The dissolution of lithium minerals in salt solutions: Implication for the lithium content of saline waters

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Lithium minerals, petalite ($\text{Li}[\text{AlSi}_4\text{O}_{10}]$) and lepidolite ($\text{K}_2(\text{Li}, \text{Al})_{5-6}[\text{Si}_{6-7}\text{Al}_{2-1}\text{O}_{20}](\text{OH}, \text{F})_4$), were reacted with seawater and NaCl solutions for 240 hours at 150 to 250°C and with a water/mineral ratio of 25 by weight, to clarify the role of dissolved salts on the enrichment of lithium in natural saline waters such as coastal thermal waters and fossil seawaters. Lithium leaching from the minerals was enhanced with increasing salt concentration and temperature. It was proved from the experiments using various salt solutions that NaCl solution and seawater are effective for the leaching of lithium from rocks and that even the altered seawaters containing low magnesium have the ability to extract lithium from rocks. This investigation suggests that the non-volcanic saline waters of high lithium content (e.g. fossil seawater) can be produced by a long term seawater-rock interaction at relatively low temperature without a contribution from the so-called "magmatic emanation".

INTRODUCTION

Many papers have been presented on the lithium content of natural waters. WHITE (1957) suggested that among the natural surface waters volcanic NaCl type waters are most enriched in lithium and it may be used as a very significant criterion to distinguish natural waters of volcanic origin. On the other hand, ELLIS and MAHON (1964) suggested that the composition of volcanic thermal water could be explained by high temperature reaction of water with rocks, and do not require contribution from a "magmatic" fluid rich in the typical hydrothermal phase elements such as Li, As, B, etc. ICHIKUNI *et al.* (1974) suggested that even the cold pore waters in sediments can be changed into waters with Li/Na and K/Na ratios resembling geothermal waters if the waters are maintained under certain conditions. In fact, some non-volcanic NaCl type waters in Japan are of the same order of magnitude as those of volcanic NaCl type waters, e.g., Kashio, $T_w = 11.0^\circ\text{C}$, $\text{Li} = 80\text{ppm}$, $\text{Li/Na} = 5.7 \times 10^{-3}$ (TAKA-

MATSU *et al.*, 1980b).

The hot springs in Japan have been classified into 4 types by SAKAI and MATSUBAYA (1974) from the hydrogen and oxygen isotopic ratio of the spring waters: Arima type, Greentuff type, coastal and volcanic thermal waters. In general, the waters except volcanic thermal waters have high salinity. Arima and Greentuff-type thermal waters which are flowing out from Neogene or pre-Neogene formations show high lithium contents and have high Li/Na ratios. On the other hand, in coastal thermal waters which are heated by conduction from the Quarternary volcanic rocks, these values are low.

The chemical composition of NaCl type waters originated from present or fossil seawater may be affected by one or some of the following mechanisms during their ascent to the surface (NADLER *et al.*, 1980): 1) reactions with rocks, 2) evaporation and precipitation of salts and 3) ultrafiltration. The first mechanism would be most significant for solutions of shallow coastal aquifers in which evaporation and ultrafiltration can not take place. It is known that

even the coastal thermal waters, that may be derived by short term seawater-rock interaction, contain more lithium than does seawater (TAKAMATSU *et al.*, 1980b). This indicates that lithium in waters may be derived from rocks by reaction with seawater and that the lithium content of non-volcanic NaCl type water may prove to be a good criterion for the degree of seawater-rock interaction.

Lithium minerals were reacted with salt solutions and seawater, to examine whether the lithium in the NaCl type waters could be derived from rocks by the reaction with the salt solutions such as seawater.

EXPERIMENTAL

Most igneous and sedimentary rocks have lithium concentrations in a restricted range of 10-70ppm (HEIER and BILLINGS, 1969). However, the lithium concentrations of rocks are too low to determine the lithium concentration of the solutions in the dissolution experiments. So lithium minerals, petalite and lepidolite, were used as our starting materials.

Petalite (Southwest of Africa) and lepidolite (South-Dakota, U.S.A.) were purchased from the Iwamoto Mineral Compnay, Tokyo. They were crushed to under 200 mesh for the use in the experiments. Their chemical compositions are given in Table 1. Reagent grade NaCl was dissolved in distilled water to prepare 0.01, 0.1 and 0.555M NaCl solutions. Natural seawater used for the experiments was collected off Torishima Island, Tokyo and passed through a 0.45 μ m cellulose membrane filter.

The lithium minerals were reacted with NaCl solutions and seawater (or diluted seawater) at moderate temperature (150, 200 and 250°C) and at a water/mineral ratio of 25 by weight. In order to elucidate the role of cations in the dissolution of lithium, petalite was reacted with 0.1 M solution of NaCl, KCl, RbCl and CsCl each at 200°C. The experiments were carried out in a shaking type autoclave using a reaction vessel made of titanium alloy. Pressure was maintained at the vapor pressure at given tempera-

Table 1. The chemical composition and the surface area of the lithium minerals

	Petalite	Lepidolite
H ₂ O	0.23	0.08
H ₂ O(+)	1.73	0.90
SiO ₂	75.58	56.40
Al ₂ O ₃	15.92	24.02
Fe ₂ O ₃	0.02	0.12
CaO	0.38	----
MgO	0.15	----
Li ₂ O	3.38	3.46
Na ₂ O	1.54	0.71
K ₂ O	0.60	8.98
MnO	0.00	0.28
F	----	3.68
Total	99.53(%)	98.63(%)
Surface area	4.0(m ² /g)	5.1 (m ² /g)

----: Not determined.

ture. The pressure effect on the dissolution of lithium was ignored in the experiments because the effect is considered to be small.

Resulting solutions were filtered through 0.45 μ m cellulose membrane filters and the pH was measured immediately. The lithium, potassium, sodium, calcium and magnesium contents of the filtrates were determined by atomic absorption spectrophotometry. The chloride and sulfate ions were determined by ion chromatography. We did not analyze the solid reaction products. Therefore, we will not discuss the alteration products in this paper.

RESULTS

Dissolution in NaCl solutions Figure 1 shows the amounts of lithium leached from petalite and lepidolite by NaCl solutions. The lithium concentrations in 0.555M NaCl solution during the reaction with petalite at 150, 200 and 250°C are shown in Fig. 2. The dissolution rate of lithium increased with increasing NaCl concentration and with temperature. The pH of the resulting solutions became slightly low with increasing NaCl concentration and temperature. The effect of NaCl on the dissolution of lithium from petalite was larger than that from lepidolite (Figs. 1 and 3). At low temperature (40-90°C), however, the effect of NaCl on the

Fig. 1. Li concentrations in salt solutions during reaction with petalite and lepidolite at 200°C and water/rock ratio of 25. Petalite: 0.555M NaCl (●), 0.1M NaCl (○), 0.01M NaCl (■) and H₂O (△). Lepidolite: 0.1M NaCl (▲), H₂O (△).

dissolution of lithium from petalite was smaller than that from lepidolite (TAKAMATSU *et al.*, 1976). This may be due to the structural difference between lepidolite and petalite; phyllosilicate and tectosilicate. The rate of release of lithium from lepidolite into the solution may reflect the rate at which the interlayer cations are removed and that from petalite may reflect the rate of attack on the tetrahedral frameworks.

Fig. 2. Li concentrations in 0.555M NaCl solution during reaction with petalite at 250°C (●), 200°C (○) and 150°C (△).

Dissolution in seawater and diluted seawater Table 2 shows the concentrations of lithium, sodium, potassium, calcium, chloride and sulfate ions found in seawater and the diluted seawater adjusted to 0.1 and 0.01M chloride concentration which reacted with petalite. The pH of the reacted solutions decreased with increasing Cl concentration and with the progress of reaction (Table 2).

Dissolution rate constants in salt solutions

From the experimental results, the dissolution of lithium minerals are considered to be incongruent. Many studies have been reported on the incongruent dissolution kinetics of feldspar and mica. PETROVIĆ *et al.* (1976) reviewed the hypotheses on the dissolution kinetics. The hypotheses involve surface reaction and diffusion through amorphous precipitates, crystalline precipitates and leached layer. The object of this study, however, is not to discuss the dissolution mechanism. We calculated an appropriate rate constant of lithium dissolution in all the experiments to know the effect of temperature and salt concentration on the dissolution of the lithium minerals. An ion exchange equilibrium will be established, when

Table 2. The pH and the concentrations of Li, Na, K, Ca, Mg, Cl and SO₄ found from the experiments of petalite and seawater and diluted seawater (adjusted to 0.1 and 0.01M chloride concentration)

	Time (hr)	pH	Li	Na	K (mg/l)	Ca	Mg	Cl	SO ₄
0.01M Cl ⁻	Start	6.72	0.00	195	7.33	7.50	23.8	353	49.0
	6	6.87	6.90	206	26.8	3.78	1.08	357	48.8
	30	7.03	11.0	196	23.4	2.09	0.23	357	48.7
	42	6.99	12.1	195	23.1	1.93	0.17	357	48.7
	66	7.14	12.8	196	22.9	1.68	0.07	353	49.5
	150	7.06	15.8	197	20.7	1.55	0.16	354	48.0
	240	7.24	18.3	198	18.6	1.48	0.11	353	47.5
0.1M Cl ⁻	Start	7.38	0.02	1,950	73.3	75.0	238	3,530	490
	6	5.47	9.00	1,940	105	84.5	198	3,600	513
	30	4.61	18.1	1,950	107	51.1	171	3,540	---
	42	5.10	21.1	1,940	105	53.6	175	3,520	413
	66	4.55	23.2	1,970	103	47.5	161	3,530	393
	150	4.74	29.2	1,960	110	46.0	157	3,530	390
	240	4.33	33.8	1,970	112	40.7	145	3,540	364
Seawater	Start	8.21	0.15	10,800	407	416	1,320	19,700	2,720
	6	5.20	10.6	10,800	450	173	1,400	19,800	2,170
	30	4.57	20.2	---	445	205	1,220	---	---
	42	4.01	22.0	10,900	437	160	1,220	19,600	2,170
	66	3.90	24.5	10,800	434	150	1,200	19,900	2,030
	150	4.10	29.9	10,900	443	142	1,160	19,800	1,990
	240	3.89	33.8	11,000	437	138	1,150	19,700	1,970

---: Not determined.

the reactions of dissolution proceed sufficiently. The reaction mechanisms will be complicated and may vary with time. In our experiments, only a few percent of lithium was dissolved in the solutions. Therefore, it is supposed that the reactions occurred at the near surface of the minerals. In order to simplify the equation for the rate constant of lithium dissolution, we assume that the order of the reaction is first with respect to the lithium concentration of the minerals. We get the following equation,

$$m = (M - m_0)(1 - e^{-kt}) + m_0 \quad (1)$$

where m and m_0 are the amounts of dissolved lithium at time t and 0, k is the dissolution rate constant for lithium and M is the amount of lithium per 1 gram of the minerals.

Substituting the values of $m(t = 6, 30, 66, 150$ and 240 hours) into Eq. (1), we calculated the dissolution rate constant k by the non-linear least squares method. Figure 3 shows the relation between the logarithm of k and the chloride concentration of the starting solution used.

DISCUSSION

Dissolution of lithium minerals in salt solutions The dissolution rate constant of lithium in seawater was smaller than that in 0.555M

Fig. 3. Relationship between rate constant and Cl concentration of salt solution. Petalite + NaCl: 250 (●), 200 (□) and 150 (○)°C. Petalite + seawater: 200 (○)°C. Lepidolite + NaCl: 200 (▲)°C. Lepidolite + H₂O: 200 (△)°C.

NaCl solution and the pH of resulting solution of seawater was smaller than that of 0.555M NaCl solution. The decrease of pH may be due to the H^+ ions produced by precipitation of Mg compound such as magnesium hydroxide sulfate. Most of lithium is exchanged with H^+ ions in the seawater experiment, while the lithium is exchanged exclusively with sodium in the NaCl solutions. These imply that the mechanisms of ion-exchange with cations are different from each other and that the dissolution rate of lithium is affected by cationic species. To examine the effect of cations on the dissolution of lithium, petalite was reacted with 0.1M solution of each NaCl, KCl, RbCl and CsCl at 200°C. The order of the dissolution rate constant of lithium was as follows: $CsCl > NaCl > RbCl > KCl$ (Table 3).

On the other hand, TAKAMATSU *et al.* (1980a) reported that the dissolution rate of lithium from petalite in NaCl solution was larger than in $NaClO_4$ solution at the same ionic strength and same pH. This indicates that the dissolution rate of lithium is also influenced by the anionic species in solution, when lithium is exchanged by a cation. YAMASHITA (1972) suggested from the investigation of the Kujyu geothermal system that the amounts of lithium dissolved from wall rocks or the Li/Na ratio vary with the anionic species in solution which attacks the rocks.

The interaction mechanism between petalite and salt solutions may not necessarily be the same as that between salt solution and common rocks. Nevertheless, it is reasonable to expect that salts in solution promote the dissolution of lithium from lithium bearing minerals. In natural hydrothermal systems, seawater whose main components are Na and Cl, may play an important role in the dissolution of lithium from rocks. This point of view is consistent with the

fact that the NaCl type waters originated from seawater in Japan contain more lithium than does seawater.

Lithium enrichment in natural NaCl type waters

The studies of chemical reactions between seawater and rocks and the analyses of submarine geothermal waters have proved that magnesium in seawater is removed during seawater-rock interaction under varying conditions (SEYFRIED and MOTT, 1977; MOTT and HOLLAND, 1978; CORLISS *et al.*, 1979; SEYFRIED and BISCHOFF, 1979 and 1981). MIZUKAMI and GREEN (1981) confirmed magnesium depletion in dacite-seawater interaction and suggested that the results are different from those of basalt-seawater interaction in that potassium increases and calcium decreases. The trends of reactions in petalite and seawater interaction agreed with their results (Table 2). ARNORSSON (1974) concluded that rock type (basalt or acid volcanics) is one of major variables governing their chemical compositions of Icelandic geothermal waters.

In order to discuss the deviation from seawater of the chemistry of NaCl type waters, we define the deviation coefficient, C_m , as follows (TAKAMATSU *et al.*, 1980b).

$$C_m = \frac{(m/Cl)_{sp}}{(m/Cl)_{sw}}$$

where m is the concentration of component m ($m = Na, K$ etc.), sp is spring water and sw is seawater. Table 4 shows the values of C_m , δD and $\delta^{18}O$ of the NaCl type waters in the Izu Islands' area. The isotopic compositions indicate that the waters are originated from seawater. The values of C_K for Hachijo and Miyake are smaller than 1, while those for Shikine and Kozu are larger than 1. The values of C_{Ca} for

Table 3. The dissolution rate constants of lithium on the dissolution experiments performed in 0.1M NaCl, KCl, RbCl and CsCl solutions at 200°C

k_{NaCl}	k_{KCl}	k_{RbCl}	k_{CsCl}	
2.26×10^{-4}	4.28×10^{-5}	6.12×10^{-5}	3.83×10^{-4}	(hr ⁻¹)

Table 4. The values of C_m , δD and $\delta^{18}O$ of the NaCl type waters in the Izu islands' area

Locality	C_{Na}	C_K	C_{Ca}	C_{Mg}	C_{SO_4}	C_{Li}	δD	$\delta^{18}O$
Hachijo 1	0.912	0.208	3.25	0.325	0.317	21.7	0.6	1.0
Hachijo 2	0.993	0.174	2.45	0.425	0.395	15.8	---	---
Hachijo 3	0.859	0.899	3.36	0.607	1.07	13.0	---	---
Miyake	1.00	0.117	2.18	0.839	0.623	5.26	-9.6	-0.6
Shikine	0.825	1.49	1.66	0.785	0.739	7.50	-9.3	0.1
Kohzu	0.953	1.14	1.06	0.990	0.957	2.89	-2.6	0.7

---: Not determined.

Isotopic analyses of oxygen and hydrogen were done in the Institute for Thermal Spring Research, Okayama University.

the former two are larger than those for the latter two. These facts may reflect the differences of the rocks with which seawater reacted; the former two springs issue from olivine-basalt, whereas the latter two are in association with rhyolite (KUNO, 1954).

On the other hand, the lithium enrichment in the solutions derived by seawater-rock interaction is almost independent of the rock type, presumably because of the restricted range of lithium content of common rocks. The relationship between C_{Li} and C_{Mg} of these waters is shown in Fig. 4. There seems to be a clear correlation between C_{Li} and C_{Mg} ($r = 0.99$) and the correlation curve passes through the point for seawater ($C_{Li} = C_{Mg} = 1$). This indicates that C_{Li} increases with the compositional change of seawater, which in turn is reflected in C_{Mg} . From the chemistry of fluids issuing from hot springs on the Galapagos Rift, COORLISS *et al.* (1979) concluded that the ridge-crest hydrothermal system is a major sink for Mg and source for Li, Mn, SiO_2 and Ba. We can conclude from these facts that the seawater-rock interaction leads to the lithium increase and magnesium decrease in seawater.

In the seawater-rock interaction, the higher temperature and larger water/rock ratio would result in the higher enrichment of heavy metals, because more H^+ ions would be supplied to seawater with deposition of Mg^{2+} (HAJASH and ARCHER, 1980 and SEYFRIED and BISCHOFF, 1981). Part of lithium might be derived by the ion exchange with H^+ ions, especially at higher temperature. However, the Li-leaching does not necessarily correspond to the Mg-depletion.

In our experiment, lithium is exchanged by Ca^{2+} and K^+ after magnesium was almost removed from the diluted seawater of 0.01 M (Table 2). This indicates that lithium is exchanged successively by the cations in salt solution and that the dissolution of Li does not necessarily require the presence of Mg in the solution. Hence, lithium can be enriched in solution by ion exchanges with cations even in low temperature waters, if these have high salinity.

In natural hydrothermal systems, the reaction time of saline waters with rocks may be another important factor for the lithium enrichment. The values of C_{Li} for the spring waters from the south-eastern part of the Izu peninsula are shown in Table 5. The chemical and isotopic evidences suggest that these waters are derived from mixtures of local surface water and seawater (MIZUTANI *et al.*, 1975). The values of

Fig. 4. Relationship between C_{Li} and C_{Mg} of the waters of the Izu Islands' area ($r = 0.99$).

Table 5. Li, Cl concentrations and C_{Li} of the spring waters from the south-eastern part of the Izu peninsula

Locality	Li(mg/l)	Cl(mg/l)	C_{Li}	Tw(°C)	Type
Atagawa	1.27	950	176	100	Reservoir
Katase	1.27	1,030	162	100	
Shirada	1.37	1,230	146	100	
Mine	0.503	1,060	85.3	100	Vein
Yazu	0.306	471	35.5	100	

Table 6. Some chemical composition of coastal, fossil and Arima type waters

Locality	pH	Tw (°C)	Na	Li	Mg (mg/l)	Cl	C_{Li}	Type
Shimogamo	8.2	100	4,048	0.605	7.40	10,370	7.66	coastal
Izusan	8.0	67.3	2,090	0.22	98	8,586	3.37	
Yashio	6.8	19.8	7,340	19.2	86.0	10,200	247	fossil seawater
Shionosawa	6.4	14.5	3,480	15.5	155	6,042	337	
Aokura	6.7	20.1	4,870	18.4	124	8,237	293	
Isobe(*)	7.7	24.5	9,720	8.05	40.7	11,800	89.6	
Arima	6.4	98.2	16,800	43.4	9.7	34,700	164	Arima
Ishibotoke(**)	6.7	19.1	5,580	13.3	442	9,260	189	
Takarazuka	6.4	15.3	4,970	14.8	58.1	8,900	218	
Kashio	7.9	16.6	11,540	62.2	101	18,800	435	

* Collected by Y. SAKAI.

** Collected by H. MASUDA.

C_{Li} for the reservoir type waters are larger than those for the vein type waters. This shows that the long term reaction of rocks with seawater or diluted seawater will lead to considerably high lithium concentration of the solutions.

The values of C_{Li} of fossil seawater and Arima type thermal waters are greater than those of coastal thermal waters (Table 6). Fossil seawaters and Arima type thermal waters might be produced by long term seawater-rock interaction at low temperature. Therefore, the reaction time of water with rocks must be one of the significant factors in the lithium enrichment in saline waters. It is difficult, however, to determine unequivocally the factors concerning lithium enrichment in natural saline waters. Further studies will be required to clarify the most significant factors in the lithium enrichment in each of the saline waters.

CONCLUSIONS

From the results of this investigation, the following conclusions are warranted.

- 1) Lithium dissolution from lithium minerals was enhanced with increasing salt concentration and with temperature.
- 2) The dissolution rate of lithium was influenced by the kinds of the salts. Salt solutions such as seawater are effective for the leaching of lithium from rocks.
- 3) The non-volcanic saline waters (e.g., coastal thermal waters and fossil seawaters) having higher lithium concentration than seawater might be accounted for by the seawater-rock interaction without the addition of a magmatic emanation.
- 4) A long term and high temperature reaction of seawater with rocks will result in high lithium concentrations of saline waters.

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