minerals

Review

Hydrochemistry, Distribution and Formation of Lithium-Rich Brines in Salt Lakes on the Qinghai-Tibetan Plateau

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Received: 30 June 2019; Accepted: 27 August 2019; Published: 30 August 2019

Abstract: Salt lakes on the Qinghai-Tibetan Plateau (QTP) are remarkable for Li-rich brines. Along with the surging demand of Li, the Li-rich brines in salt lakes on the QTP are of great importance for China's Li supply. Previous studies reported the geological, geographical, geochemical signatures of numerous salt lakes on the QTP; however, conclusive work and the internal relationships among the hydrochemistry, distribution and geological setting of Li-rich salt lakes are still inadequate. In this study, major and trace (Li, B) ionic compositions of 74 Li-rich salt lakes on the QTP were reviewed. The Li-rich brines cover various hydrochemical types (carbonate, sodium sulfate, magnesium sulfate, and chloride types) and present horizontal zoning from the southwest to the northeast along with the stronger aridity. The Li concentrations and Mg/Li ratios in these salt lakes range from 23 to 2895 mg/L, 0.0 to 1549.4, respectively. The distribution of these salt lakes is close to the major suture zones. Geothermal water is proposed to be the dominant source of Li in the investigated salt lakes, while weathering of Li-bearing sediments and igneous rocks, and brine migration provide a minor part of Li. Four factors (sufficient Li sources, arid climate, endorheic basin and time) should be considered for the formation of Li-rich brines in salt lakes on the QTP.

Keywords: Li-rich brine; salt lake; hydrochemistry; distribution; formation; Qinghai-Tibetan Plateau

1. Introduction

Lithium (Li) is the lightest alkaline metal and an excellent conductor of electricity and heat. Over the last decade, the Li demand has been boosted due to its use in Li battery industry, which is playing a critical role in electrical vehicles and storage of energy [1–3]. Lithium-rich brines, as major raw materials for Li and its compounds production, account for 66% of the world's Li resources and >60% of global Li production [4,5]. In China, 78% of identified Li resources (4.5 million tons) are brine resources [6] and 86.8% of Li brine resources occur in the salt lakes on the Qinghai-Tibetan Plateau (QTP) [7,8]. In addition, Li brine deposits are also reported in the Sichuan Basin, Jianghan Basin, Jitai Basin and Lop Nur Salt Lake in China (Figure 1a) [9–11].

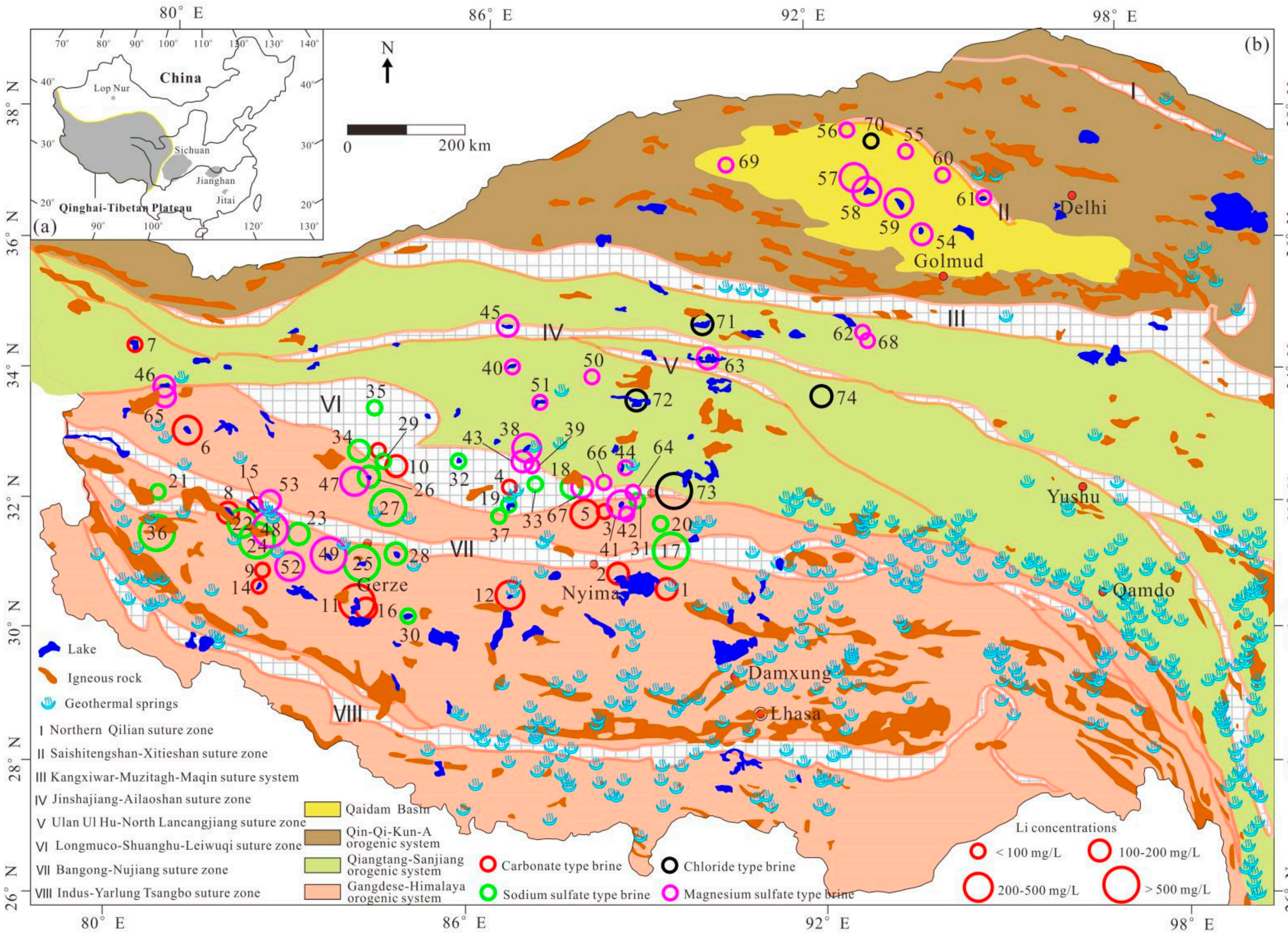

Figure 1. (**a**) Map showing the location of Qinghai-Tibetan Plateau (QTP); (**b**) the distribution and Li concentrations of salt lakes on the Qinghai-Tibetan Plateau. The location of geothermal springs is from [12]; the distribution of suture zones and orogenic systems is from [13]. The name and Li concentrations of salt lakes can be seen from Table 1.

Since 1980s, significant efforts have been directed towards investigating on regional geology, evaporitic mineral assemblages, geochemical signatures of brines and sediments, and potential evaluation of valuable elements (such as K, B, Li, Cs, Rb, Br) in salt lakes on the QTP [14–18]. After that, two dominant Li brine deposits have been delineated and developed, including the Zabuye Lake in the Tibet and terminal lakes (Yiliping playa, Xitai and Dongtai lakes, Bieletan section in the Qarhan playa) of Nalenggele River in the Qaidam Basin. In recent years, along with the surging demand of Li and its compounds, preparatory evaporation experiments of brines from several Li-rich salt lakes, including the Laguo Co, Dangxiong Co, Jieze Chaka, Chabo Co, Longmu Co, etc. on the QTP have been completed for future Li extraction [19–31]. In addition, studies on the formation of Li brine deposits in several salt lakes on the QTP have been carried out, including the Zabuye Lake [32], Dongtai and Xitai salt lakes [33–35], Da Qaidam Salt Lake [36,37], Duogecuoren Co. [38], Eya Co [39], Kangru Chaka [40], Rejue Chaka [41].

Even though studies on the hydrochemistry and formation of specific salt lakes on the QTP have been reported, all-round studies on the Li-rich salt lakes on the QTP are still inadequate. Similarly, the relationship between the distribution and evolution of Li-rich salt lakes on the QTP is unclear until now. Since a summary of existing studies would be of great benefit both for improving knowledge of Li brine resources and for further developing brine Li resources, this study reviews and compiles the major and trace (Li, B) ionic compositions of 74 Li-rich salt lakes on the QTP, and attempts to (i) elucidate the hydrochemistry and distribution of Li-rich salt lakes on the QTP and (ii) constrain the formation of Li brine deposits in these salt lakes. In addition, large amounts of research studies on the famous "Lithium Triangle" in South America, which contains the largest Li deposits on Earth, have been reported. Hundreds of geochemical data (major and trace elemental concentrations, and isotopic compositions) of brines in this region were published [42–47]. These studies provide insights into the hydrochemistry, distribution and formation of brines and salts in the salars on the Central Andes. Related literature has been examined in order to draw comparisons with the salt lakes on the QTP.

2. Overview of Analytical Methods

Most of the geochemical data of the Li-rich salt lakes on the QTP were reported from the Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. The analyses for major ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$, Cl^-, $HCO_3{}^-$, $CO_3{}^{2-}$) of brines generally followed the procedures of The Introduction to Analyzing Methods of Brines and Salt Deposits [48]. K^+ and $SO_4{}^{2-}$ concentrations were measured by gravimetric methods through precipitation of potassium tetraphenylborate and $BaSO_4$, respectively. Ca^{2+} and Mg^{2+} were determined by the ethylene diamine tetraacetic acid (EDTA) titration. Cl^- concentrations were determined by $AgNO_3$ potentiometric titration. $HCO_3{}^-$ and $CO_3{}^{2-}$ were analyzed by the hydrochloric acid (HCl) titration. Na^+ concentrations were calculated by charge balance (($NCO_3{}^{2-}$ + $NHCO_3{}^-$ + NCl^- + $NSO_4{}^{2-}$)−(NK^+ + NCa^{2+} + NMg^{2+})) (N represents ionic equivalent value). The analytical errors for major cations and anions are better than 2%. B concentrations were usually determined by inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo Fisher Scientific, Waltham, MA, USA) with errors ≤3% or by mannitol titration with errors ≤2%. Li concentrations were generally determined by the atomic absorption spectrometer (AAS) (Perkin Elmer, Waltham, MA, USA) with errors ≤0.5%.

3. The Hydrochemistry and Distribution of Li-rich Brines in Salt Lakes on the QTP

There are more than 300 salt lakes (total dissolved solids (TDS) >35 g/L, which defines the lower limit of the salinity of a salt lake) among numerous lakes (~2500) with an area of >1 km^2 on the QTP [12,13]. These salt lakes are mainly distributed in the western part of the QTP, which is in accord with the stronger aridity of this area compared to the eastern part of the QTP [49]. It is reported that over 80 salt lakes on the QTP contain brines (surface and/or intercrystalline brines) with Li^+ >50 mg/L [50]. Of which, seventy-four salt lakes (containing brines with Li^+ >25 mg/L, which is the industrial requirement for comprehensive utilization of brines in China [11]) were compiled in this study (Figure 1). The water chemistry and B, Li concentrations of the other Li-rich salt lakes were unavailable until now. In addition, it is noteworthy that there are three Li-rich lakes (Daze Co, Selin Co and Dangreyong Co) (Figure 1) that are not salt lakes, but their Li^+ concentrations are 34 mg/L, 41 mg/L and 51 mg/L, respectively.

Most of Li concentrations of brines in these Li-rich salt lakes on the QTP range from 100 to 300 mg/L, which is lower than those (mean Li concentrations varying from 82–1400 mg/L) of brines from salars in the South America, such as Uyuni, Salar de Atacama and Hombre Muerto salars [2,47]. These Li-rich brines in salt lakes on the QTP can be classified as the carbonate, sodium sulfate, magnesium sulfate, and chloride types according to the Kurnakov-Valyashko hydrochemical classification. From the southwest to northeast, the carbonate-type, the sodium sulfate-type and the magnesium sulfate-type salt lakes are presented sequentially and present horizontal zoning (Figure 1). This zoning is in agreement with the evolution of natural lake waters along with the increasing aridity from the south to the north on the QTP. Similarly, there are three areas on the QTP, where the Li-rich salt lakes are clustered, the Tibet, Hoh Xil area and the Qaidam Basin (Figure 1). Tectonically, Li-rich salt lakes in the Lhasa and Qiangtang terranes are close to the Bangong-Nujiang and Longmucuo-Shuanghu suture zones, and those in the Songpan-Ganzi-Hoh Xil terranes are near the Jinshajiang-Ailaoshan and Kangxiwar-Mutztagh-Maqin suture zones (Figure 1) [18]. This suggests that the vicinity to the suture zone may be a controlling factor for the Li-enrichment in the studied brines. The Li-rich salt lakes in the Qaidam Basin, which is the largest intermontane basin on the northern QTP, are mainly distributed in the central of the basin. The terminal lakes (Yiliping playa, Xitai and Dongtai salt lakes, Bieletan section of Qarhan playa) of Nalenggele River, originating from eastern Kunlun Mountain, have higher Li concentrations than other lakes in the Qaidam Basin (Table 1).

Different types of brines have distinct major-ion compositions. Generally, the solutes in most brines are dominated by Na and Cl with less Mg and SO_4 (Figure 2a). The Ca and CO_3 + HCO_3 have elevated concentrations only in the carbonate-type brines (Figure 2a). Compared to the sodium sulfate-type brines, the magnesium sulfate-type brines have higher Mg^{2+} concentrations (Figure 2a). The TDS of the Li-rich brines in salt lakes on the QTP range from ~35 to 555 g/L. The average TDS of brines are carbonate-type (143 g/L) < sodium sulfate-type (169 g/L) < magnesium sulfate-type (247 g/L) < chloride-type (295 g/L), while the average Li concentrations of brines are magnesium sulfate-type (183 g/L) < chloride-type (196 g/L) < carbonate-type (224 g/L) < sodium sulfate-type (322 g/L) (Figure 3a). No obvious correlation between the TDS and Li concentrations is observed in these brines (Figure 3a).

Table 1. Major and trace (Li, B) ionic compositions, lake areas, hydrochemical types, Mg/Li ratios of different Li-rich salt lakes on the Qinghai-Tibetan Plateau.

No.	Name	Water Type	Sample Type [1]	Area (km^2)	TDS (g/L)	Na^+ (g/L)	K^+ (g/L)	Mg^{2+} (g/L)	Ca^{2+} (g/L)	Cl^- (g/L)	SO_4^{2-} (g/L)	HCO_3^- (g/L)	CO_3^{2-} (g/L)	B^{3+} (mg/L)	Li^+ (mg/L)	Mg/Li Ratio	Data Source
1	Bange Co	Carbonate	Inter-brine	140	174	54	13	0	0	42	43	5	14	1110	245	0.0	[14]
			Surface brine		222	62	8	0	0	40	1	12	7	849	127	0.4	
2	Dujiali Lake	Carbonate	Surface brine	80	114	41	3	0	0	16	43	3	6	461	112	0.0	[14]
			Inter-brine		126	51	8	0	0	41	37	0	12	1150	150	0.2	
3	Beilei Co	Carbonate	Surface brine	20	131	45	3	0	0	59	16	4	3	195	40	1.6	[14]
4	Gangtang Co	Carbonate	Surface brine	11	72	25	4	0	0	39	2	0	2	480	41	1.5	[14]
5	Pengyan Co	Carbonate	Surface brine	40	96	35	2	0	0	48	8	3	1	75	254	0.1	[30]
6	Jieze Chaka	Carbonate	Surface brine	104	146	44	3	0	0	67	3	0	3	258	192	2.1	[24]
7	Akesayi Lake	Carbonate	Surface brine	164	56	20	1	1	0	32	2	2	0	-	94	5.9	[14]
8	Aweng Co	Carbonate	Surface brine	55	87	37	2	1	0	25	18	0	2	863	140	4.5	[14]
9	Chalaka Co	Carbonate	Surface brine	10	105	40	4	0	0	26	27	0	3	1270	90	0.3	[14]
10	Caimaer Co	Carbonate	Surface brine	32	191	61	16	0	0	90	17	0	6	625	130	0.0	[14]
11	Zhabuye Lake	Carbonate	Surface brine	250	414	130	41	0	0	156	39	0	44	3377	1048	0.0	[51]
			Inter-brine		369	119	25	0	0	138	47	1	27	2616	1085	0.0	[14]
12	Dangxiong Co	Carbonate	Surface brine	56	151	54	7	0	0	68	7	0	11	405	360	0.0	[21]
13	Cona Co	Carbonate	Surface brine	48	33	12	1	0	0	6.2	8	1	3	851	33	2.5	[14]
14	Gangma Co	Carbonate	Surface brine	13	81	29	2	0	0	34	10	0	4	230	56	3.3	[14]
15	Nawu Co	Carbonate	Surface brine	46	106	35	1	0	0	14	48	1	5	213	23	12.1	[14]
16	Leen Co	Carbonate	Surface brine	1	58	18	3	0	0	19	8	0	3	1762	106	0.4	[14]
17	Zanzong Co	Sodium Sulfate	Surface brine	8	413	95	17	3	0	162	106	0	2	952	2756	0.1	[14]
18	Kongkong Chaka	Sodium Sulfate	Surface brine	36	334	124	4	2	0	189	14	0	0	59	140	10.9	[14]
19	Yibu Chaka	Sodium Sulfate	Surface brine	100	97	34	1	1	0	43	17	0	0	68	43	21.0	[14]
20	Angdaer Co	Sodium Sulfate	Surface brine	45	181	69	3	0	0	92	8	1	6	219	64	3.4	[14]
21	Rebang Co	Sodium Sulfate	Surface brine	27	70	21	3	0	0	19	25	0	1	506	29	11.1	[14]
22	Qia Chaka	Sodium Sulfate	Surface brine	3	199	70	8	0	0	97	20	0	0	869	250	1.4	[14]
23	Bieruoze Co	Sodium Sulfate	Surface brine	40	145	32	3	5	0	4	65	2	0	1436	150	33.0	[14]
24	Nieer Co	Sodium Sulfate	Surface brine	33	215	40	17	16	0	92	43	0	0	1507	655	24.8	[14]
25	Laguo Co	Sodium Sulfate	Surface brine	86	91	27	6	2	0	42	12	0	1	714	530	3.0	[14]
26	Chabo Co	Sodium Sulfate	Surface brine	32	199	63	10	4	0	110	12	0	0	241	165	24.2	[27]
27	Duoma Co	Sodium Sulfate	Surface brine	18	117	33	5	3	0	72	2	0	0	529	570	4.4	[14]
28	Dong Co	Sodium Sulfate	Surface brine	100	140	24	6	3	0	25	37	0	1	433	190	15.4	[14]
29	Buerga Co	Sodium Sulfate	Surface brine	12	136	42	5	4	0	65	18	1	0	177	55	67.6	[14]
30	Dawa Co	Sodium Sulfate	Surface brine	110	36	8	1	1	0	4	20	0	0	272	31	32.2	[14]
31	Dirangbi Co	Sodium Sulfate	Surface brine	26	110	19	1	3	0	19	28	0	0	252	35	79.6	[12]
32	Gemu Co	Sodium Sulfate	Surface brine	76	275	105	2	0	0	160	6	0	0	111	65	6.0	[52]
33	Jiaomu Chaka	Sodium Sulfate	Surface brine	12	40	13	1	1	1	23	2	0	0	71	46	20.3	[52]
34	Taoxing Co	Sodium Sulfate	Surface brine	5	213	77	3	1	0	106	24	1	0	175	125	9.9	[52]
35	Xin Co	Sodium Sulfate	Surface brine	25	63	12	2	7	0	31	10	1	0	122	55	124.0	[52]
36	Gaerkunsha Lake	Sodium Sulfate	Inter-brine	2	365	118	21	0	3	187	28	0	0	1436	2895	0.0	[14]
37	Yanjian Co	Sodium Sulfate	Surface brine	5	42	9	1	3	1	13	15	1	0	83	27	123.6	[14]
38	Maerguo Chaka	Magnesium Sulfate	Surface brine	80	323	100	6	13	1	189	13	0	0	313	320	40.7	[14]

Table 1. *Cont.*

No.	Name	Water Type	Sample Type [1]	Area (km^2)	TDS (g/L)	Na^+ (g/L)	K^+ (g/L)	Mg^{2+} (g/L)	Ca^{2+} (g/L)	Cl^- (g/L)	$SO_4{}^{2-}$ (g/L)	$HCO_3{}^-$ (g/L)	$CO_3{}^{2-}$ (g/L)	B^{3+} (mg/L)	Li^+ (mg/L)	Mg/Li Ratio	Data Source
39	Kangru Chaka	Magnesium Sulfate	Surface brine	10	323	117	3	3	0	186	12	0	0	89	77	43.5	[14]
40	Maergai Chaka	Magnesium Sulfate	Surface brine	80	324	28	1	1	0	45	3	0	0	406	30	25.5	[14]
41	Eya Co	Magnesium Sulfate	Surface brine	4	150	35	7	12	0	82	7	0	0	205	180	67.0	[19]
42	Biluo Co	Magnesium Sulfate	Surface brine	24	323	90	14	12	0	194	11	0	0	328	61	199.1	[14]
43	Rejue Chaka	Magnesium Sulfate	Surface brine	19	146	49	4	4	0	85	5	0	0	75	160	23.4	[14]
44	Daerwocuowen Co	Magnesium Sulfate	Surface brine	45	136	45	2	4	1	80	6	0	0	-	64	55.2	[14]
45	Yongbo Co	Magnesium Sulfate	Surface brine	40	314	107	5	5	1	187	8	1	0	0	166	29.8	[14]
46	Longmu Co	Magnesium Sulfate	Surface brine	97	143	33	4	12	1	86	7	0	0	273	110	107.3	[29]
47	Chana Co	Magnesium Sulfate	Surface brine	4	329	85	10	20	0	183	26	0	0	600	300	67.1	[14]
48	Zhacang Chaka	Magnesium Sulfate	Surface brine	35	341	106	11	8	0	178	35	0	0	425	505	16.6	[14]
			Inter-brine		221	42	10	9	0	86	18	1	0	615	553	15.4	
		Magnesium Sulfate	Surface brine	60	290	61	10	9	0	111	19	0	0	453	436	21.1	
			Inter-brine		268	17	18	13	0	169	16	0	0	522	780	16.4	
		Magnesium Sulfate	Surface brine	33	308	94	10	8	0	169	24	0	0	375	800	10.5	
			Inter-brine		323	88	16	14	0	172	29	0	0	522	1207	11.5	
49	Mami Co	Magnesium Sulfate	Surface brine	94	174	49	10	6	0	93	17	0	1	859	1227	4.6	[14]
50	Yupan Co	Magnesium Sulfate	Surface brine	20	-	120	2	7	0	-	8	1	0	1323	62	115.9	[14]
51	Coni Co	Magnesium Sulfate	Surface brine	67	57	19	1	2	1	31	8	0	0	276	40	52.5	[12]
52	Baqian Co	Magnesium Sulfate	Surface brine	15	216	58	10	10	1	123	7	0	0	1169	410	24.9	[28]
53	Purang Chaka	Magnesium Sulfate	Surface brine	35	340	96	11	17	0	186	28	2	0	170	187	91.9	[52]
54	Bieletan playa	Magnesium Sulfate	Inter-brine	1120	213	23	23	64	0	240	7	0	0	292	124	517.3	[14]
55	Mahai Lake	Magnesium Sulfate	Inter-brine	2000	465	112	12	122	1	304	30	0	0	535	150	810.5	[14]
56	Kunteyi playa	Magnesium Sulfate	Inter-brine	1680	329	54	12	38	7	217	1	0	0	243	27	1414.8	[14]
57	Yiliping playa	Magnesium Sulfate	Inter-brine	360	327	86	11	22	0	193	20	0	0	303	244	89.7	[31]
58	Xitai Lake	Magnesium Sulfate	Inter-brine	570	335	101	8	16	0	184	35	0	0	757	256	61.5	[14]
59	Dongtai Lake	Magnesium Sulfate	Surface brine	201	332	117	4	6	0	187	18	0	0	428	141	40.3	[14]
60	Da Qaidam Lake	Magnesium Sulfate	Surface brine	240	274	88	3	10	1	156	17	0	0	939	85	114.2	[14]
61	Xiaoqaidam Lake	Magnesium Sulfate	Surface brine	152	350	106	3	13	0	184	32	0	0	-	36	374.4	[14]
62	Yanhu Lake	Magnesium Sulfate	Surface brine	32	221	72	2	7	1	123	16	1	0	80	62	107.7	[53]
63	Xijinwulan Lake	Magnesium Sulfate	Surface brine	346	357	93	3	3	0	152	4	0	0	180	101	24.6	[14]
64	Caiduo Chaka	Magnesium Sulfate	Surface brine	44	151	57	1	2	1	76	13	1	0	168	40	46.4	[12]
65	Mang Co	Magnesium Sulfate	Surface brine	12	101	33	2	3	0	56	7	0	1	75	111	26.5	[52]
66	Qiagang Co	Magnesium Sulfate	Surface brine	20	42	15	1	1	0	24	2	0	0	22	26	17.3	[52]
67	Zhaqiongema Co	Magnesium Sulfate	Surface brine	10	262	97	3	2	0	146	14	1	0	161	164	9.9	[52]
68	Duoxiu Lake	Magnesium Sulfate	Surface brine	5	306	102	2	12	1	182	8	0	0	116	67	173.9	[54]
69	Gas Hur Lake	Magnesium Sulfate	Surface brine	103	333	77	5	30	0	176	45	0	0	108	25	1190.8	[14]
70	Niulangzhinv Lake	Chloride	Surface brine	30	555	0	1	72	100	382	0	0	0	535	47	1549.4	[14]
71	Lexiewudan Lake	Chloride	Surface brine	227	90	30	2	1	2	54	1	0	0	79	103	11.2	[55]
72	Duogecuoren Co	Chloride	Surface brine	260	148	53	3	1	12	86	2	0	0	47	104	11.9	[38]
73	Queer Chaka	Chloride	Surface brine	8	330	110	13	3	5	195	1	1	0	251	548	5.0	[52]
74	Goulu Co	Chloride	Surface brine	35	308	105	3	5	6	188	1	0	0	475	111	43.4	[53]

[1] Inter-brine represents intercrystalline brine. "-" means no data available.

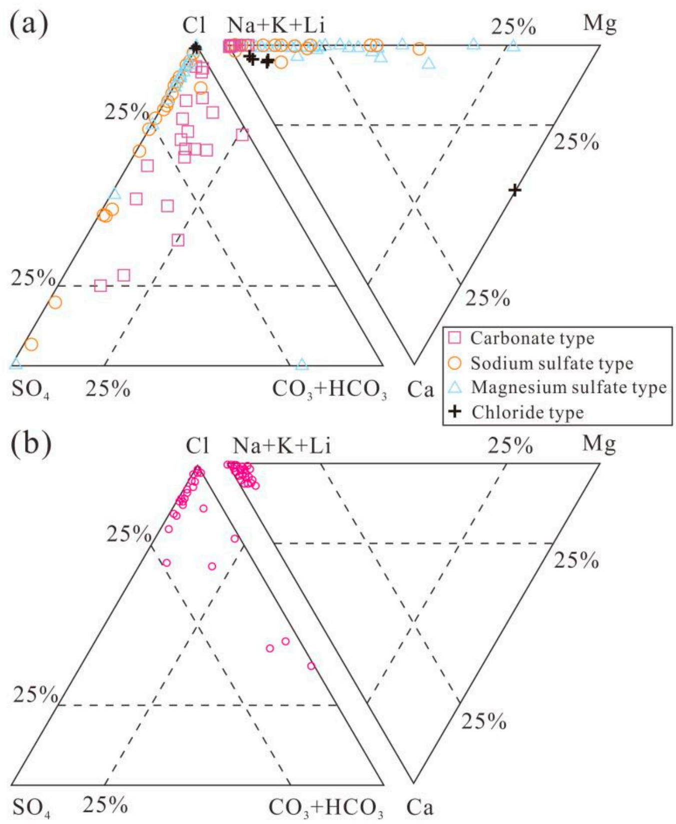

Figure 2. (**a**) Brine compositions of Li-rich salt lakes on the Qinghai-Tibetan Plateau; (**b**) brine compositions of Bolivian salars (from [42]). The data of salt lakes on the QTP can be seen in Table 1.

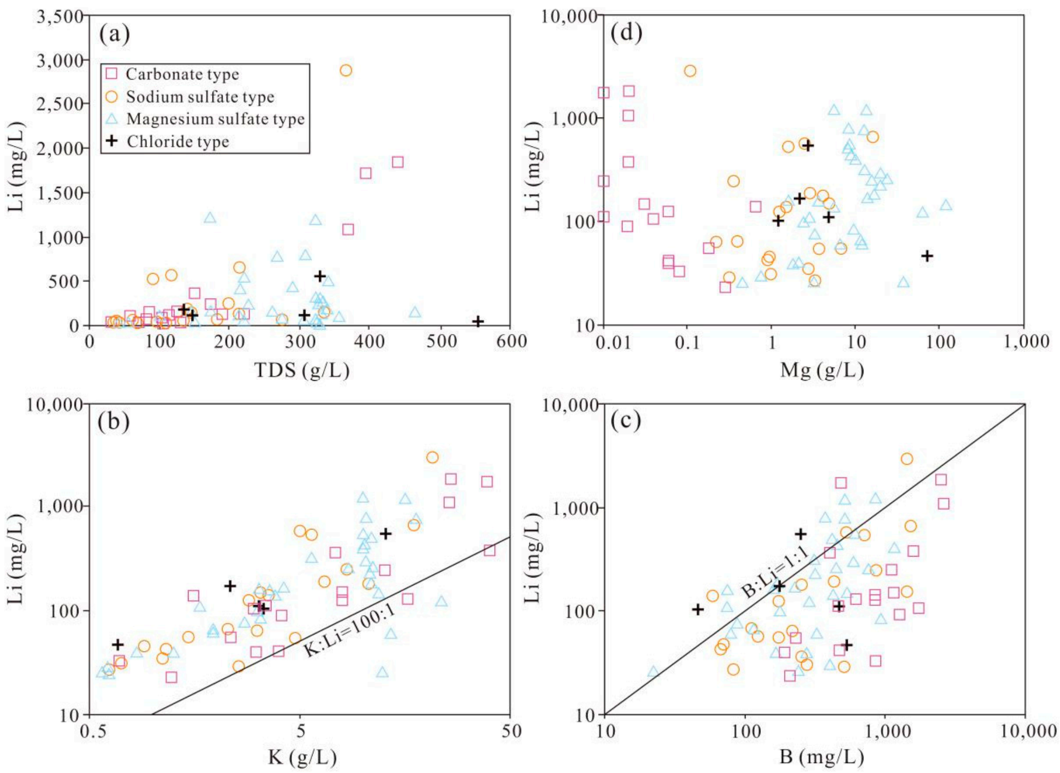

Figure 3. (**a**) Li vs. total dissolved solids (TDS) of different type brines in salt lakes; (**b**) Li vs. K of different type brines in salt lakes; (**c**) Li vs. B of different type brines in salt lakes; (**d**) Li vs. Mg of different type brines in salt lakes. The data of salt lakes on the QTP can be seen in Table 1.

Brines in the Li-rich salt lakes on the QTP are also characterized by high B^{3+} and K^+ concentrations. Positive correlations have been determined among Li, K and B in different brine types, suggesting common sources and similar geochemical behavior for these ions (Figure 3b,c). The K^+ and B^{3+} concentrations are usually one or two orders of magnitude higher than the Li^+ concentrations in these brines (Figure 3b,c), which indicate the potential of comprehensive exploitation of Li, B and K in the Li-rich salt lakes on the QTP.

In addition, the Mg/Li ratio is a critical factor for evaluating the brine quality due to that Mg and Li cations have similar ionic properties and separating Mg^{2+} from Li^+ is a challenging problem during the Li extraction. No unequivocal correlation between Mg^{2+} and Li^+ is observed (Figure 3d), indicating different sources of Mg and Li in brines on the QTP. Compared with the salars in the Andean Plateau (Figure 2b), salt lakes on the QTP are generally characterized by high Mg^{2+} and $SO_4{}^{2-}$ concentrations [42]. Yu et al. [56] defined that brines with Mg/Li ratios ≤8 are the low-Mg/Li-ratio brines and brines with Mg/Li ratios >8 are the high-Mg/Li-ratio brines. According to this definition, almost all carbonate-type brines are low-Mg/Li-ratio brines (Mg/Li ratios ranging from 0.0 to 5.9, averaging 1.5) except for Nawu Co (12.1), while most of sodium sulfate-, magnesium sulfate- and chloride-type brines are high-Mg/Li-ratio brines (Mg/Li ratios ranging from 0.0 to 124.0, 4.6 to 1414.8, 5.0 to 1549.4, averaging 24.6, 151.2, 324.5, respectively) (Table 1). Based on the Li concentrations and Mg/Li ratios, carbonate-type brines are the most promising Li resources, which is conducive to the Li extraction. This is supported by the fact that most of the carbonate-type salt lakes have been conducted the evaporation experiments for future exploitation of Li resources [19–31]. Most of the sodium sulfate-type, magnesium sulfate-type, and chloride-type brines are disadvantageous for Li extraction because of the high Mg/Li ratios. However, when considering the large lake areas and high Li concentrations, these salt lakes show great potential of Li resources. Recent studies focus on investigating the separation of Mg and Li and the recovery of Li from the high-Mg/Li-ratio brines. The emerging technologies include solvent extraction, ion sieve adsorption, electrochemical approaches, membrane separation [57–61].

4. The Formation of Li Brine Deposits in Salt Lakes on the QTP

4.1. The Sources of Li in Brines in Salt Lakes

Lithium in the salt lakes on the QTP may be derived from one or more processes [15,33,62–71]: (1) weathering of igneous or volcanic rocks; (2) geothermal fluids involved in nearby volcanic systems or underlying magma chambers; (3) weathering of Li-rich sedimentary sequence; (4) Li-bearing brine migration through faults or topographic evolution (Figure 4).

The first two types of sources have been widely accepted by the geological community and supported by the Li-rich brines on the notable Andean salars. Weathering and erosion of widespread volcanic rocks and active or ancient hydrothermal springs related to volcanism contribute to the formation of Li-rich brines in most of the salars on the Central Andes [45,68–72]. In contrast to widespread Cenozoic volcanic rocks in the Central Andes, there are restricted magmatic rocks on the QTP (Figure 1). Cenozoic volcanism on the QTP is the volcanic response to the India–Asia continental collision. The volcanism on the QTP showed regular displacement in space and time, which occurred mainly in the southern plateau at 65–40 Ma, in the central plateau at 45–26 Ma, in the southern plateau at 26–10 Ma and in the northern plateau from ~18 Ma to the present [73]. The patched volcanic rocks may restrict the formation of Li-rich salt lakes on the QTP. However, geothermal systems are well-developed on the QTP (Figure 1) [17,74–77]. Hydrochemistry of modern geothermal waters on the QTP has been reported extensively and they are generally enriched in Li (0.08–96 mg/L) [37,53,74,76,78,79]. Although Risacher and Fritz [42,43] and Risacher et al. [45] proposed that hydrothermal activity is not specifically responsible for the formation of high Li concentrations in brines of salt lakes studied in the Andes, these geothermal waters on the QTP play evidently important roles in the formation of Li-rich salt lakes. An isothermal evaporation experiment of geothermal waters from the Kawu

Geothermal field on the QTP reported that zabuyelite, which was first discovered in the Zabuye Lake, precipitated, suggesting that geothermal water inflow may be the primary source for Li accumulation in the salt lakes [67]. Moreover, previous studies reported that the combined action of surrounding rocks' weathering, paleo-lake migration, leaching of former evaporites and upflow of deep underground brines contributed to the formation of Li brine deposits in the Bieletan section in the Qarhan playa, Dongtai and Xitai salt lakes, and Yiliping playa in the Qaidam Basin on the QTP [80]. However, recent studies certified that these Li brine deposits were formed by the supply of the Nalenggele River [33–35]. Compared to other rivers originated from the eastern Kunlun Mountain, the Nalenggele River has higher Li concentrations (0.416–0.756 mg/L) because its upper reaches (Hongshui River) are supplied by geothermal springs related to volcanism along the Kunlun Fault. Limited studies on water chemistry of hot springs in this area reported high Li concentrations (0.41–96.0 mg/L) [53]. This conclusion also deciphers the fact that Li-rich salt lakes in the Qaidam Basin seems to have no collection with sutures. These lakes receive Li from the suture zones through rivers which can transport solutes for a long distance.

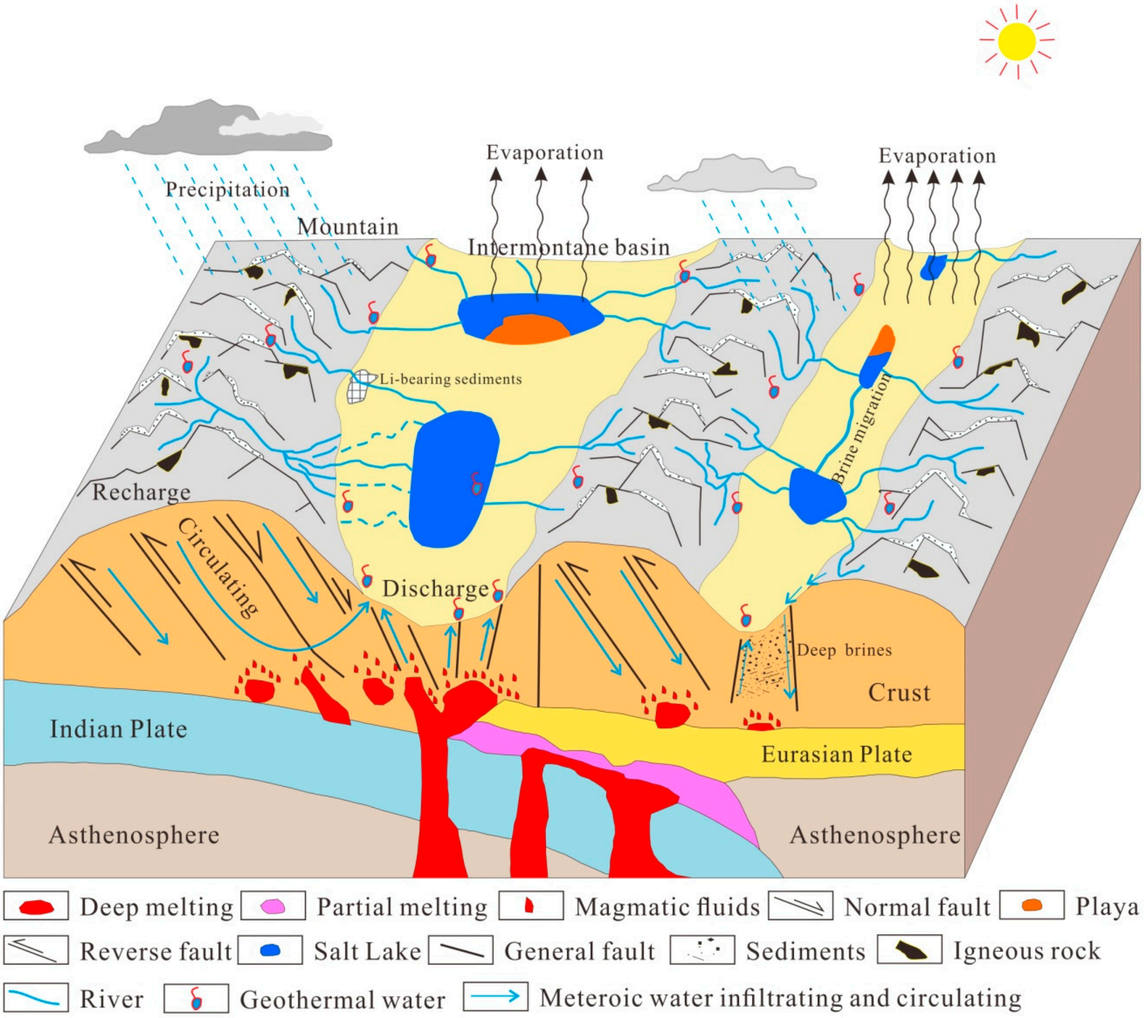

Figure 4. Schematic model for the formation of Li-rich brines in salt lakes on the Qinghai-Tibetan Plateau (after [78]).

The formation of geothermal springs is interpreted as the infiltration and circulation of meteoric waters along some stretching tensile active tectonic belts or suture zones [77,81]. The meteoric water was heated by the crustal remelting magmas, then discharged as hot springs (geothermal waters) at the surface [77,81]. During this process, water-rock interaction and magmatic residuals may contribute abundant Li to the waters [69,81]. This conclusion may shed light on the phenomenon that Li-rich salt lakes mainly distributed around the suture zones. Besides the widespread modern geothermal springs, ancient geothermal activities were also intensive on the QTP, certified by extensive geyserites and travertine deposits with high concentrations of Li, Rb, Cs and B [82,83]. Geyserites or travertine deposits are widespread in several Li-rich salt lakes, such as Dangxiong Co, Zabuye Lake, Duogecuoren Co, etc. In the Zabuye Lake, ancient travertine deposits occur extensively along the faults in the central and western parts. Some travertine mounds are still active and spring waters supply into the Zabuye Lake. These spring waters usually contain high Li concentrations (0.02–4.70 mg/L), which is an important source of Li in the Zabuye Lake.

Zheng and Liu [15] reported a Miocene Li-rich (20–111 μg/g) volcanic-sedimentary sequence in the northwestern part of Ngangla Ringco Lake on the QTP, and emphasized that weathering of these rocks provides significant part of Li in the salt lakes in this region. Similarly, in the Zabuye Lake, Li is also enriched in inflowing rivers (0.2–1.1 mg/L) and has an increasing trend from the upper to lower reaches, suggesting that weathering of surrounding rocks and sediments also provides Li to the lake.

Besides the above three sources of Li, brine migration also takes part in the formation of Li-rich brines in several salt lakes on the QTP. The low-lying Laguo Co receives a significant part of solutes from the neighboring topographical-high Jibu Chaka, Jiangge Co and Xizha Co. A similar process is also observed from the high-altitude Rejue Chaka to low-lying Kangru Chaka, the Songmuxi Co to Longmu Co, and the Taruo Co to Zhabuye Lake [40,41,84].

In recent years, Li-rich deep brines (a potential Li resources with Li concentrations ranging from 0.22–1890 mg/L), discovered in some anticlines in the western Qaidam Basin, may be another Li source for the salt lakes in this region [85,86]. The deep geothermal waters related to felsic volcanic rocks may provide Li to the deep brines in the western Qaidam Basin [80].

4.2. The Formation Model of Li Brine Deposits on the QTP

Zheng and Liu [15] and Li et al. [11] emphasized the climate and tectonic-geomorphologic conditions for the high Li concentrations in salt lakes on the QTP. These conclusions are of great importance to understanding the formation of Li brine deposits in salt lakes on a large scale.

The primary condition for the formation of Li-rich salt lakes on the QTP should be the sufficient sources of Li, including the geothermal waters, weathering of igneous rocks and Li-rich sediments, which were discussed in the Section 4.1. Salt lakes in the Xinjiang and Inner Mongolia provinces, western China, have barely any Li brine deposits due to lack of geothermal activities. Even on the QTP, Li-rich salt lakes are mainly clustered in major suture zones and igneous/volcanic rock areas, which can be supplied by Li-rich geothermal/river waters. Then, endorheic basins related to topographical low, such as the Qaidam Basin, provide suitable residual places for the Li-rich spring or river waters. Finally, under arid climate, suggesting strong evaporation and less precipitation, these waters can evolve to Li-rich brines with sufficient time. Salt lakes on the QTP are mainly distributed in the west part of the QTP with the stronger aridity; meanwhile Li-rich salt lakes are not presented in the southern and eastern part of the QTP where geothermal activities are very strong (Figure 1). This is due to the relatively humid climate and extensive exorheic watershed in the southern and eastern QTP. Even though there are sufficient Li sources, arid climate and endorheic basin in the Yahu Lake in the Qaidam Basin, Li brine deposit is not formed because of the short residual time. Thus, the above four factors jointly constrain the distribution, Li grades of Li-rich salt lakes on the QTP. The schematic formation model of Li-rich salt lakes on the QTP is shown in Figure 4.

In addition, when studying the formation of Li brine deposits in salt lakes on the QTP, some basin scale processes, including absorption of Li by clay, evaporites formation, should be considered. For example, Li reserves in the Bielatan and Yiliping playas, Dongtai and Xitai salt lakes are 2.3 million tons; however, according to the recharge time (>10,000 years), the annual runoff (~10.83×10^8 m^3), Li content (0.727 mg/L) of the supplying Nalenggele River water, the total Li (~7.9 million tons Li) supplied by river is much larger than the present reserves [33–35]. The Li may be lost during the river transportation process and/or the evaporation and concentration process in the lake area. However, the mechanisms controlling the Li ionic behavior during the transportation and enrichment processes are unclear and the extent of Li scavenging by clay and evaporites has not been assessed in this area.

5. Perspectives for Future Work

As mentioned above, there are over 300 salt lakes on the QTP, among which over 80 salt lakes contain brines with Li^+ concentrations >50 mg/L. However, the hydrochemistry of many lakes on the QTP is not reported because of the harsh environments and Li^+ concentrations of some lakes were not analyzed in previous investigations. Since the increasing demand for Li and its compounds in China has stimulated the exploitation of Li-rich salt lakes on the QTP, a more extensive geological survey is needed in order to identify the Li-rich salt lakes on the QTP, which is also helpful to understand the relationship between the formation and evolution of these salt lakes and the geological background of the QTP. Moreover, while systematic hydrochemical studies have been performed in the Andean salars [42,43,45], similar studies on the hydrogeology and geochemistry of supplying rivers or springs, neighboring sediments and rocks in salt lakes on the QTP are limited and needed to better constrain the formation of Li-rich salt lakes. In addition, even though many scientists approved that geothermal activities and weathering of igneous rocks are related to the formation of Li-rich salt lakes on the QTP, solid (hydrogeological, hydrochemical, isotopic) evidence to support this idea is still lacking. Few works on the sources of Li and formation of Li-rich brines in specific salt lakes on the QTP are reported.

For the Zhabuye Lake, Dongtai and Xitai salt lakes where geochemistry of waters and surrounding rocks has been investigated systemically, future work should focus on providing a robust data set in order to calculate the mass balance of Li and elucidate the geochemical behavior of Li transported from the source to the sink, where complex hydrogeochemical processes happened. Detailed monitoring works and evaporation experiments should be started in the future. The influence of basin-scale processes, such as evaporation and clay absorption, on the Li brine resources is also needed to be assessed quantitatively.

In addition, compared to hydrochemistry of the Andean salars, Li-rich salt lakes on the QTP are generally characterized by high Mg concentrations, resulting in problems in Li extraction. Identifying the sources of Mg in salt lakes on the QTP is of significance to further develop the Li resources in the salt lakes.

Author Contributions: Q.L. sorted out the data and wrote the paper; Q.F., J.W. and Z.Q. conceived of and designed the paper; X.Z., H.W., Y.D., F.S. provide writing, reviewing and editing work.

Funding: This research was funded by the National Natural Science Foundation of China (Grant Nos. 41872093 and 41671521), the Ministry of Science and Technology of the People's Republic of China (Grant No. 2018YFC0406605) and the One-Thousand Innovative Talent Project of Qinghai Province (Grant to Q.S. Fan).

Acknowledgments: We thank Liyan Shao for helping with the data collection. Four anonymous reviewers are thanked for providing valuable comments and suggestions.

Conflicts of Interest: The authors declare no conflict of interest.

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