Fractionation of Lithium Isotopes by Intercalation in Layered Inorganic Ion Exchangers

Yoji Makita,* Hirofumi Kanoh, Takahiro Hirotsu, and Kenta Ooi*
Shikoku National Industrial Research Institute, 2217-14, Hayashi, Takamatsu 761-03

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Layered titanium phosphates and heat-treated tin phosphate showed high separation factors (1.015-1.018) for lithium isotopes; the fractionation properties could be explained by considering two factors: the degree of Li^+ dehydration in the solid phase and the affinity of the ion-exchange site toward Li^+.

The lithium element consists of two stable isotopes which are ^6Li and ^7Li in their natural states. The study of lithium isotope effects is important, not only for industrial nuclear science, but also for fundamental material and geological sciences. Lithium isotope fractionation by ion-exchange reaction has been studied extensively since the first work carried out by Taylor and Urey.[1] However, the fractionation mechanism of ion-exchange has not been clearly elucidated yet because the fractionation phenomena are complicated depending on the kinds of ion-exchangers used as well as on the conditions of ion-exchange. In the present paper, we describe the fractionation properties of layered inorganic ion exchangers (metal phosphates and magadiite) for lithium isotopes in order to elucidate the isotope fractionation mechanism, and with a view to developing novel isotope separation materials. The layered exchangers have different ion-sieve properties depending on the basal spacing between a neighboring pair of layers.

α-titanium phosphate ($Ti(HPO_4)_2 \cdot nH_2O$), α-zirconium phosphate ($Zr(HPO_4)_2 \cdot nH_2O$), and α-tin phosphate ($Sn(HPO_4)_2 \cdot nH_2O$), were supplied by Toagosei Co., Ltd. Heat-treated samples were prepared by heating them at 200 or 400 °C in air for 4 h. We denote MP, MP(200) and MP(400) (M : Ti, Zr, Sn) for the original $\alpha\text{-}M(HPO_4)_2 \cdot nH_2O$ and the samples heat-treated at 200 and 400 °C in air, respectively. Hydrogen type magadiite (H-magadiite) was prepared by acid treatment of magadiite ($NaSi_7O_{13}(OH)_3 \cdot 3H_2O$) which was synthesized by the hydrothermal method.[2]

Fractionation of lithium isotopes was studied by a batch method. The layered inorganic ion exchanger (0.19g) was added to a lithium-containing (0.03M LiCl + 0.07M LiOH) solution ($8cm^3$) and shaken for about 2 weeks. After the equilibrium, the ion exchanger was filtered off with a membrane filter and the Li^+ concentration in the supernatant solution was determined by atomic absorption spectrometry. The Li^+ uptake by the exchanger was calculated by subtracting the final concentration of Li^+ from the initial. The lithium isotope ratio in the supernatant solution was measured using a surface ionization mass spectrometer. The standard deviation of $^7Li/^6Li$ measurement was less than 0.02%. The separation factor (S) of the lithium isotope was calculated using the following equation:[3]

$$S = (^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{solution}} / (^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{exchanger}}$$

where the lithium isotope ratio in the solid phase, $(^7\mathrm{Li}/^6\mathrm{Li})_{\mathrm{exchanger}}$, was calculated from the lithium isotope ratios and the lithium concentrations of the solution phase before and after the intercalation reaction.

Lithium uptakes and isotope separation factors for the layered ion exchangers are given in Table 1. TiP and TiP(200) showed high isotope separation factors 1.017 and 1.018, respectively. SnP(400) also gave a relatively high separation factor (1.015) although the unheated sample SnP gave a low S value. The S value larger than 1 indicates that the lighter isotope, ^6Li, was preferentially fractionated into the solid phase, and the heavier isotope, ^7Li, was enriched in the solution phase. These S values are comparable to that of crystalline antimonic acid ($Sb_2O_5 \cdot nH_2O$) with a cubic structure,[3,4] which has, to the best of our knowledge, the highest lithium isotope separation factor (1.025) among the inorganic ion-exchangers studied so far. ZrP and H-magadiite produced a low fractionation effect for lithium isotope in spite of the fact that they have layered structures similar to TiP. The above results indicate that the fractionation properties of layered exchangers are influenced greatly by the chemical species of the central metal atoms as well as the degree of heat treatment.

In the preceding paper,[3] we proposed two factors for the origin of lithium isotope fractionation: (1) the difference in hydration circumstances between a solid and a solution phase and (2) the Li^+ stabilization in the solid phase. In the present paper, the former factor was investigated by measuring the changes of interlayer water contents, and the latter by measuring distribution coefficients for Li^+ and Na^+.

Interlayer water contents were calculated from the weight loss by heating up to 380 °C on the TG curves.[5] The changes of chemical composition after Li^+ intercalation and the increases ($\Delta H_2O/Li$) of water content by intercalation per mole of Li atoms are given in Table 1. The samples with low $\Delta H_2O/Li$ tend to have higher separation factors for lithium isotopes, except for SnP. The low $\Delta H_2O/Li$ value corresponds to the extensive

Table 1. Lithium uptakes and isotope separation factors

Sample	Li^+ uptake / mmol/g	Separation factor	Composition before	Composition after	$\Delta H_2O/Li$
TiP	2.6	1.017	$Ti(HPO_4)_2 \cdot 0.97H_2O$	$Ti(H_{0.67}Li_{0.33}PO_4)_2 \cdot 1.16H_2O$	0.28
TiP(200)	3.7	1.018	$Ti(HPO_4)_2 \cdot 0.99H_2O$	$Ti(H_{0.52}Li_{0.48}PO_4)_2 \cdot 1.06H_2O$	0.07
ZrP	4.1	1.001	$Zr(HPO_4)_2 \cdot 0.97H_2O$	$Zr(H_{0.38}Li_{0.62}PO_4)_2 \cdot 1.83H_2O$	0.70
ZrP(200)	4.3	1.003	$Zr(HPO_4)_2 \cdot 0.92H_2O$	$Zr(H_{0.36}Li_{0.64}PO_4)_2 \cdot 1.81H_2O$	0.69
SnP	3.2	1.003	$Sn(HPO_4)_2 \cdot 1.58\ H_2O$	$Sn(H_{0.46}Li_{0.54}PO_4)_2 \cdot 1.85H_2O$	0.25
SnP(400)	4.0	1.015	$Sn(HPO_4)_2 \cdot 1.02\ H_2O$	$Sn(H_{0.34}Li_{0.66}PO_4)_2 \cdot 1.47H_2O$	0.34
H-Magadiite	1.3	1.003	$HSi_7O_{13}(OH)_3 \cdot 0.52H_2O$	$H_{0.40}Li_{0.60}Si_7O_{13}(OH)_3 \cdot 2.39H_2O$	3.09

$\Delta H_2O/Li$ shows increase of water content by intercalation per mole of Li atoms.

dehydration of Li^+ in the solid phase, since Li^+ has a hydration number of about 4 in an aqueous solution.[6] Thus, the present result suggests that the dehydration of Li^+ is a cause of lithium isotope fractionation by Li^+ intercalation, similar to the case of ion-sieve exchangers.[3]

X-ray diffraction patterns of unheated samples before and after intercalation are given in Figure 1. Basal spacings were calculated from the XRD (002) peaks for the metal phosphates and from the (001) peak for H-magadiite (Table 2). The basal spacings were nearly constant regardless of Li^+ intercalation for TiP and SnP. On the other hand, those of ZrP and H-magadiite increased markedly with Li^+ intercalation, indicating that these materials swelled easily in an aqueous medium. This property is disadvantageous to lithium isotope fractionation since Li^+ can intercalate smoothly in the solid phase without dehydration.

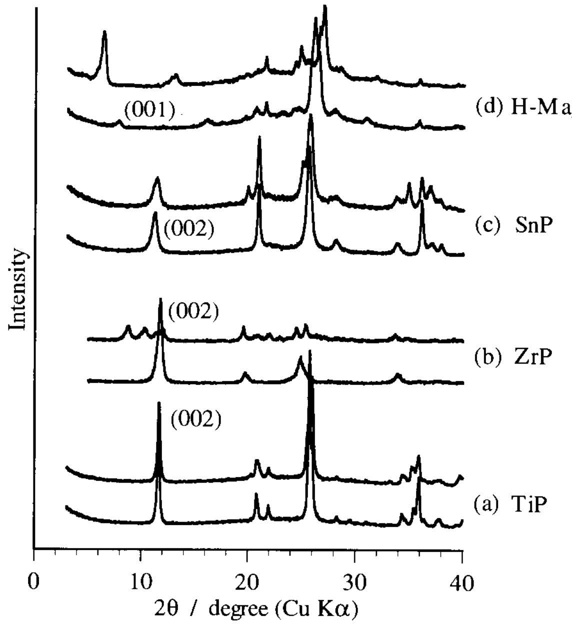

Figure 1. XRD patterns of TiP (a), ZrP (b), SnP (c) and H-magadiite (d). The lower and upper lines show XRD patterns before and after Li^+ intercalation, respectively.

Table 2. Basal spacings and distribution coefficients

Sample	Basal spacing (nm)		Kd (cm^3/g)	
	before	after	Li	Na
TiP	0.764	0.760	1600	530
TiP(200)	0.760	0.756	650	750
ZrP	0.751	1.006, 0.860, 0.741	<5	<5
ZrP(200)	0.749	1.013, 0.856, 0.739	<5	<5
SnP	0.784	0.776	370	27
SnP(400)	0.771	0.808	510	2000
H-Magadiite	1.147	1.380	14	54

$$Kd = \frac{\text{the amount of the ion taken up per 1 g of the adsorbent}}{\text{the amount of the ion remaining per 1 cm}^3\text{ of the solution phase}}$$

Distribution coefficients were measured by a batch method using a NH_3-NH_4Cl buffer solution (pH8.2) containing 1mM LiCl and 1mM NaCl. The Kd values are summarized in Table 2. TiP and TiP(200) gave high Kd values for both Li^+ and Na^+. These results agree well with that in the literature where TiP showed a sodium ion-sieve property (exchangeable for Li^+ and Na^+ but not for the other alkali metal ions with ionic radii larger than Na^+).[7] ZrP, ZrP(200) and H-magadiite gave low Kd values for both Li^+ and Na^+ in spite of the fact that they had large ion exchange capacities. Since they can intercalate cations nonselectively, due to the expansion of basal spacing, most of the sites are probably exchanged by NH_4^+, the major cation in the buffered solution. SnP showed a lithium ion-sieve property (high Kd(Li), low Kd(Na)), while SnP(400) showed a sodium ion-sieve property. These results indicate that the isotope fractionation is highly correlated with the sodium ion-sieve property.

A theoretical study of isotope fractionation showed that the heavier isotope was more stable in the molecule, while the lighter isotope favored the isolated form of atoms.[8] This notion indicates that ^6Li is more enriched in the solid phase if lithium ions are more dehydrated (the isotopic effect of dehydration) and that ^7Li is more fractionated to the solid phase if lithium ions are more strongly bound (the isotopic effect of Li^+ stabilization). The result in Table 1 demonstrates that the isotopic effect of dehydration determines principally the *S* values of the layered inorganic ion exchangers. However, the isotopic effect of dehydration is reduced by the isotopic effect of Li^+ stabilization. The low *S* value on SnP can be explained by its Li^+ stabilization effect, which is inferred from the affinity of the ion-exchange site toward Li^+.

Table 1 and 2 demonstrate a close correlation between the isotope separation factors and the affinity for Na^+. The present results gives a new approach to design layered ion exchangers effective for lithium isotope separation.

References and Notes

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