Separation of Lithium Isotopes. I. Incomplete Precipitation of Lithium Carbonate from Ammoniac Alkaline Solution

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Isotopic separation factors for the incomplete and slow precipitation of lithium carbonate from ammoniac alkaline solution have been measured. Mean separation factors for the 30-40 wt. % precipitation at 0°C and 18°C are 1.015±0.004 and 1.011± 0.003, respectively.

1. Introduction

Lithium comprises two kinds of stable isotopes. L_i^6 has an abundance of approximately 7.5 %[1] and a cross section for thermal neutron absorption of 945 barns[2]. L_i^7 which has very small cross section for thermal neutron absorption comprises the remaining approximately 92.5 % of normal lithium. This large difference in the thermal neutron cross sections has sustained current interest in the separation of lithium isotopes. Recently, many reports[3,4] on the separation of lithium isotopes by electromagnetic, electrochemical and molecular distillation methods have been published.

Besides this, lithium is one of the elements those natural isotopic abundances have yet been undecided. This uncertainty is mainly due to two different reasons. The one is the mass discrimination effect in the course of mass spectroscopic measurements, and the other is the separation of lithium isotopes which may be caused by various physical changes and chemical reactions.

In recent years the present authors have continued the measurements of the natural abundance of lithium isotopes, and it is interesting for the present authors to study the fractionation of lithium isotopes under simple chemical treatments.

2. Experimental

Materials.——First grade reagent of *lithium chloride* of the Wako Chemicals was used in the subsequent experiments without further purification. *Hydrochloric acid, sulfuric acid, ammonium hydroxide* and *ammonium carbonate* were all extra pure grade reagents of the Wako Chemicals and no further purification was processed.

Apparatus.——Each experiment for the precipitation of lithium carbonate was carried out in the thermostat of an usual type, and the temperature variation of the thermostat was never greater than ±0.2°C. A single focusing mass spectrometer of the

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90° sector type (the radius of curvature of the analyser tube is 135 mm) was employed
for the relative measurements of the isotopic abundance ratio of lithium in solid and
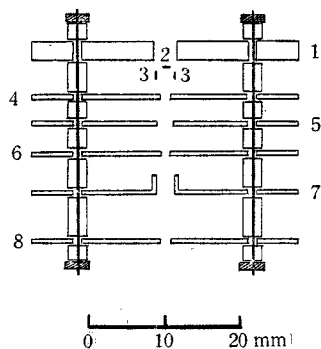liquid phases. The schematic diagram of the triple filament ion source of the mass spectrometer is shown in Fig. 1. The slit widths and the potential arrangement of the ion source are summarized in Table 1.
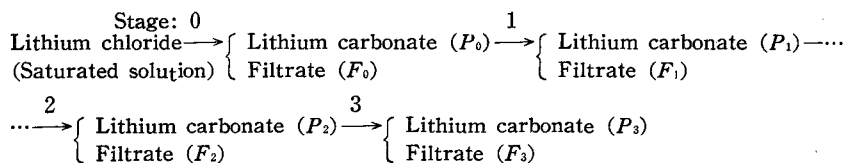

Fig. 1. Triple filament ion source.
1: Guard plate (non-magnetic stainless steel, 2.5 mm in thickness),
2: Center filament (tungsten, $0.75 \times 10 \times 0.025$ mm),
3: Sample filament (tungsten, $0.75 \times 10 \times 0.025$ mm),
4: Ion accelerating plate (Nichrome V, 0.8 mm in thickness),
5: Lens plate (Nichrome V, 0.8 mm in thickness),
6: Defining plate (Nichrome V, 0.8 mm in thickness),
7: Ion deflecting plate (Nichrome V, 0.8 mm in thickness),
8: Buffer plate (Nichrome V, 0.8 mm in thickness).

Table 1. Slit widths and potential arrangement of the triple filament ion source.

Plates and filaments	Slit widths (mm)	Source potentials (V)
1	——	1105
2	——	1105
3	——	1105
4	0.75×10	1100
5	1.50×10	1010
6	0.25×10	earth
7	2.50×10	earth
8	0.50×10	earth

Procedure.——Experimental procedure for the precipitation of lithium carbonate
is schematically shown as follows.

$$
\begin{array}{c}
\text{Stage: 0} \qquad\qquad\qquad 1 \\
\text{Lithium chloride} \longrightarrow \Big\{ \begin{array}{l} \text{Lithium carbonate } (P_0) \\ \text{Filtrate } (F_0) \end{array} \longrightarrow \Big\{ \begin{array}{l} \text{Lithium carbonate } (P_1) \longrightarrow \cdots \\ \text{Filtrate } (F_1) \end{array}
\end{array}
$$

$$
\begin{array}{c}
2 \qquad\qquad\qquad\qquad 3 \\
\cdots \longrightarrow \Big\{ \begin{array}{l} \text{Lithium carbonate } (P_2) \\ \text{Filtrate } (F_2) \end{array} \longrightarrow \Big\{ \begin{array}{l} \text{Lithium carbonate } (P_3) \\ \text{Filtrate } (F_3) \end{array}
\end{array}
$$

Lithium carbonate (P_0) was quantitatively precipitated from the saturated aqueous
solution of lithium chloride by the addition of concentrated ammonium carbonate
solution.   After separation of the filtrate (F_0), greater part of the precipitate (P_0)
was dissolved in dilute hydrochloric acid and the resulting solution was neutralized
with ammonium hydroxide, and then lithium carbonate (P_1) was partially precipitated
by dropping the calculated quantity of ammonium carbonate solution. Other precipitates
$(P_2$ and $P_3)$ and filtrates $(F_2$ and $F_3)$ were obtained by further repetition of similar
treatments.   In the course of these procedures, the initial concentration of lithium
ions and the dropping rate of ammonium carbonate solution were kept nearly constant.

Each precipitate of lithium carbonate was dissolved in dilute sulfuric acid and the resulting solution was evaporated and heated to dryness, and finally 0.5 mole lithium sulfate solution was prepared and used for abundance ratio measurements. After addition of small quantity of concentrated sulfuric acid, each filtrate was treated in the similar manner and finally about 0.5 mole lithium sulfate solution for abundance ratio measurements was prepared. A micro-quantity of the resulting lithium sulfate solution (approximately 1 μg of lithium) was used for each measurement of surface ionization. The isotopic abundance ratio of lithium was determined as the ratio of the graphically integrated ion intensities of $(L_i^7)^+$ to that of $(L_i^6)^+$.

3. Results and Discussion

The isotopic abundance ratio of lithium measured for each separation stage was summarized in Tables 2 and 3. In these tables the mass discrimination effect of lithium isotopes in the course of mass spectroscopic measurements was neglected. It is worthwhile to notice that the precipitation of lithium carbonate (P_1, P_2 and P_3) very slowly proceeded and about 20 hours were needed for the precipitation of 30~40 wt. percent of lithium.

Table 2. Separation of lithium isotopes under each precipitation stage at 0°C.

Stages	Phases and wt.% of L_i ppted.	Approx. wt. of L_i used for each measurement (μg)	Relative abundance ratio (Li^7/Li^6)
0	P_0 (98%)	0.7-1.5	12.37±0.01
0	F_0	0.9-1.2	12.38±0.02
1	P_1 (43%)	1.0-1.4	12.26±0.02
1	F_1	0.8-1.5	12.45±0.03
2	P_2 (27%)	0.9-1.5	12.14±0.02
2	F_2	0.8-1.5	12.31±0.02

Table 3. Separation of lithium isotopes under each precipitation stage at 18°C.

Stages	Phases and wt. % of L_i ppted.	Approx. wt. of L_i used for each measurement (μg)	Relative abundance ratio (L_i^7/L_i^6)
0	P_0 (98%)	0.9-1.2	12.37±0.01
0	F_0	0.7-0.9	12.38±0.02
1	P_1 (41%)	0.6-1.5	12.30±0.02
1	F_1	1.0-1.3	12.41±0.02
2	P_2 (35%)	0.8-1.5	12.20±0.02
2	F_2	0.9-1.4	12.35±0.01
3	P_3 (32%)	1.1-1.5	12.10±0.02
3	F_3	1.0-1.5	12.24±0.02

The separation factors for each separation stage are shown in Table 4. Table 4 indicates that the mean separation factors for a single stage in which 30~40 wt. percent of lithium was precipitated are 1.015 ±0.004 at 0°C and 1.011 ±0.003 at 18°C.

Table 4. Separation factors for incomplete precipitation of lithium carbonate.

Temp. (°C)	Precipitation stage	wt.% of Li ppted.	Separation factor $\alpha = \left(\dfrac{Li^7}{Li^6}\right)_l / \left(\dfrac{Li^7}{Li^6}\right)_s$
0	1	43	1.016 ± 0.004
0	2	27	1.014 ± 0.003
18	1	41	1.009 ± 0.003
18	2	35	1.012 ± 0.002
18	3	32	1.011 ± 0.003

These results suggest the possibilities of the fractionation of lithium isotopes in the course of various chemical treatments——e. g. partial extraction and purification of lithium from terrestrial materials. But, since the separation factors measured by the present experiments also contain some uncertainties and rate of separation was not measured, more detailed experiments must be continued in order to discuss the mechanism of the fractionation of lithium isotopes.

Acknowledgment

References

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