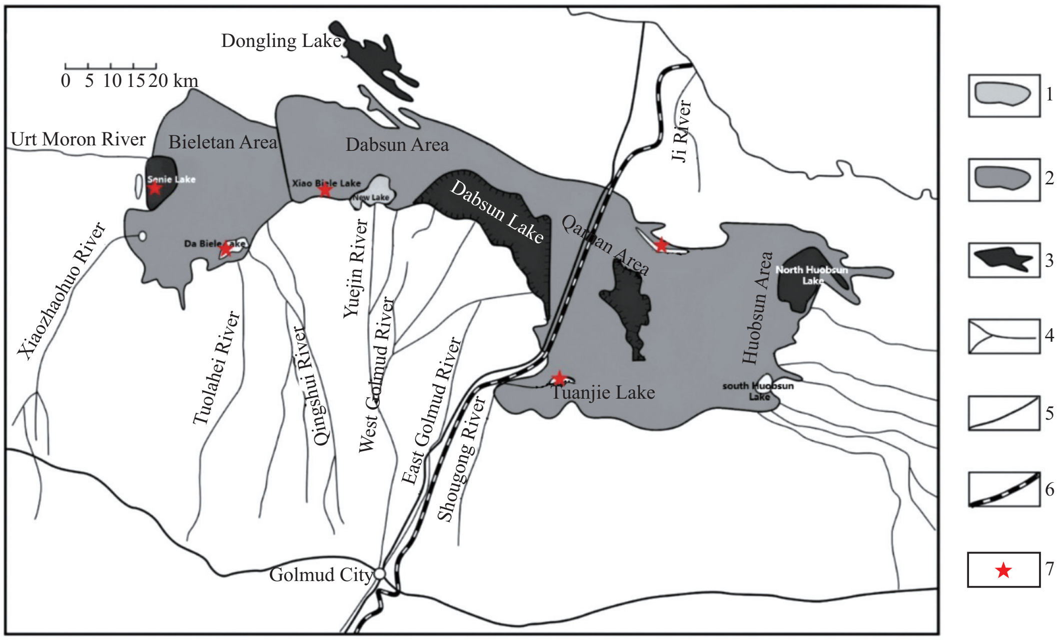

Fig. 3. The section divisions of the Qarhan salt lake (modified from Li BT et al, 2010). 1:water lake; 2:playa; 3:salt lake with solid and liquid; 4:river; 5:road; 6:railway; 7:location.

Table 1. The chemical properties of lithium - rich salt lake in Qaidam Basin.

Salt Lake Name		TDS/(g/L)	pH	Li$^+$/(mg/L)	Mg/Li	Hydrochemical Types	References
Gasikule salt lake		333.278	7.56	25	1188	MS	Zhang PX, 1987
Yiliping salt lake (J)		327.243	7.32	262	92	MS	Zhang PX, 1987
Kunteyi salt lake (J)		328.916	6.20	26.8	1415	CL	Zhang PX, 1987
East Taijinar salt lake		331.533	7.75	141	40	MS	Zhang PX, 1987
West Taijinar salt lake		336.328	7.70	202	67	MS	Zhang PX, 1987
Qarhan salt lake area	Qarhan area (L)	/	/	1600	75	CL	Li et al., 2016
	Dabuxun area	470.180	5.32	88.4	1342	MS	Zhang PX, 1987
	Bieletan area (J)	358.000	6.51	124	517	MS	Zhang PX, 1987
	Xiezuo lake	358.489	5.5	28.6	2261	CL	Zhang PX, 1987
	Tuanjie lake	425.266	5.4	59	1672	MS	Zhang PX, 1987
	Da Biele lake	362.885	7.00	37	837	MS	Zhang PX, 1987
	Xiao Biele lake	386.922	6.2	66.3	1230	MS	Zhang PX, 1987
	Senie lake	332.247	7.10	191	63	MS	Zhang PX, 1987
Mahai salt lake (J)		/	7.3	58.7-67.1	66-77	MS	Zhang PX, 1987
Da Qaidam salt lake		274.438	7.95	84.9	114	MS	Zhang PX, 1987
Xiao Qaidam salt lake		339.074	7.80	35.8	374	MS	Zhang PX, 1987

Notes: j=intercrystalline brine; L=residual brine from solar ponds; “/” =lake of data; The same below.

Tibet are divided into the carbonate type (CT), sodium sulfate subtype (NS) and magnesium sulfate subtype (MS). The chemical properties of lithium-rich brine of the salt lakes in Tibet are shown in Table 2.

As shown in Table 2, the range of brine TDS varies widely, from 30-400 g/L. The pH ranges from 7 to 9.5, mostly alkaline. The ratio value of Mg/Li is lower in carbonate salt lakes than that in magnesium sulfate subtype and sodium sulfate subtype salt lakes.

3.1.3. Lithium-rich brine of Salt Lakes in the Hoh Xil region

Hoh Xil is located in the western hinterland of Qinghai-Tibet plateau, including an area south of Kunlun Mountain, and the vast area north of Tanggula Mountain. Its area is 83 000 km^2, with an elevation of 4500-5000 m (Han FQ, 2001). There are a large number of lakes in Hoh Xil. According to the preliminary statistics, there are 359 of all lakes with an area of over 1 km^2, including twenty-one salt lakes, 172 semi-saline lakes and 166 fresh water lakes. Among the 21 salt lakes, there are only three lithium-rich Yanhu lakes, namely Salt Lake, Xijinwulan Lake and Lexiewudan Lake(Zheng XY et al., 2002).

These lithium-rich salt lakes are controlled by the Cenozoic intermountain tectonic faults, with the sediment of the lake bottom dominated by halite. In addition, mirabilite, bloedite, water glauberite and gypsum lie among the sediments. The

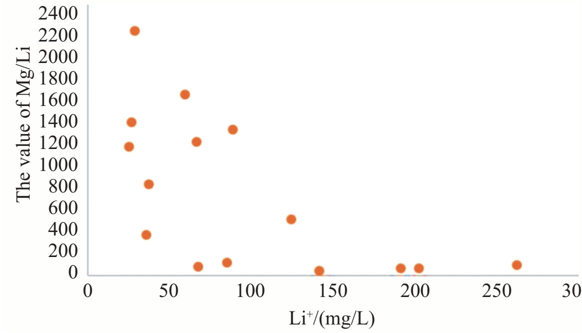

Fig. 4. The relationship between the content of Li^+ and the Mg/Li value of lithium-rich salt lakes in Qaidam Basin.

chemical properties of lithium - rich brine of salt lakes in Hoh Xil Region is showed in Table 3. The hydrochemical types of these lithium-rich salt lakes are magnesium sulfate subtype(MS) and chloride type(CL), lack of sodium sulfate subtype(NS) and carbonate type(CT). The pH is close to neutral. The value of Mg/Li is relatively high.

3.1.4. Li-bearing brine of Lop Nur salty lake in the Tarim Basin

Tarim Basin is one of the largest inland basins of the world, bounded by the Tianshan Mountains to the north, the Pamir Mts to the west, the West Kunlun Mts to the south, and the Altun Mts to the southeast. Lop Nur lake is located in the eastern corner of the Tarim Basin, being a playa, and is the lowest part in the Tarim basin. The Lop Nur sub-basin is a faulting basin with an area of about 18056 km^2, controlled mainly by near NS and EW striking faults (Liu CL et al., 2006).

A super large brine-potash deposit has been found in the Luobei sub-basin in the northern Lop Nur depression, and the potassium-rich brine is stored in glauberite intercrystalline pores(Wang ML et al., 2001, 2005).The evaporite-bearing strata are mainly middle Pleistocene, upper Pleistocene and Holocene, and the structure of the brine-bearing layers is characterized by a phreatic aquifer and five main confined aquifers, which are stratoid and lenticular, and a burial depth ranging from 1m to 150 m (Liu CL et al., 2009). According to Valyashko’s classification (Valyashko MG, 1965), brine of Lop Nur salt lake belongs to the magnesium sulfate subtype. The concentration of lithium in the brine increases rapidly with the increase in salinity, from 5mg/L to 45 mg/L. So the old brine after extracting potassium is enriched with a lot of lithium, and the Li^+ in residual brine is up to 304 mg/L, much more than industrial grade, and the inferred amount of LiCl in the brine is 210.23 Mt (Wang ML et al., 2001).

3.2. The deep-buried underground lithium-rich brines in China

3.2.1. The deep-buried underground lithium-rich brines in the western Qaidam Basin

From the Late Mesozoic to the Cenozoic, a series of faults and folds in a NW-SE direction were formed in the western Qaidam Basin, due to the Himalayan Movement. This kind of tectonic setting, which favors the migration of deep water and the aggregation of the weathering products in peripheral mountain, provides salt-depositing spaces in depth up to about 1000 m in the western Qaidam Basin (Fan QS et al., 2007). The lithology of these sediments is mainly carbonate, mudstone and rock salt and this combination provides an ideal reservoir setting for underground brine. The content of Li is higher than industrial grade and is mainly distributed in Xiaoliangshan, Nanyishan, Youquanzi and Kaitemilike. The hydrochemical characteristics of the brine in the western Qaidam Basin are shown in Table 4.

As shown in Table 4, the deep-buried lithium-rich underground brine has a high salinity, main ions being Na^+ and Cl^-. The hydro-chemical type is chloride type. The Li content of Nanyishan is very high, up to 983 mg/L. The value of Mg/Li is relatively low, which is mainly due to the water-rock interaction between the medium acidic volcanics and the volcanic geothermal water.

3.2.2. The deep-buried underground lithium-rich brines in the Sichuan Basin

The Sichuan Basin has an area of about 230000 km^2, located in the southwest of China. The stratigraphic series of the basin are from the Proterozoic to the Cenozoic period, and have a total thickness of 9 km (Tong CG, 1985). Brine is widespread in the Sichuan Basin across all of the stratigraphic levels from the Sinian to the Cretaceous. There are nine principal brine reservoir units, namely the marine carbonate-evaporite series in the Sinian, the marine carbonate-evaporite series in the Cambrian, the shallow marine carbonate series in the Ordovician, the marine carbonate series in the Carboniferous, the shallow marine carbonate series in the Triassic, the carbonate - evaporite series in the middle-Lower Triassic, the coastal-river-lacustrine facies detrital rock series in the Upper Triassic, the river lacustrine facies detrital rock - limestone series in middle-Lower Jurassic and the continental detrital rock - evaporite series in the the Upper Cretaceous (Xiong SJ et al., 1996).

The formation and development of the basin took place during the Indosinian movement, and stopped after the Himalayan Movement. The basin can be sequentially divided into three tectonic zones, namely the eastern, middle and western ones. The lithium-rich brine is mainly distribute the eastern and western area of the basin. Detrital rocks and carbonate rocks act as two important brine bearing rocks, because of their lower porosity, lower osmotic potential and higher compactness. The chemical properties of the brines in the Sichuan Basin is shown in Table 5.

As can be seen from Table 5, the salinity of the brine is supersaturated and higher in the western than in the eastern area. Li^+ is higher in the western than in the eastern, and the value of Mg/Li display a similar relationship. All of the characteristics are dependent on the sedimentary environment and

Table 2. The chemical properties of lithium-rich brine of salt lakes in Tibet (modified from Zheng XY et al., 2002).

Salt Lake Name	TDS/(g/L)	pH	Li^+/(mg/L)	Mg/Li	Hydrochemical Types
Maergai Chaka	323.55	9.5	30.15	25.44	MS
Kangru Chaka	322.80	7.0	77.00	43.45	MS
Cangmu Co	173.54	8.8	1227.30	4.57	MS
Zhaxi Chaka	166.74	7.8	139.80	72.25	MS
Lungmu Co	173.60	7.8	169.80	84.59	MS
Eya Co	227.74	/	229.10	88.08	MS
Chana Co	329.35	7.6	299.5	67.07	MS
Maerguo Chaka	323.00	7.3	319.90	40.72	MS
Zhacang Chaka	313.027	7.8	579.93	14.93	MS
Yupan Co	161.00	7.3	62.4	115.91	MS
Gangtang Co	72.3	9.5	41.40	1.47	CT
Chalaka Co	105.3	8.5	90.30	0.25	CT
Caimaer Co	190.8	8.8	130.00	0.032	CT
Awong Co	87.00	9.2	140.00	4.54	CT
Guojialin Co	125.91	8.8	131.00	0.14	CT
Bange Co	154.63	8.7	158.67	0.36	CT
Pengyan Co	393.80	9.0	374.70	0.057	CT
Zabuye Chaka	307.00	9.2	1552.33	0.012	CT
Beilei Co	131.11	9.0	39.8	1.56	CT
Rebang Co	70.00	9.2	29.00	11.08	NS
Dawa Co	35.55	9.3	31.30	31.84	NS
Yibu Chaka	96.82	8.2	43.00	20.99	NS
Buerga Co	135.50	7.9	55	67.56	NS
Kongkong Chaka	333.53	7.4	140.00	10.88	NS
Bieruoze Co	144.98	8.7	150.00	33.02	NS
Chabo Co	141.10	8.2	179.90	23.07	NS
Qia Chaka	198.57	7.9	249.60	1.44	NS
Dong Co	139.7	8.9	190.00	15.38	NS
Laguo Co	91.29	8.5	530.00	3.04	NS
Nier Co	215.00	8.0	654.90	24.81	NS

reservoir strata. The western region was controlled by the fault tectonic zones, and the eastern region was influenced by mainly anticlines. The brine in the western area is mainly in the reservoir units of Upper Triassic and middle-Lower Triassic, and the brine in the eastern area is mainly in the Triassic (Yang et al., 1993).

3.2.3. The deep-buried underground lithium-rich brines in the Jianghan Basin

The lithium-rich brine of the Jianghan Basin is mainly distributed in the Jiangling Depression and the Qianjiang Depression, and they therefore can be discussed separately.

(1) The Jiangling Depression

Jiangling Depression is located in the south-central part of the rift basin in the southern block of China. It is a secondary depression in the western part of the Jianghan Basin, with an area of 6500 km^2. The maximum depositional thickness of Cretaceous-Neogene in the depression is nearly 10000 m. Evaporite is mainly deposited in the Shashi member of the Paleocene series and the Xingouzui member of the Eocene series, the brine mainly being found in the Shashi member and the Xingouzui member. The brine is retained in the pores and crannies of sand rock, basalt, diabase and dolomite rock (Pan et al., 2011; Liu CL et al., 2016), the burial depth being average about 3500 m. According to the lithology, the salt-bearing strata can be divided into lower carbonate segments, salt-bearing segments and upper sulfate segments. The lithology of the lower carbonate segments is a gray argillaceous dolomite, including local thin layers of gypsum, paste mudstone and siltstone; the lithology of the salt-bearing segments is white and gray anhydrite halite, brown mudstone, and siltstone; the lithology of the upper sulfate segment is dark gray mudstone, argillaceous stone, glauberite, siltstone (Liu CL et al., 2016).

The Jiangling Depression is well-known for its deep, potassium-rich brine. Meanwhile, the deep brine is enriched in lithium, and the chemical properties of deep brines in the Jiangling Depression are shown in Table 6.

As can be seen from Table 6, the salinity of the deep brine is saturated. The concentration of Li^+ has reached industrial grade, because of deep materials brought up by intense volcanic activities, and pulsed transgressive seawater during the Cretaceous-Paleogene acting as the major provenance for the deep brine (Liu CL et al., 2016). The value of Mg/Li is very low, resulting from the metamorphosis of the brine, resulting

Table 3. The chemical properties of lithium-rich brine of salt lake in Hoh Xil Region (modified from Zheng XY et al., 2002).

Salt Lake Name	TDS/(g/L)	pH	Li^+/(mg/L)	Mg/Li	Hydrochemical Types
Salt Lake	221.40	6.85	62.00	107.66	MS
Lexiewudan Lake	135.50	7.00	171.00	12.81	CL
Xijinwulan Lake	356.7	7.13	100.6	24.64	MS

Table 4. The chemical properties of deep brines in western Qaidam Basin (modified from Tan HB et al., 2007).

Distribution	TDS/(g/L)	pH	Li^+/(mg/L)	Mg/Li	Hydrochemical Types
Xiaoliangshan	154.10	/	36	9.17	CL
Nanyishan	402.23	/	983	5.15	CL
Youquanzi	360.17	/	91.6	22.39	CL
Kaitemilike	220.42	/	33.8	47.35	CL

Table 5. The chemical properties of deep brines in Sichuan Basin.

Distribution	TDS/(g/L)	pH	Li^+/(mg/L)	Mg/Li	Hydrochemical Types	References
The western	377.27	/	90.00	35.22	Cl	Lin et al., 1996
The eastern	352.69	/	32.00	3.94	Cl	Jiang, 2013

in the removal of Mg (Pan et al., 2011), and this is a great advantage of the brine in the Jiangling Depression making it worthy of mining.

(2) Qianjiang Depression

The Qianjiang Depression is located in the middle part of the Jianghan Basin, which is a typical Mesozoic-Cenozoic faulted basin with an area of 2500 km^2. Since the late Eocene to early Oligocene the Qianjiang Depression has become the subsidence, water catchment and concentration center of the whole basin, under closed and strongly evaporative conditions, forming a unique continental evaporate sedimentary basin with characteristics sedimentary filling; the thickness of the strata is more than 3500 m, and the thickness of the salt sediments accumulates to 1800 m (Liu Q et al., 1983). The deep brine occurs mainly in the Qianjiang member and is found in the sandstone.

The hydrochemical type of the deep brine is mainly sodium sulfate subtype and chloride type, and is secondarily magnesium sulfate subtype and carbonate type (Qu JY et al., 1984; Yu SS, 1994; Ma LC et al., 2015; Huang et al., 2015). The vertical zoning of the brine is obvious, and the salinity increases with the depth of the brine, which can be divided into three layers, respectively, the brine layer which is buried at depth of 500-1280 m with a salinity reaching 270 g/L at 1280 m, the brine layer which is buried at a depth of 1280-2190 m with a salinity gradually becoming more saturated, namely 270 to 300 g/L, and the brine which is buried beneath 2190 m with a salinity of more than 300 g/L (Huang et al., 2015). The chemical properties of the deep brines in the Qianjiang Depression are shown in Table 7.

As can be seen from Table 7 the lithium of the brine is more than industrial grade. Similar to the Jiangling depression, the value of Mg/Li is very low, and the pH is slightly acidic perhaps for the same reason as with the Jiangling Depression.

3.2.4. The deep-buried underground lithium-rich brines in the Jitai Basin

The Jitai Basin, a continental dustpan lake basin with an area of about 4550 km^2, is located in the central part of Jiangxi Province, and the tectonic structure is the Ji-an Depression of the South China Folded System (Lu QY, 1991). Along with the Qingjiang basin, Fuzhou basin and Ganzhou basin, the Yanshan Period-Himalayan Period basin group is formed in the middle-north of Jiangxi Province. Around the Jitai basin, there are three deep faults, respectively Huang-ao, Jishui, Suichuan-Dexing, and dozens of smaller faults. These faults have good connectivity ability between the deep and shallow strata, and the brine is transported upward along the deep faults under the strata pressure and is retained in the pores and crannies of the sedimentary formations (Liu CL et al., 2016). The brine-bearing fault strikes to the north-east and dips to the south-west. Currently, the extent of the fault is about 2000 m. The brine is reserved in the Cretaceous Zhoutian member, in which has been formed a tectonic fracture.

As can be seen from Table 8, the salinity of the brine is saturated, and the lithium is much higher than industrial grade. The value of Mg/Li is very low. The hydrochemical type is chloride type. The chemical properties of the deep brines in the Jitai Basin are similar to those of the Jiangling Depression and the Qianjiang Depression, perhaps because of their formation being related with rifting.

4. The formation of lithium-rich brine

4.1. Lithium-rich brine in Salt Lakes

Lithium-rich salt lakes are usually formed in a closed catchment basin which has an environment of strong wind, dry climate and a lack of rainfall. Around the basin, Cenozoic volcanic activity is frequent, faults develop and the surround-

Table 6. The chemical properties of deep brines in Jiangling Depression.

Name of the well	TDS/(g/L)	pH	Li^+/(mg/L)	Mg/Li	Hydrochemical Types	References
Sha 4#	329.50	/	65.00	0	CL	Pan YD et al., 2011
Lu 9#	337.56	/	60.00	0.017	CL	Pan YD et al., 2011
GK 1#	336.98	/	52.00	3.27	CL	Li et al., 2013
SK 4#	308.80	/	43.00	0.21	CL	*

Notes: "*" MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences.

Table 7. The chemical properties of deep brines in Qianjiang Depression (modified from Ma LC et al., 2015).

Name of the well	TDS/(g/L)	pH	Li^+/(mg/L)	Mg/Li	Hydrochemical Types
Guang 14#	331.97	6.09	110.00	4.09	CL
Hao 19#	332.09	6.56	88.00	0.0011	NS

Table 8. The chemical properties of deep brines in Jitai Basin.

Name	TDS/(g/L)	pH	Li^+/(mg/L)	Mg/Li	Hydrochemical Types	Reference
Taihe Depression	323.23	/	100.00	1.20	CL	*

Notes: "*" MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences.

ing rock is enriched in lithium. Magmatic hydrothermal activity and volcanic ejecta provide a rich source of material for the brine. Under the influence of long-term geological and climatic conditions, the lithium-rich salt lakes deposits are formed (Zheng MP, 2001).

Lithium-rich salt lakes in China are distributed throughout the Qinghai-Tibet Plateau. The formation and chemical composition of the salt lakes in the Tibetan plateau are influenced by its unique set of geographical and geochemical factors. One is the climate. The uplift of the plateau blocks the warm moist airflow from the Indian Ocean, making the plateau climate tend toward dry cold. The cold dry or warm dry climatic conditions of the plateau allow the brine to be concentrated in the catchment area (Zheng MP, 2001; Wang QS, 2015), forming numerous salt lakes in the middle, west and north of the Qinghai-Tibet Plateau. This is mainly because the lithium can be dissolved during the process of chemical weathering. In a closed basin, especially in a strong evaporation area, most of the lithium is retained in the brine. Another factor is the topography and landforms. The Tibetan plateau is a huge lozenge-shaped block. The plateau is composed of a series of fault-block mountains and faulted valleys. The basins are surrounded by mountains, and the elevation difference between mountain and basin is huge. Thousands of meters of elevation difference between the mountains and the basin forms the effect of a rain-shadow. The high mountains block the monsoons, and there is a lot of rainfall in the windward area of the mountain, and the leeward area is extremely dry (Warren JK, 2010). The third factor is the material source. There are three main sources of metallogenic materials. The Cenozoic magma intrusion and volcanic eruption are active in the Qinghai-Tibet Plateau, forming a large number of hot springs. The fault activities of the basin bring or form the excretion of the deep circulation brine. There are a lot of lithium-bearing rocks, such as granitic, granite-porphyry, felsic tuff, lithium-bearing pegmatite and clay, in the Qinghai-Tibet Plateau, that provide important sources of lithium for the lakes. As a result, in the closed system, under the extremely arid climate and strong evaporation conditions, seasonal waters from the mountains flow into the basin, and the lithium-rich hot spring water supplies the lakes with a plenty of Li and other elements. Finally, lithium of the brine enriches to form ore deposits (Zheng MP et al., 1995; Zhao YY et al., 2010). The model of Li-rich salt lake formation in the Qinghai-Tibet Plateau is shown in Fig. 5.

4.2. The deep-buried lithium-rich brine

4.2.1. The water-rock interaction type in western Qaidam Basin

This type is especially suitable for the western part of the Qaidam Basin. The deep brine in the west of Qaidam Basin is very different from the modern salt-lake brine in Qaidam basin, and it is obvious that there is no direct relationship between the deep brine and the Quaternary salt lakes (Liu CL et al., 2016). Yang Q, 1986, Wei XJ et al., 1993, Li TW et al., 2006, Fan QS et al., 2007 and Tan HB et al., 2007 have studied the deep brine of the western part of the Qaidam Basin, and believe it is mainly due to the following reasons that the deep brine is formed.

There is an amount of intermediate-acid rock bodies, volcanic and detrital rocks which are from the Indosinian and Yanshanian surrounding a large area of the Qaidam Basin. These rocks are rich in potassium, sodium, calcium, magnesium and lithium. Because of water-rock interaction, the useful components, which are form the rocks that are weathered and leached, are enriched in the water. Near the fault zone of the mountains, which form the periphery of the Qaidam Basin, there is a lot of geothermal water formed by the volcanic during the activity Mesozoic, the geothermal water is rich in po-

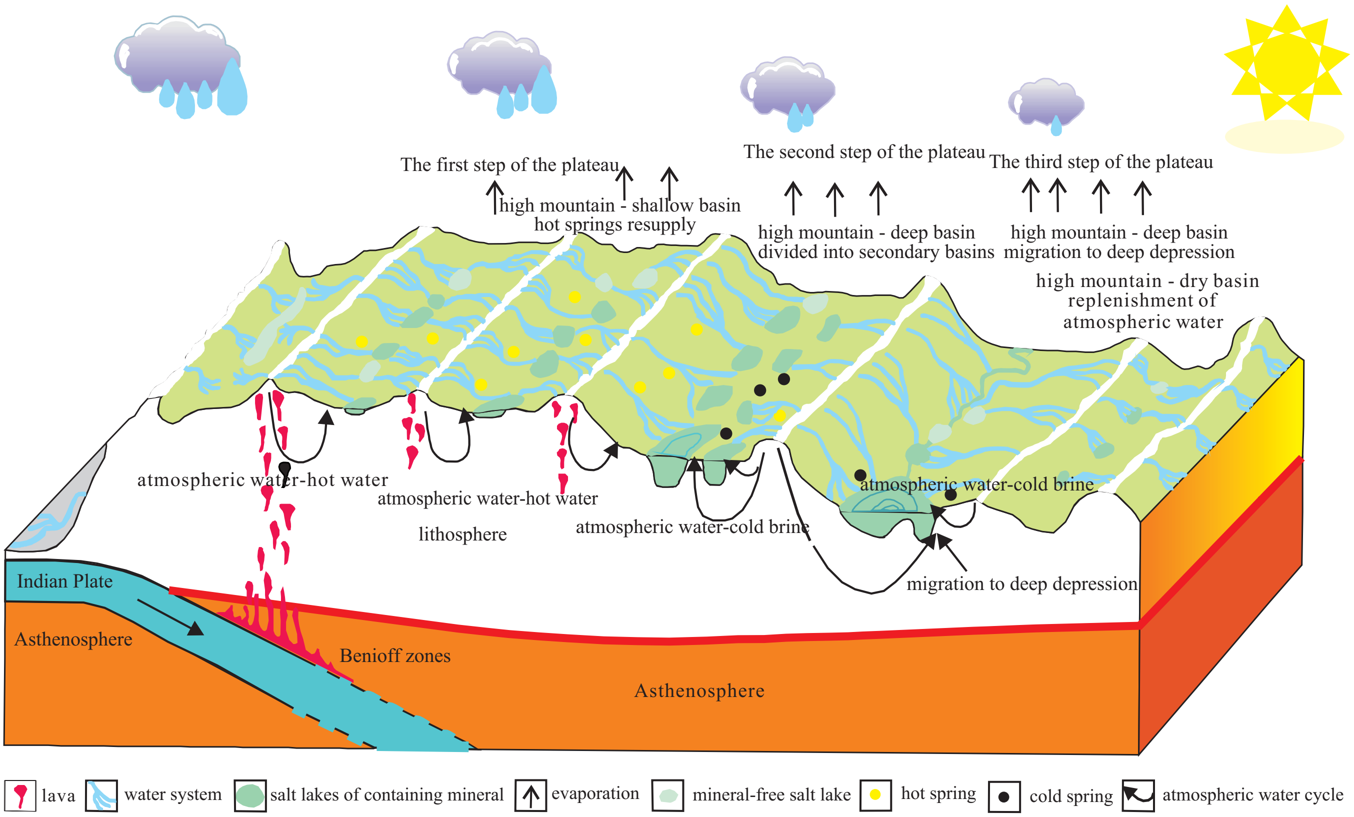

Fig. 5. The metallogenic model of K and Li-rich brine deposits of salt lakes in the Qinghai-Tibet Plateau (modified from Liu CL et al., 2016).

tassium, boron and lithium, etc., is collected in the western part of the basin, and then enters into the underground brine. In addition, there is considerable underground dissolution of the evaporate. Consequently, a large amount of lithium-rich brine is formed in the western part of the Qaidam Basin.

4.2.2. The marine-evaporitic type in Sichuan Basin

The deep underground brine in the Sichuan basin is the product of the Triassic sea water evaporation. In a strong evaporative environment, when the Triassic sea in the upper Yangtze platform was retreated, the remaining seawater was evaporated and salt lakes were developed, finally the brine was buried and transferred into the deep underground brine within marine sedimentary formation. Potassium, bromine, boron and lithium are rich in brine. Under the influence of positive metamorphism, the degree of mineralization increases with the increase of metamorphic grade, and the brine is increasingly enriched in potassium, bromine, boron and lithium (Lin YT et al., 1996; 2001; 2002). Its generation is attributed to a composite formation involving both the metamorphism of sedimentary brine and the dissolution-filtration of solid salts (Lin et al., 2004; Liu et al., 2016).

4.2.3. The continental-rifting type in southeast China

This type is suitable for the Jiangling Depression, the Qianjiang Depression and the Jitai Basin.

During the Cretaceous period, a series of Mesozoic-Cenozoic rift basins were formed in the South China Continental Block (Liu CL et al., 2016). There is a large amount of deep brine which is rich in potassium and lithium in these rift basins. The genesis of this brine may be through the following conditions and processes. Analysis from the tectonics indicates that the lithosphere of the Mesozoic-Cenozoic basins in South China had undergone extensive thinning during the process of tectonic transition from compression to extension. Under the extension background, there occurred massive magmatic activity. Therefore, there are a lot of igneous rocks in the rift basins, and higher level of potassium and lithium in these basins are related to the basalt eruption and granite intrusion in this region. During the Cretaceous-Paleogene period, this region was in a dry climate, and the basin was deposited within abundant evaporites. According to above analysis, the formation process of potassium and lithum-rich brines in the rift basin has been proposed (Fig. 6; Fig. 7).

The model can be depicted as two stages and three processes. The first stage is the interaction between the surface of the salt lake and the solar energy. The second stage is the effect of the buried magmatic energy. The three processes are respectively evaporation-deposition, sedimentary-leaching, and metamorphism-modification.

5. Conclusions

(1) The metallogenic epoch of China's lithium-rich brine deposits has a large span, from Triassic to Quaternary. The lithium-rich brine of salt lakes belongs to the Quaternary, and the deep-buried brines are present in Triassic, Cretaceous, Pa-

leogene and Neogene. The spatial distribution of rich lithium brine in China has obvious regional characteristics. The lithium-rich salt lakes are mainly distributed in the Qinghai-Tibet Plateau. The deep-buried lithium-rich brines are mainly distributed in South China, such as those of Sichuan, Hubei, Jiangxi, and some are in the western part of the Qaidam Basin.

(2) The hydrochemical types of the lithium-rich brines in China include chloride type, sulfate type, and carbonate type. The deep-buried lithium-rich brines are mainly of chloride type. On the whole, the value of Mg/Li in deep brine is generally lower than that of brine in the salt lakes, which is an advantage of deep brine.

(3) The salt lakes in Qaidam Basin are mainly sulfate type in hydro-geochemical classification. The pH value is from 5.4 to 7.95. The value of Mg/Li is high, and the content of Li^+ in these salt lakes has a significant inverse relationship with the value of Mg/Li. In Tibet, the salt lakes belong to chloride type, sulfate type, and carbonate type. The sulfate type lakes are basically neutral and slightly alkaline, the carbonate type lakes are slightly alkaline, and the chloride type lakes are mildly acidic. The value of Mg/Li in carbonate type lakes is lower than that in sulfate type lakes and chloride type lakes.

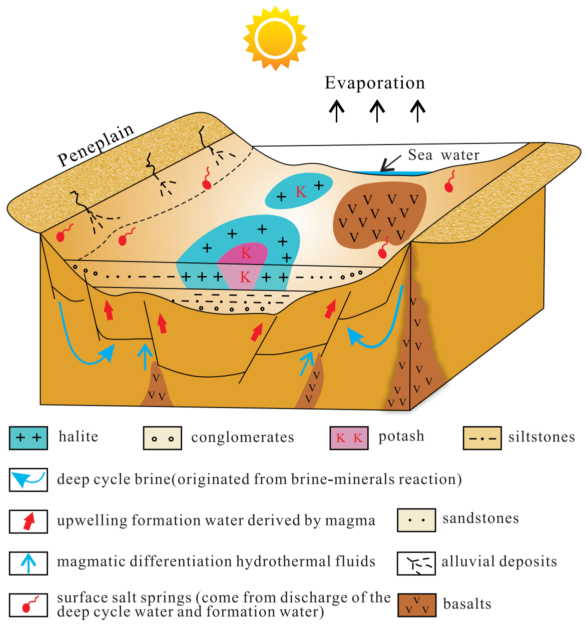

Fig. 6. Schematic diagram showing the formation of potash salts in the rift basin (modified from Liu CL et al., 2013; 2016).

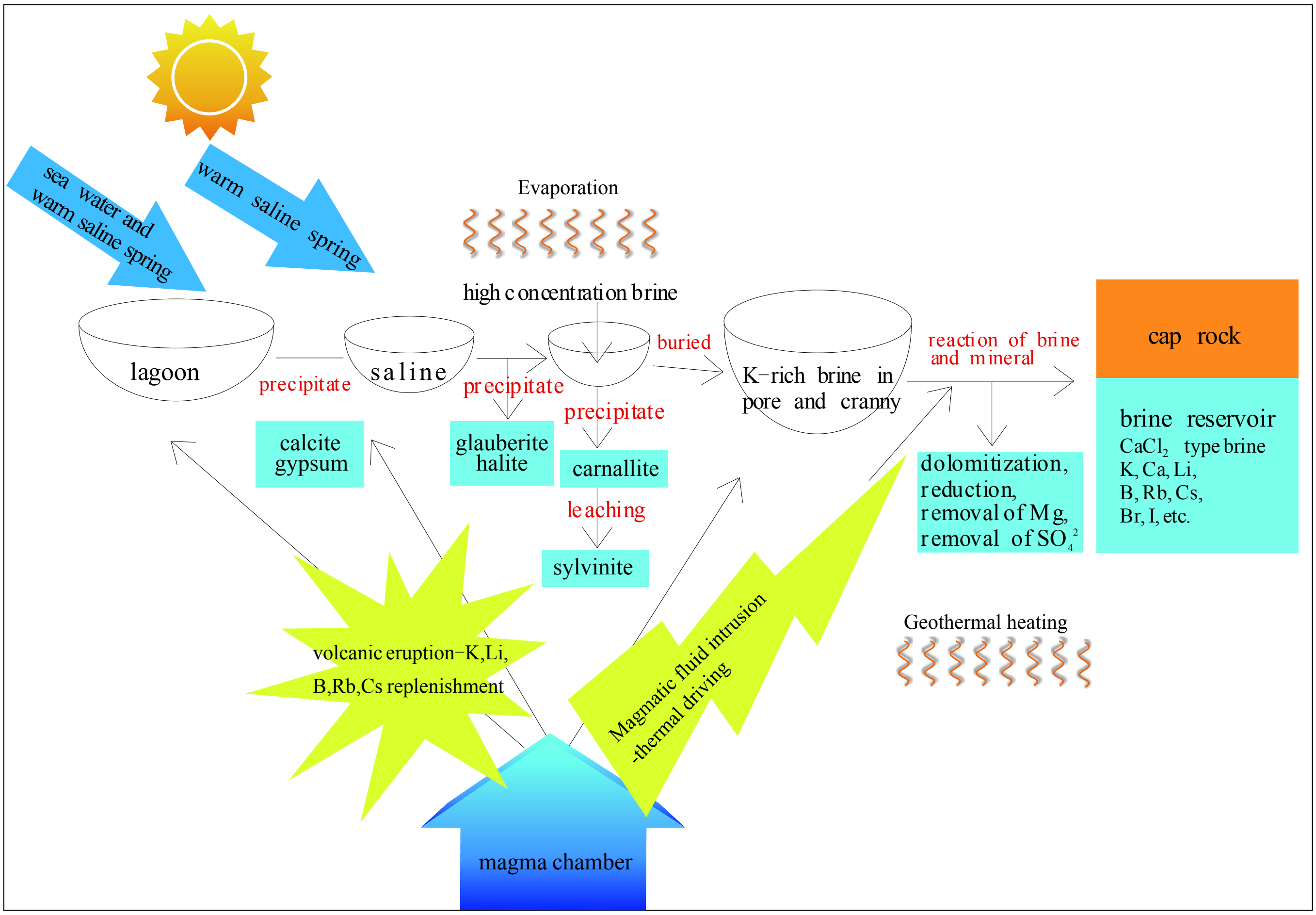

Fig. 7. Schematic diagram showing the formation process of the deep-buried potassium and lithum-rich brines in the rift basin (modified from Liu CL et al., 2013, 2016).

(4) The formation of lithium-rich brine in China is remarkably diverse. There are generally three types of genesis, ie., evaporation of lake water supplied with the Li-bearing geo-thermal water, then residual brine of paleo-sea water evaporation, finally rock-water reaction and evaporation.

Acknowledgements

The National Basic Research Program of China (973 program 2011CB403007), Basic Scientific Research Program of Chinese Academy of Geological Sciences (YYWF201607), and the Prospecting Investigation and Evaluation of Potash Minerals in western China which belongs to Level Two Geological Survey Program of China Geological Survey (DD2016 0054) provide the funding for this study. We are grateful to two anonymous reviewers for their constructive comments on the manuscript.

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