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Lithium isotopic composition of submarine basalts: implications for the lithium cycle in the oceans

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ABSTRACT

We have measured the Li isotope composition of young, pristine basalts from active ocean ridge crests, of progressively older basalts along a dredging transect, and a limited number of hydrothermally altered basalts. The data significantly extend our limited knowledge of the isotopic abundance ratio of Li in geological material. Fresh mid-ocean ridge basalts have $\delta^6\text{Li}$ values of between -3.4 and -4.7‰ relative to isotope standard L-SVEC. During low-temperature weathering on the seafloor, the isotopic composition of the rock becomes increasingly heavier due to addition of seawater Li ($\delta^6\text{Li} = -32.3\text{‰}$). The oldest (46 m.y.) and most altered rock studied has an isotopic composition of -14‰ . A linear relationship exists between $\delta^6\text{Li}$ and the inverse of Li concentration, suggesting that Li in weathered basalts can be regarded as a two-component mixture of basaltic Li and seawater-derived Li that has been incorporated in alteration minerals, most likely secondary clays such as smectite and phillipsite. The inferred Li isotopic composition of the alteration endmember indicates an apparent isotopic fractionation factor of 1.019 relative to the seawater source. Thus Li uptake by secondary minerals from the low-temperature weathering process and, by analogy, incorporation in similar authigenic minerals in marine sediments provides a mechanism for preferential removal of the lighter Li isotope from ocean water. However, isotopic fractionation due to authigenic clay formation alone cannot account for the isotopic difference between seawater and its principal sources, unless the hydrothermal flux is comparable to the river flux. Alternatively, more important sinks of ^6Li must exist if the steady state isotopic composition of Li in ocean water is to be maintained.

1. Introduction

Lithium actively participates in the chemical exchange between seawater and oceanic crust. Laboratory experiments [1,2] and chemical studies of submarine basalts [see summary in 3] and hydrothermal fluids [4–10] have shown that lithium transfer is strongly dependent on temperature. At high temperatures ($> 200^\circ\text{C}$), seawater extracts Li from basalt, while at low temperatures ($< 150^\circ\text{C}$), Li is removed from seawater into alteration phases. A recent study [11] revealed that the Li isotopic composition of mid-ocean ridge basalt is distinct from that of seawater, and therefore may be used to study both low-temperature weathering and hydrothermal processes of the oceanic crust. We have carried out the first measurements of the lithium isotopic composition of

fresh and weathered basalts from the East Pacific Rise (EPR), of progressively older and altered basalts along a dredging transect on the Mid-Atlantic Ridge (MAR) at 23°N , and of hydrothermally altered basalts. The objective of the study was to evaluate the behavior of lithium isotopes during the interaction of seawater and seafloor basalts. The isotope systematics not only carry implications for the oceanic cycle of lithium but also place constraints on the importance of the interaction of seawater with oceanic crust at low temperature relative to hydrothermal circulation at the ridge crest. Furthermore, unlike other light stable isotopes, the geochemistry of lithium isotopes is not well characterized. Thus, in a broader sense, this work contributes to the overall understanding of the terrestrial variation of the isotopic abundance ratio of Li.

2. Samples and method

The samples analyzed include fresh basalts recovered from the axial valleys of the EPR at 21°N and 13°N, and the MAR at 23°N. In addition, in order to study the progressive change with age, we analyzed a suite of basalts collected along a transect from the median valley of the west flank of the MAR at 23°N. The location of the seafloor transect is shown in fig. 1 in Ludden and Thompson (1979) [12]. These samples represent a time sequence of basalts from the same axial point of extrusion over the past 46 m.y. Thus Li abundance and isotopic differences attributable to mantle source variations are minimized. Dredged basalts from this transect have been subjected to reaction with seawater at ambient temperature (ca. 2°C). The effects of low-temperature weathering on the major and trace element composition of the transect samples have been reported [12,13]. Most notably, the water and K contents of pillow interiors and margins increase and the FeO contents decrease with age. Clay-bound trace elements such as B, Rb and Ba are also enriched with alteration. For comparison with the low-temperature altered basalts, we have also analyzed a small number of hydrothermally altered basalts (metabasalts) from the ridge axis at the same latitude.

Powdered samples of pillow basalts were prepared from the outer 1 cm glassy margins and from sections through the whole of the interiors.

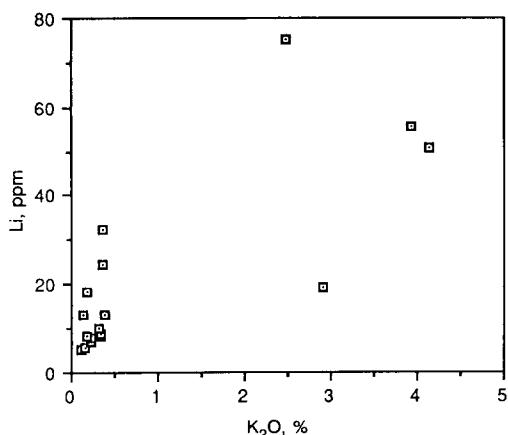


Fig. 1. Li concentration vs. K concentration in fresh and altered basalts from the Mid-Atlantic Ridge at 23°N. The correlation coefficient, r^2 , is 0.603.

In addition, samples were also prepared from chips from the interior representing different degrees of alteration. Total dissolution was carried out by low-temperature HF-HClO₄ digestion [14] followed by final conversion to perchlorate salts. The lithium contents were determined by flame emission using a Perkin Elmer 560 atomic absorption spectrophotometer. This method yielded a Li concentration of 12.3 ppm for BCR-1 and 12.4 ppm for BEN, in good agreement with the recommended values of 12.8 ppm [15] and 12 ppm [16] respectively for these reference rocks.

K was determined for the same solutions used for Li concentration and isotope analyses as a measure of the extent of low-temperature weathering (Tables 1 and 2). There is only a very broad relationship between K and Li contents of weathered basalt ($r^2 = 0.603$), indicating different sinks for these two elements (Fig. 1). Li may be associated primarily with secondary clays [2,3], while K may be present in both clays and secondary K-feldspars [17]. The mineralogy of the studied basalts was determined from thin section observations and, on selected samples, by X-ray diffraction analysis.

The isotopic analysis of Li is rendered difficult by the susceptibility of the low-mass isotopes to instrumental fractionation, and the absence of a third naturally occurring isotope to correct for the effect of mass fractionation on the measured ⁶Li/⁷Li values. Recently a new mass spectrometric technique has been developed in which Li isotopic composition is determined by thermal ionization mass spectrometry of lithium tetraborate to a precision of 1.3‰ [18]. In this study, a modified procedure was adopted using lithium sodium tetraborate as the ion source. The latter method has two advantages: (a) LiNaB₄O₇ has a lower ionization potential and hence produces LiNaBO₂⁺ at a lower current, and (b) the masses of the molecular ion measured are higher, thereby reducing isotopic fractionation during analysis.

Rock solutions containing 0.5 μmol Li were processed for isotope ratio measurements. Li was quantitatively separated by cation exchange chromatography (AG 50X8) in the form of chloride. It was subsequently converted to hydroxide using an AG 1X8 anion exchange column (2 ml resin volume) which was preconditioned with 1 N NaOH. After the eluted sample is irradiated by ultraviolet

TABLE 1

Lithium isotopic composition of fresh basalts

Location	Sample	Position	Li (ppm)	K ₂ O (%)	$\delta^6\text{Li}$ (‰) *
MAR	1679-1	23°22.3' N, 44°58.1' W	5.60	0.16	-6.3 ± 1.6
	1680-4	23°22.2' N, 44°57.1' W	5.36	0.11	-4.7 ± 0.8
	1685-1	23°13.0' N, 44°57.0' W	6.04	0.13	-3.8 ± 1.1
	AII 114 1-1	22°58.3' N, 44°55.7' W	5.47	0.07	-3.4 ± 1.1
EPR		21°N	6.10		-4.7 ± 0.7
		13°N	6.90	0.22	-6.8 ± 1.0

* Errors in $\delta^6\text{Li}$ values are $2\sigma_m$ in isotopic ratios of individual samples.

let light to oxidize all organic carbon, Li is converted to tetraborate by reacting with ¹¹B-enriched boric acid. Attempts to synthesize LiNaB₄O₇ by stoichiometric combination of Li and Na salts with boric acid were unsuccessful. However, LiNaBO₂⁺ ions are produced in the thermal ionization process, although only pure Li solution is passed through the anion exchange column. This is apparently due to the presence of a trace amount of Na on the ion exchange resin

after preconditioning with NaOH, even after washing with 11 bed volumes of distilled water. This residual Na combined with Li in the sample to form a mixture of tetraborates: Li₂B₄O₇, LiNaB₄O₇ and Na₂B₄O₇.

Isotopic analysis was performed at the MIT on a solid source mass spectrometer with a 6 in radius and a 90° magnet sector. The sample was loaded in sub-boiling distilled water on to a pre-baked tantalum filament following the procedure

TABLE 2

Lithium isotopic composition of 23°N transect basalts and other altered basalts from MAR

Sample	Position	Age (m.y.) *	K ₂ O (%)	Li (ppm)	$\delta^6\text{Li} \pm 2\sigma_m$ (‰)	Type **
AII 78 1-1	23°13' N, 44°43' W	< 1	0.04	4.61	+2.1 ± 0.8	metabasalt
AII 78 1-2		< 1	0.03	1.79		metabasalt
AII 78 3-105	23°13' N, 44°55' W	< 1	0.23	7.84	-7.6 ± 1.0	basalt, w. int.
AII 78 3-105				6.97		basalt, int.
AII 78 6-3	23°04' N, 45°10' W	2.5	0.34	8.15		basalt, w. int.
AII 78 6-3			0.31	10.26	-9.8 ± 0.8	basalt, mar.
AII 78 6-3			0.19	8.17	-7.4 ± 0.8	basalt, int.
AII 78 8-16	22°58' N, 45°51' W	5	2.91	19.28		basalt, mar.
AII 78 8-16			0.14	13.18	-9.4 ± 1.0	basalt, w. int.
AII 78 10-3	23°00' N, 46°13' W	7	0.18	18.49	-11.8 ± 1.0	basalt, w. int.
AII 78 10-3			0.35	8.88	-7.8 ± 1.1	basalt, int.
AII 78 12-2	23°11' N, 48°46' W	30.5	0.36	32.46	-12.1 ± 0.8	basalt, w. int.
AII 78 12-2				26.67		basalt, int.
AII 78 14-4	23°16' N, 49°13' W	35	0.36	24.50	-13.5 ± 0.9	basalt, w. int.
AII 78 14-4			0.40	12.13	-11.0 ± 1.0	basalt, int.
AII 78 15-4	23°24' N, 50°45' W	46	2.47	75.3		basalt, mar.
AII 78 15-4			4.13	50.9		basalt, w. int.
AII 78 15-4			3.93	55.6	-13.4 ± 1.1	basalt, int.
1682-4	23°25' N, 45°01' W	1		9.23	-9.1 ± 1.0	basalt, int.
AD 2-1	20°40' S, 13°16' W			9.4	-8.4 ± 1.0	basalt, mar.
1689-1	23°10' N, 45°01' W			18.6	-5.8 ± 1.0	metabasalt

* Ages have been determined by sample positions relative to magnetic anomalies.

** w. int. = whole interior; mar. = margin; int. = interior.

described in [18]. Upon thermal ionization, the Na_2BO_2^+ signal was detected first at a filament current of about 1 A, followed by the appearance of LiNaBO_2^+ and finally Li_2BO_2^+ at successively higher currents. The measurement of the relative intensity of the LiNaBO_2^+ ions at mass positions 72 and 73 (I_{72}/I_{73}) was taken when the ion current of the mass 73 peak was most prominent relative to the emissions of Na_2BO_2^+ and Li_2BO_2^+ . The ${}^6\text{Li}/{}^7\text{Li}$ ratios were obtained from the measured I_{72}/I_{73} and the B isotopic ratio in the added spike:

$${}^6\text{Li}/{}^7\text{Li} = I_{72}/I_{73} - ({}^{10}\text{B}/{}^{11}\text{B})_{\text{spike}}$$

Replicate analyses of an NBS isotopic standard (L-SVEC) with this technique yielded a value of 0.083013 ± 0.000090 (1 s.d.), giving a relative precision of about 1.1‰. The ${}^6\text{Li}/{}^7\text{Li}$ ratio of the standard has been determined by the lithium tetraborate method to be 0.083062 ± 0.000054 (1 s.d.). Note that this is a revised value resulting from long-term measurements of the same standard reported in Chan, 1987 [18]. The values obtained by the two methods are not significantly different and both agree within analytical uncertainty with the reported absolute ratio of 0.08302 ± 0.0002 for the same standard [19]. In this report the isotopic ratios of the samples are expressed as $\delta^6\text{Li}$:

$$\delta^6\text{Li} = \left[\frac{({}^6\text{Li}/{}^7\text{Li})_{\text{sample}}}{({}^6\text{Li}/{}^7\text{Li})_{\text{std}}} - 1 \right] \times 1000$$

where $({}^6\text{Li}/{}^7\text{Li})_{\text{std}} = 0.083062$. The isotopic data for the studied basalts are presented in Tables 1 and 2.

3. Results

3.1. Fresh basalts

The pillow basalt fragments from the axial valleys of the EPR and MAR are fresh glass (1680–4 of MAR; 21°N, EPR), sparsely crystalline plagioclase-olivine basalt (1679–1 and 1685–1) or aphyric basalt (AII 114 1–1). These basalts contain 5–6 ppm of Li (Table 1), which is typical of mid-ocean ridge tholeiitic basalts [14]. The freshest rocks ($\text{K}_2\text{O} < 0.13$ ppm) have $\delta^6\text{Li}$ values of between -3.4 and -4.7 ‰ (Table 1).

Sample 1679–1 has a slightly higher K_2O content, and minor Fe hydroxide in the groundmass. Its relatively large analytical error also makes it a less precise representation of pristine basaltic composition. The sample from 13°N EPR has slightly higher Li and K concentrations. Its $\delta^6\text{Li}$ value also reflects slight alteration of this fine crystalline basalt. A fresh glass from 21°N, EPR has a $\delta^6\text{Li}$ value of -4.7 ‰, falling in the range of the MAR basalts. From these limited data, no systematic difference in the Li isotopic composition is evident between the two oceanic ridge systems.

3.2. Weathered basalts

The Atlantic transect samples show increasing alteration with age. They have been oxidized to Fe oxyhydroxides and altered to clay minerals and saussuritized feldspars in which K-spar is present. Previous studies have shown that submarine basalts that have undergone low-temperature weathering have elevated lithium concentrations [3 and references therein]. Along the MAR 23°N transect, Li contents of the whole interiors of pillows generally increase with age, and the margins are more enriched than the interiors (Table 2). The highest whole-interior concentration (56 ppm) was found in the 46 m.y. old rock. This is similar to the Li concentration (55 ppm Li) in a basalt from DSDP Hole 417A that has been completely altered to smectite and palagonite by direct exposure to seawater over a long period [20]. This may be representative of the endmember Li concentration of alteration products in weathered basalts. The margin of the oldest rock shows the highest enrichment (75.3 ppm). This sample is highly oxidized, with abundant Fe oxyhydroxides and with trace smectite and phillipsite. There is a possibility that some Li may be carried on the Fe oxyhydroxides.

Li enrichment in weathered basalt is accompanied by a shift of $\delta^6\text{Li}$ to more negative values, confirming a preliminary study by Chan and Edmond [11]. The relationship between isotopic composition and concentration is shown in a $\delta^6\text{Li}$ versus $1/\text{Li}$ plot (Fig. 2). The isotopic composition of seawater has been determined to be -32.3 ‰ [11], which is 27–29‰ heavier than the value for unaltered basalt. Consequently, subma-

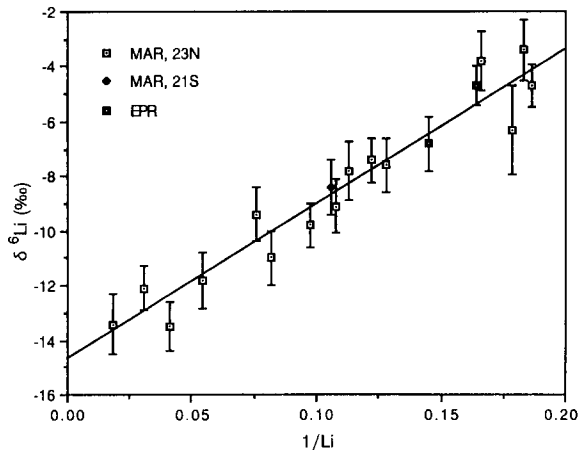


Fig. 2. $\delta^6\text{Li}$ vs. $1/\text{Li}$ concentration of fresh and weathered basalts from various sites on the Mid-Atlantic Ridge and East Pacific Rise. All samples follow a single mixing trend and a linear regression line for MAR 23°N is described by the equation $y = 56.37x - 14.69$ ($r^2 = 0.934$). Errors shown are $2\sigma_m$ uncertainties in the isotopic ratios.

rine basalt becomes enriched in ^7Li as oceanic Li is progressively added to the rock during weathering. The weathered rim of a basalt from the MAR at 21°S (AD2 of Engel et al. [21]) is also included in Fig. 2 for comparison. A single linear correlation exists for samples within the same rocks, and among rocks from different sites, and for rocks representing the two ridge systems.

3.3. Metabasalts

A detailed isotope study of the high-temperature alteration of basalt is beyond the scope of this paper. However, a small number of metabasalts are included for comparison with the isotopic characteristics of the basalt weathered at low temperature. Two metabasalts (AII 78 1-1 and 1-2) from the median valley of the MAR at 23°N (Table 2) are sparsely plagioclase-phryic basalts. The groundmass of the first metabasalt has been altered to chlorite with minor amphibole, and that of the second metabasalt to amphibole with minor chlorite. Both are depleted in Li relative to fresh basalt, apparently as a result of extraction by circulating fluids. AII 78 1-1 has a very light $\delta^6\text{Li}$ value of +2.1‰. Another metabasalt (1689-1, an amphibolite), also from the MAR axis, whose groundmass has been totally altered to amphibole, epidote and chlorite,

is rich in Li (18.6 ppm) and exhibits an isotopic composition of -5.8‰.

4. Discussion

4.1. The behavior of Li isotopes during low-temperature weathering

The linear relationship between $\delta^6\text{Li}$ and $1/\text{Li}$ suggests that Li in weathered basalt can be regarded as a two-component system, most likely a mixture of basaltic Li and seawater Li that is incorporated in alteration minerals. Extrapolation to the oldest and most Li-rich rock of Fig. 2 gives an empirical $\delta^6\text{Li}$ value of about -14‰ for the endmember alteration products. This indicates an apparent isotopic fractionation factor ($\alpha_{\text{mineral-water}} = (^6\text{Li}/^7\text{Li})_{\text{mineral}} / (^6\text{Li}/^7\text{Li})_{\text{water}}$) of about 1.019 for the clay mineral-seawater system at ambient bottom-water temperature.

The low-temperature alteration process mainly involves the transformation of igneous minerals to smectites, mixed-layer clays and hydroxides [22]. The principal alteration products observed in the transect samples are smectite, phillipsite and Fe oxyhydroxides. Li is known to be concentrated in clays. An experimental study shows that Li can be partitioned into zeolites, smectites and chlorites during reaction of seawater with basalt glass especially at low temperatures [2]. Li is believed to substitute for Mg and Fe in the octahedral sites of chlorites and smectites or for Na in zeolites [2]. It can also occupy exchangeable positions in interlayers of these layer aluminosilicates [2,23] although its adsorption energy is less than that of the larger alkalis. The mineralogy of the margin of the oldest, most Li-rich sample (AII78 15-4) is dominated by Fe oxyhydroxides together with smectite and phillipsite. Whether Fe oxyhydroxides carry a significant amount of Li cannot be determined from the present data.

The consistency of the linear correlation is surprising in view of the fact that Li may be incorporated in more than one alteration phase and the fractionation factor of individual minerals may differ. The good fit to the straight line (correlation coefficient $r^2 = 0.934$) implies that the mineralogical compositions of the mixing endmembers in the basalts are largely homogeneous and that the alteration minerals are in isotopic

equilibrium with seawater. The mechanisms of the isotopic fractionation have not been determined. The most likely cause could be the difference between the binding energies of the two isotopic ions with water and with atoms in the clay structure. It is interesting to note that the observed isotope fractionation is in the same direction and of comparable (but lower) magnitude as that observed during Li exchange with zeolite [23]. Regardless of the mechanism, the inferred isotopic fractionation factor for Li suggests that the alteration products preferentially take up the lighter Li isotope from ocean water during low-temperature processes.

Oxygen isotopes have been established as a sensitive measure of the extent of low-temperature weathering and a broad correlation has been observed between $\delta^{18}\text{O}$ and the Li content of weathered basalts [24]. The oxygen isotope systematics have been explained by considering the weathered basalt as a binary mixture of fresh basalt ($\delta^{18}\text{O} = 5.7\text{‰}$) and an iron-rich montmorillonite ($\delta^{18}\text{O} = 27\text{‰}$) formed from reaction with seawater [24]. A similar model is used to explain the alkali element ratios of altered oceanic basalts [25]. The interpretation of the Li system is consistent with these mixing models for oxygen isotopes and heavier alkali elements. Thus the Li isotopic composition, especially used in conjunction with Li content, can be used to define the nature and extent of alteration of seafloor basalt.

4.2. Metabasalt

The metabasalts studied show both depletion and enrichment in Li content relative to fresh basalt. Li depletion in metabasalts is expected as a result of extraction by hydrothermal solutions. The positive $\delta^6\text{Li}$ value of the Li-depleted metabasalt ($+2.1\text{‰}$) mirrors the more negative isotopic values of hydrothermal solutions relative to fresh basalt [11,26,27,28] (see further discussion later). This demonstrates that Li is not quantitatively extracted by the circulating fluid but may be partially retained in the greenschist facies minerals during hydrothermal activity, the lighter isotope being preferentially taken up in the solid phase. The metabasalt with the highest content of Li (18.6 ppm) exhibits an isotopic composition of -5.8‰ . If the excess Li is solely derived from

seawater during retrograde low-temperature alteration, the altered basalt should have a $\delta^6\text{Li}$ of -11.5‰ (Fig. 1). Thus this metabasalt must contain a light Li component which could only be derived from fresh basalt. It may be that Li initially extracted into hydrothermal solution is later incorporated in the metamorphic minerals. This is consistent with the observation of Humphris and Thompson that Li is highly mobilized during hydrothermal alteration [29].

4.3. Implication for the Li cycle in the ocean

The principal inputs of Li to the ocean are continental weathering products carried by rivers, and hydrothermal fluids associated with high-temperature reactions of seawater and newly formed basalt at ocean spreading centers. The only known removal mechanism is uptake by basalt during low-temperature alteration of the oceanic crust. Several authors have estimated the Li fluxes into and out of the ocean and have shown that the uptake by weathered basalt is insufficient to balance the riverine and hydrothermal inputs [1,3,13]. It is generally believed that the deficit is balanced by marine sediments, possibly with authigenic clays as the dominant sinks [3].

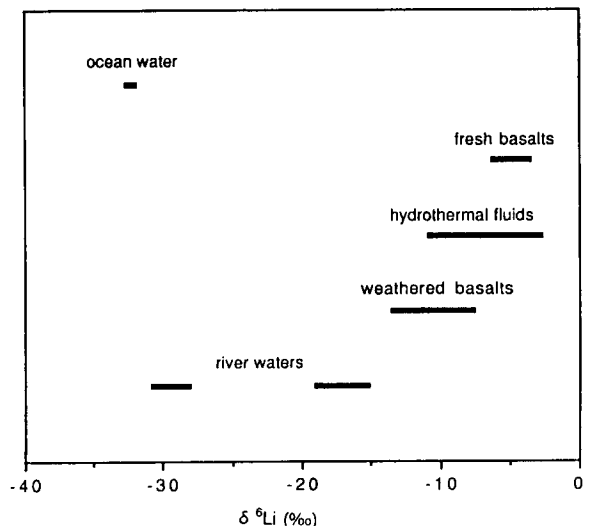


Fig. 3. $\delta^6\text{Li}$ values of some major Li reservoirs. Data are from this work and Chan and Edmond [11,26,27,28 and unpublished data].

TABLE 3

Li isotopic composition of rivers

River	Li ($\mu\text{mol/kg}$)	$\delta^6\text{Li}$ (‰)
Amazon	0.11	-29.4 ± 1.5
Mississippi (low flow)	1.66	-15.3 ± 1.4
Mississippi (high flow)	0.45	-17.7 ± 0.9
Jordan at Yarmouk	4.74	-16.2 ± 1.2
Jordan at Allenby	11.7	-18.5 ± 1.2

We now examine the oceanic cycle of Li from the standpoint of isotope balance. Figure 3 summarizes the present state of knowledge of the isotope geochemistry of Li [11,26,27,28]. The survey of rivers to assess global delivery of Li isotopes to the oceans is in progress. The available data are listed in Table 3. It is significant that rivers draining mixed volcanic and sedimentary terrains such as the Mississippi and Jordan Rivers have lithium isotopic compositions of between -15‰ and -19‰ . The Amazon is low in Li and has a relatively negative value (-29.4‰) for the lithium isotopes. This is probably due to the fact that the ancient shield terrains in the river basin have been almost completely weathered and most of the dissolved Li is derived from marine evaporites, which are abundant in the Andes [30]. Li behaves conservatively in estuaries [31,32] and the isotopic composition of the river flux is not altered by processes in the freshwater–seawater mixing zone. The Li isotopic ratios of high-temperature hydrothermal fluids from different tectonic settings have been measured [11,26,27,28]. The values from mid-ocean ridge crests (EPR and MAR) range from -6‰ to -11‰ . It is clear that submarine hydrothermal fluids bear the isotopic imprint of fresh basalt.

TABLE 4

Estimates of Li fluxes and isotopic composition

Parameter	Best estimate (range)	Reference
River flux ($\times 10^{10}$ mol/yr)	1.4 (1.1 to 1.7)	[3,6,34]
Hydrothermal flux ($\times 10^{10}$ mol/yr)	14 (9.5 to 19)	[4,6]
$(\delta^6\text{Li})_{\text{river}}$ (‰)	-19 (-14 to -25)	Table 3
$(\delta^6\text{Li})_{\text{hydrothermal}}$ (‰)	-9 (-6 to -11)	[11,26,27,28]
f_{river}	0.091 (0.053 to 0.168)	
$(\delta^6\text{Li})_{\text{input}}$ (‰)	-10 (-6.4 to -13.4)	eqn. (2)
$(\delta^6\text{Li})_{\text{seawater}}$ (‰)	-32.3 (-31.8 to -32.8)	[11]
Computed α	1.023 (1.019 to 1.027)	eqn. (1)

The deviation from basaltic composition may be attributed to partial retention of Li in greenschist facies minerals during high-temperature reactions [1]. Fluids from sediment-covered spreading centers (Guaymas Basin and Escanaba Trough) have a wider range of isotopic ratios (-2.6 to -10.2‰), which are attributable to the interaction of hydrothermal fluids with marine sediments. It appears that seawater is isotopically heavier than its principal sources. To maintain the steady state isotopic composition of seawater the lighter isotope must be preferentially removed from the ocean. Following Schwartz et al. [33], the following equation may be written for Li isotope balance under steady state conditions:

$$\begin{aligned} T^6/T^7 &= 1/\alpha = (A^6/A^7)/(F^6/F^7) \\ &= (A^6/A^7)/(R^6/R^7) \end{aligned} \quad (1)$$

where T is the mean residence time of the isotopes in the ocean, α is the isotopic fractionation factor, A is the content of the isotopes in the ocean, F is the input flux and R is the removal rate, and the superscripts denote the mass of the isotopes. F^6/F^7 may be expressed as the $\delta^6\text{Li}$ value of the integrated input to the ocean:

$$\begin{aligned} (\delta^6\text{Li})_{\text{input}} &= f_{\text{river}}(\delta^6\text{Li})_{\text{river}} \\ &\quad + f_{\text{hydrothermal}}(\delta^6\text{Li})_{\text{hydrothermal}} \\ &= f_{\text{river}}(\delta^6\text{Li})_{\text{river}} \\ &\quad + (1 - f_{\text{river}})(\delta^6\text{Li})_{\text{hydrothermal}} \end{aligned} \quad (2)$$

where f_{river} and $f_{\text{hydrothermal}}$ are fractions of the total flux due to river and hydrothermal inputs, respectively.

In Table 4 we present the best estimates and ranges of various parameters for the considera-

tion of isotope balance. The river flux has been estimated to be $(1.4 \pm 0.3) \times 10^{10}$ mol/yr [3,6,34]. The global hydrothermal fluxes of Li have been computed to be $9.5\text{--}19 \times 10^{10}$ mol/yr on the basis of the $^3\text{He}/\text{heat}$ ratio of ridge crest hot springs at Galapagos and the EPR at 21°N [4,6], as the ^3He -heat relationships at these centers combined with the oceanic ^3He inventory give rise to the estimated global heat flux. This model yields a ridge water flux of 1.3×10^{14} kg/yr [4], which is in good agreement with that obtained from the Sr isotope budget [36]. The mean Li isotopic composition of rivers is estimated to be $-19 \pm 6\text{‰}$ from available river data (Table 4) and that of the hydrothermal input is taken to be $-9 \pm 2\text{‰}$ based on the measurements from the hot springs of sediment-free spreading centers [28]. By applying these constraints to eqns. (1) and (2), we obtain a best estimate of 1.023 for the magnitude of α required to account for the observed isotopic difference between seawater and its inputs, with lower and upper limits at 1.019 and 1.027.

This calculation shows that the low-temperature weathering process alone is insufficient to account for isotopic difference between seawater and its inputs unless the most extreme conditions shown in Table 4 are operating to yield a $\delta^6\text{Li}$ of -14‰ for the total Li input. Two other possibilities may be envisaged: First, additional mechanism(s) with larger isotopic effects exist to maintain the isotopic balance. As Li in weathered basalts is most likely to be concentrated in secondary clays, by analogy authigenic clays formed in marine sedimentary processes may also be sinks of the lighter isotope. However, if equilibrium with authigenic clays cannot be the sole control of the Li isotopic composition of seawater, there must be other sedimentary sinks that more efficiently concentrate the lighter Li isotope. The second alternative is that the hydrothermal flux is not as large as presently calculated. It has been observed that the ^3He heat ratios of hydrothermal vents vary by an order of magnitude [37], suggesting that the ratio observed at Galapagos and the EPR may not be representative of all hydrothermal systems. Using the best estimate isotopic values for rivers and ridge crest hot springs (Table 4) the observed isotopic fractionation between secondary clay and seawater

would require the hydrothermal flux to be comparable to the river flux. This is more compatible with the geophysical model, which predicts lower hydrothermal fluxes [35]. A comprehensive study is in progress to characterize the sources and sinks of Li isotopes in the marine regime so that the magnitude of fluxes may be better constrained.

5. Summary and conclusion

The present study has led to the characterization of the Li isotopic compositions of variously altered submarine basalts which strongly reflect the extent and pathway of Li exchange between seawater and oceanic crust. The following observations may be made from the isotopic systematics:

(1) The Li isotopic composition of basalts altered at low temperature is determined by the simple mixing of basaltic Li and Li incorporated in alteration minerals from seawater. Li isotope abundance ratios are therefore consistent with other indicators of the extent of low-temperature alteration.

(2) The isotopic composition of Li in the estimated alteration endmember is -14‰ , indicating an apparent isotopic fractionation factor of 1.019 relative to seawater during the low-temperature uptake process.

(3) The isotopic characteristics of low-temperature weathered basalts are distinct from those of metabasalt. Thus Li isotopic ratios can be used to discriminate hydrothermal alteration from low-temperature processes in the rock record.

(4) Seawater is isotopically heavier than the integrated input from its principal sources. Incorporation of light Li in secondary minerals resulting from the low-temperature weathering process and, by analogy, in similar authigenic minerals in marine sediments, could provide a mechanism for preferential removal of the light isotope from ocean water as required by a steady state ocean. However, isotopic fractionation due to authigenic clay formation alone cannot account for the isotopic difference between seawater and its inputs, unless the hydrothermal flux is comparable to the river flux in magnitude, and not greatly larger as presently calculated.

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