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Temperature-dependent isotopic fractionation of lithium between clinopyroxene and high-pressure hydrous fluids

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Abstract The fractionation of lithium isotopes between synthetic spodumene as representative of Li-bearing clinopyroxene and Cl- and OH-bearing aqueous fluids was experimentally determined between 500 and 900°C at 2.0 GPa. In all the experiments, ^7Li was preferentially partitioned into the fluid. The fractionation is temperature dependent and approximated by the equation $\Delta^7\text{Li}_{(\text{clinopyroxene}-\text{fluid})} = -4.61 \times (1,000/T \text{ [K]}) + 2.48$; $R^2 = 0.86$. Significant Li isotopic fractionation of about 1.0‰ exists even at high temperatures of 900°C. Using neutral and weakly basic fluids revealed that the amount of fractionation is not different. The Li isotopic fractionation between altered basalt and hot spring water (350°C) in natural samples is in good agreement with our experimentally determined fractionation curve. The data confirm earlier speculations drawn from the Li isotopic record of dehydrated metamorphic rocks that fluids expelled from a dehydrating slab carry heavier Li into the mantle wedge, and that a light Li component is introduced into the deeper mantle. Li and Li isotopes are redistributed among wedge minerals as fluids travel across the wedge into hotter regions of arc magma production. This modifies the Li isotopic characteristics of slab-derived fluids erasing their source memory, and explains the absence of cross-arc variations of Li isotopes in arc basalts.

Introduction

Lithium is a fluid-mobile element that tends to preferentially partition into the fluid phase during fluid–rock interaction processes (e.g., Brenan et al. 1998). It has two stable isotopes, ^7Li and ^6Li with abundances of 92.5

and 7.5%, respectively. The large mass difference of about 17% between both isotopes facilitates strong isotopic fractionation during geological processes leading to natural isotopic variations of larger than 50‰ (Tomascak 2004; Fig. 1). The isotopic composition of lithium in fluids, melts, and rocks from subduction-zone settings has, therefore, a great potential for quantifying mass transfer processes at convergent margins. Due to the high $\delta^7\text{Li}$ of seawater of about +32‰, low temperature sea floor alteration generates rocks enriched in heavy Li relative to those present in fresh mid-ocean ridge basalts (e.g., Chan et al. 1992; Moriguti and Nakamura 1998a; for a review see Tomascak 2004, and references therein). Slab metamorphism releases fluids that are believed to be depleted in Li and are isotopically heavier than rocks (e.g., Tomascak et al. 2002; Elliott et al. 2004; Nishio et al. 2004; Seitz et al. 2004), and continuous dehydration of pelagic sediments and altered oceanic crust would produce rocks depleted in heavy Li. In fact, Zack et al. (2003) have shown that relatively dry eclogites derived from altered oceanic crust have low Li contents and $\delta^7\text{Li}$ -values down to -11‰. If so, further subduction of high pressure rocks into deeper parts would contribute to a light Li isotopic component within the mantle. On the other hand, slab-derived fluids may transfer isotopically heavier Li into the overlying mantle wedge and possibly up to the site of arc magma generation. Whether island arc volcanic rocks still have a memory of the slab-derived Li isotopic signature (Moriguti and Nakamura 1998a) or whether this memory has been erased due to fluid–mineral exchange of Li and its isotopes when fluid percolated through mantle rocks up to the site of melt generation (Tomascak 2004; and references above) is still a matter of debate. One of the crucial points is that the overall fractionation effect is identified, however, quantitative information is urgently needed.

A prerequisite to the quantitative understanding of these processes is that temperature-dependent Li isotopic fractionation factors between minerals and coexisting fluids must be known. Direct determinations have

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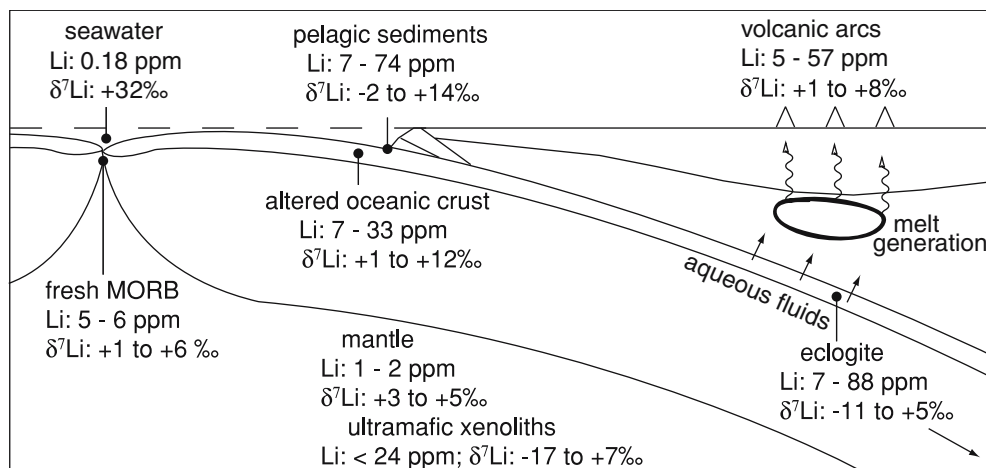


Fig. 1 Schematic cross section through a subduction zone with ranges of lithium concentrations and $\delta^7\text{Li}$ values typical for natural reservoirs. Data for lithium concentrations and $\delta^7\text{Li}$ are from Tomascak et al. (1999a) for seawater, Bouman et al. (2004) for pelagic sediments, Moriguti and Nakamura (1998a); Tomascak and Langmuir (1999) and Nishio et al. (2002) for fresh MORB,

Bouman et al. (2004) for altered oceanic crust, Ryan and Langmuir (1987) and Teng et al. (2004) for mantle, Moriguti and Nakamura (1998a) and Tomascak et al. (2002) for island arc magmas, Nishio et al. (2004) for ultramafic xenoliths, and Zack et al. (2003) for eclogites

been made, so far, only for natural fluid–whole rock systems and using basalt–seawater leaching experiments (Seyfried et al. 1998; Chan et al. 1992, 1993, 1994; James et al. 2003). The Li isotopic fractionation between altered basalt and seawater at 2°C is about -18‰ and at 350°C -5 to -6‰ , in line with the assumption of fluids being enriched in ^7Li compared to rocks. Experiments designed for mineral–fluid Li isotopic fractionation are lacking. These are particularly necessary for higher temperatures and pressures, i.e., for eclogite facies rocks, as dehydration and subsequent release of fluids into the overlying mantle wedge continues during high-pressure metamorphism. A recent experimental study based on Li isotope exchange between quartz, muscovite, and saline fluids at 400–500°C and 50–100 MPa, however, suggests that fluids were considerably lighter than quartz and muscovite (Lynton et al. 2005). This appears to be contradictory to what is known from basalt–seawater fractionations and also from the Li isotopic record of dehydrated metamorphic rocks, the reason of which is unknown. It is clear that the problem needs further experimental clarification.

Clinopyroxene is the most important carrier of Li in eclogitic assemblages, and contains always much more Li than coexisting phengite (Woodland et al. 2002). In line with that, Zack et al. (2003) have shown that there is a good correlation between the Li isotopic composition of eclogite whole rocks and the corresponding omphacite mineral separates from Trescolmen, Switzerland, and that omphacite is the best representative of $\delta^7\text{Li}$ in high-pressure rocks. We, therefore, present experimentally determined Li isotopic fractionation factors between clinopyroxene and high-pressure fluids at temperatures of 500–900°C and 2 GPa using spodumene, $\text{LiAlSi}_2\text{O}_6$, as representative of clinopyroxene. Spodumene is particularly suitable because it is easily

synthesized with coexisting fluid as a single solid phase over a wide temperature range and because the crystal-chemical constraints of Li incorporation into the clinopyroxene structure are well understood. Using these new data, we speculate how Li isotopic ratios of expelled high-pressure fluids may be recorded in overlying rocks of the mantle wedge and possibly also in arc magmas. Furthermore, we discuss the similarities and differences when compared to isotopic ratios of other light elements, such as B, which are used as tracers for fluid transfer processes in subduction zones.

Experimental technique

Synthetic spodumene, $\text{LiAl}[\text{Si}_2\text{O}_6]$, of endmember composition was chosen as a representative for lithium-bearing clinopyroxene. Oxide mixtures of stoichiometric spodumene composition with an excess of 3 wt.% SiO_2 were used as solid starting materials. The starting fluids were either aqueous LiCl- or LiOH-solution both in about 0.1 M concentration. All experiments were performed in a piston-cylinder press at 2.0 GPa. Experimental temperatures ranged from 500 to 900°C (in steps of 100°C) and lasted between 2 and 12 days (Table 1). Two sealed gold capsules both containing 5–20 mg of the solid mixture plus 1–2 μl of one of the fluids were positioned in a high-pressure cell, which consisted of rock salt, a steel furnace, and a mantled chromel–alumel thermocouple. For details on the experimental techniques see Wunder et al. (1999). After fast quench of the experiment reaching 200°C in less than 15 s, the capsules were cleaned, checked for leakage, and opened by piercing in doubly distilled water. After filtration, the total amount of fluid was 100 ml. Solid products were separated from the fluid by filtration and characterized

Table 1 Summary of experimental and analytical results

Run No.	P (GPa)	T (°C)	<i>t</i> (d)	Products (‰)		
				$\delta^7\text{Li}_{\text{spd}}$	$\delta^7\text{Li}_{\text{fluid}}$	$\Delta^7\text{Li}_{\text{spd-fluid}}$
Experiments using 0.1 M LiOH-solution						
# 566	2.0	500	2	+ 14.3	+ 18.1	−3.8
# 564	2.0	500	12	+ 14.6	+ 17.9	−3.3
# 562	2.0	600	5	+ 14.4	+ 17.1	−2.7
# 558	2.0	700	7	+ 14.1	+ 16.9	−2.8
# 568	2.0	800	5	+ 14.3	+ 16.2	−1.9
Experiments using 0.1 M LiCl solution						
# 567	2.0	500	2	+ 15.9	+ 19.2	−3.3
# 565	2.0	500	12	+ 15.8	+ 19.3	−3.5
# 563	2.0	600	5	+ 15.6	+ 18.2	−2.6
# 559	2.0	700	7	+ 14.9	+ 17.1	−2.2
# 569	2.0	800	5	+ 15.2	+ 17.2	−2.0
# 570	2.0	900	5	+ 15.7	+ 16.4	−0.7
# 581	2.0	900	7	+ 16.0	+ 17.8	−1.8

1 σ -uncertainty in $\delta^7\text{Li}_{\text{spd-fluid}}$ is 0.5‰. *spd* spodumene

optically and by X-ray powder diffraction (XRD) using the Rietveld method.

Isotopic analyses are given as per mil variations in the lithium composition of a sample relative to the lithium isotopic standard NIST 8545, according to $\delta^7\text{Li} = \{[(^7\text{Li}/^6\text{Li})_{\text{sample}}/(^7\text{Li}/^6\text{Li})_{\text{standard}}] - 1\} \times 1,000$. Lithium isotope separation and determination were done as follows. Solids were dissolved in HNO_3/HF and HClO_4 ; the fluids were dried. The samples were taken up in 2% HNO_3 to determine the Li content of the sample using mass ^7Li and a 200 ppb NIST 8545 standard solution as reference. For ion-chromatography using a one-step setup modified after Tomascak et al. (1999a) and Strehlow et al. (1974), an aliquot of the sample containing 1–2 μg Li was re-dissolved in 6 ml 1 N HNO_3 and 3 ml methanol. Each series of Li separation by ion exchange included the Li standard and seawater as additional samples. To control the chromatographical separation, we collected the 15 ml pre-eluate, i.e., the solution eluted from the column before the lithium, and the 5 ml eluate after lithium to check for loss of lithium, which would cause isotopic fractionation. Typically, loss of Li was less than 0.1% of the total Li in the sample and thus did not cause a detectable isotopic shift due to sample purification by ion exchange. The estimated total procedure blank during this project ranged from 50 to 900 pg Li and had no influence on the isotopic composition of the Li in the samples.

Content and isotopic composition of lithium were determined using a ThermoFinnigan Neptune MC ICP-MS. Separated samples were diluted in 2% HNO_3 to approximately 200 ppb Li. Lithium isotopes were collected simultaneously on Faraday collectors H4 and L4. Operating conditions for the Li measurements under hot wet plasma are listed in Table 2. Each measurement including peak centre, baseline, and acquisition of 20 ratios takes about 10 min. Samples have been measured repeatedly and sequential data collection was performed in the standard—sample—standard bracketing mode.

Each bracketing sequence consists of blank 1, standard 1, blank 2, sample 1, blank 3, and standard 2; standards and samples being corrected for the measured blank. The delta value of the sample was calculated relative to the mean of the neighbouring 200 ppb NIST 8545 standards, and adjusted relative to the standard that passed through the entire chemistry. The variation of the NIST 8545 over a sequence of 6–8 h typically was less than 1‰. The short-term drift over 40 min, including two standard measurements over a bracketing sequence, was better than 0.2‰. International standard rock materials and seawater measured during this study are reported in Table 3 and fall in the range of published data. The starting materials had the following isotopic composition ($\delta^7\text{Li}$): Li_2O : +14.8‰; 0.1 M LiOH: +12.5‰; 0.1 M LiCl: +327‰.

Results

All experiments produced spodumene as the sole Li-bearing solid phase together with small amounts of quartz, the amount of which varied between 0 and 6 wt.% and was determined by XRD using the Rietveld method for quantitative phase analysis. Cell dimensions

Table 2 Operating conditions for the Li isotopic measurements during this project

Inlet system	ThermoFinnigan stable introduction system (SIS) (low-flow PFA nebulizer together with tandem quartz glass spray chamber), standard (H)-Ni cones, quartz injector tube $d = 1.75$ mm; plug in torch
Gas flows	Cool gas 14–15 l/min; Aux gas 0.7–0.8 l/min Sample gas 0.9–1.1 l/min
Power	1,200 W
Blank	15–35 mV on ^7Li for 2% HNO_3
Sensitivity	35–40 V on ^7Li per ppm
$^7\text{Li}/^6\text{Li}$ NBS 8545	14.50–14.85 (over 10 month)

Table 3 International reference samples and seawater measured during this study and comparison with published data

Reference material	This study			Literature		
	$\delta^7\text{Li}$ (‰) mean \pm 1SD ^a	n^b (°) ^c	Li (ppm)	$\delta^7\text{Li}$ (‰) mean	Li (ppm)	Sources ^d
JB-2 (basalt)	4.27 \pm 0.13	2 (3)	8	4.3–6.8	7.9–8.34	1, 2, 4–9
JB-3 (basalt)	4.12 \pm 0.32	2 (3)	7.6	3.9	7.55	2, 3, 5, 6, 9
JR-2 (rhyolite)	3.78 \pm 0.16	2 (4)	75	4.2	10	5
JG-2 (granite)	−0.07 \pm 0.22	2 (4)	40	3.8–3.9	73.9–83	2, 3, 6, 9, 11
Seawater	30.85 \pm 0.7	1 (3)		−0.4–0.3	42.9	2, 3, 6, 9, 12
				29.3–33.3	41–43.4	1, 6, 11
					0.189	1, 5, 6, 10, 13–15
						1

^aSD of all independent measurements of all sample dissolutions

^bNumber of sample dissolutions

^cNumber of independent measurements of one sample dissolution

^dSources (1) Jeffcoate et al. (2004); (2) Magna et al. (2004); (3) Chan and Frey (2003); (4) Chan et al. (2002); (5) Nishio and Nakai (2002); (6) James and Palmer (2000); (7) Tomascak et al. (1999a, b); (8) Moriguti and Nakamura (1998b); (9) Potts et al. (1992); (10) Moriguti and Nakamura (1998a); (11) Oi et al. (1997); (12) Govindaraju (1994); (13) Tomascak et al. (1999a, b); (14) You and Chan (1996); Chan and Edmond (1988)

of synthetic spodumene from all the experiments are in excellent agreement with literature values, indicating that the synthetic spodumene was of stoichiometric composition.

Results of lithium isotope fractionation are summarized in Table 1 and are shown in Fig. 2. In all the

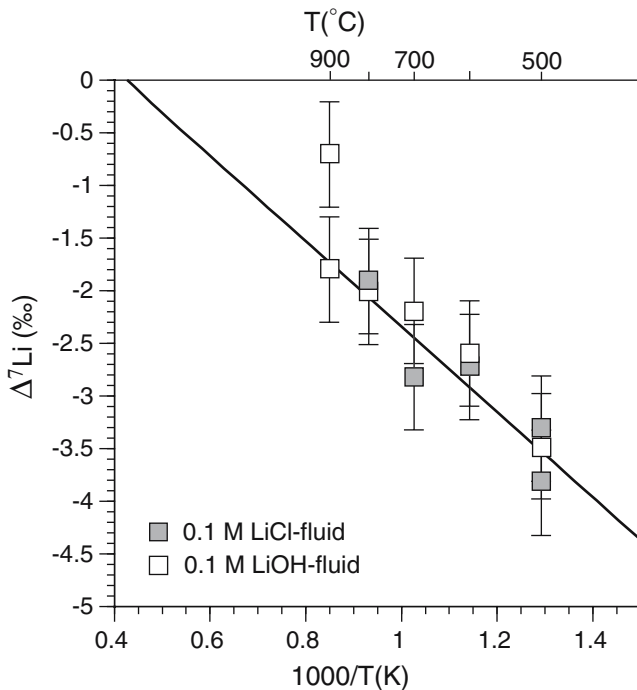


Fig. 2 Plot of experimentally determined lithium-isotope fractionation versus reciprocal temperature between spodumene and 0.1 M LiCl-fluid and between spodumene and 0.1 M LiOH-fluid. Solid line is a least squares regression of the lithium-isotope fractionation between spodumene and fluid calculated from all experiments, resulting in $\Delta^7\text{Li} = -4.61 \times (1,000/T [\text{K}]) + 2.48$; $R^2 = 0.86$ (see text)

experiments, ^7Li was preferentially fractionated into the fluid. Within the range of uncertainty in $\Delta^7\text{Li} = \delta^7\text{Li}_{\text{spd}} - \delta^7\text{Li}_{\text{fluid}}$, no significant difference in the isotopic fractionation between spodumene and neutral and weakly basic fluid, respectively, was observed. Duplicate experiments at the lowest temperature of 500°C (Table 1), varying the duration between 2 and 12 days, resulted in a reproducibility in $\Delta^7\text{Li}$ within 0.2–0.5‰ and indicates that equilibrium fractionation was reached in all the experiments. The experiments using LiCl-bearing fluid started with a fluid extremely enriched in ^7Li (+327‰), whereas that using LiOH had only 12.5‰. Consequently, the $\delta^7\text{Li}_{(\text{spd})}$ - and $\delta^7\text{Li}_{(\text{fluid})}$ -values were significantly higher than those for the LiOH experiments (Table 1). Even though, the resulting $\Delta^7\text{Li}_{\text{spd-fluid}}$ values are nearly identical irrespective of the different initials, which indicates that the isotopic exchange between fluid and solid was very effective and rapid, providing a further strong argument for equilibrium fractionation in our experiments. The low concentration of lithium within the fluids warranted that all dissolved lithium remained in the fluid during quenching. No evidence of quench crystallization was found in any of the runs given in Table 1. Furthermore, no significant Li loss occurred during the experiments (except experiment # 570, Table 1), indicating that lithium did not diffuse through the Au-capsule of 0.2-mm thickness for the conditions chosen in our experiments.

The temperature-dependent Li isotopic fractionation is approximated by $\Delta^7\text{Li}_{\text{spd-fluid}} = -4.61 \times (1,000/T [\text{K}]) + 2.48$; $R^2 = 0.86$, from the least squares linear regression, which is derived from ten of the eleven experiments given in Table 1. Experiment # 570 (at 900°C; Fig. 2), which was showing a slight deviation of about 1‰, was excluded from linear regression. This sample had a significantly lower Li-concentration in the product fluid than predicted by mass balance, the reason

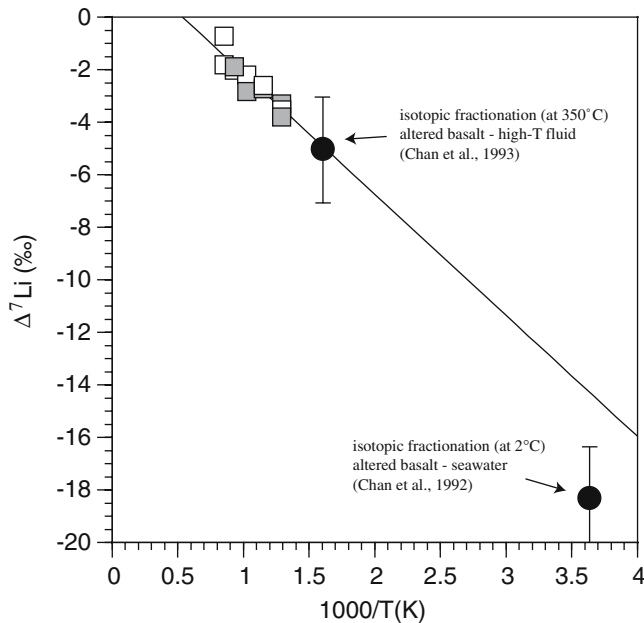


Fig. 3 Experimentally determined lithium-isotope fractionation between spodumene and fluid and resulting linear regression (see text), together with Li isotope fractionation data between altered basalt and seawater (Chan et al. 1992) and data between altered basalts and high-T fluids inferred from mid-ocean ridge hot springs (Chan et al. 1993)

of which is unknown. The temperature dependence is not very pronounced but significant, so that $\Delta^7\text{Li}_{\text{spd-fluid}}$ is $-3.5 \pm 0.5\text{‰}$ at 500°C and $-1.5 \pm 0.5\text{‰}$ at 900°C . The Li isotopic fractionation of about -5‰ between altered basalt and seawater at 350°C (Chan et al. 1993) falls perfectly onto the regression line, and that between altered basalt and seawater of -18‰ at 2°C (Chan et al. 1992) falls slightly off, but follows the general trend (Fig. 3).

Discussion

Fractionation behaviour

There is overall agreement that, besides temperature, the differences in coordination among coexisting phases are the first-order effects that control isotopic fractionation and that the lighter isotope preferentially occupies the more highly coordinated site (Oi et al. 1989). In most silicates, Li substitutes for Mg in octahedral coordination, and this is certainly true for spodumene synthesized in this study. The coordination of Li in high temperature and pressure fluids is unknown. In weakly basic fluids at ambient conditions, $[\text{Li}(\text{H}_2\text{O})_4]^+$ is the main cluster in aqueous fluids, which is probably responsible for the mineral–fluid fractionation of Li isotopes (Yamaji et al. 2001). Clusters with five and six water molecules occur in smaller amounts, but it is unclear up the extent to which these cluster types vary with changing P–T conditions. In Cl-bearing supercritical fluids, Li may show similar

behaviour to other alkali chlorides, such that the dissociation constant and speciation of Li is strongly dependent on P–T conditions. High temperature/low pressure would favour formation of neutral LiCl^0 monomers (e.g., Webster et al. 1989), whereas high pressure favours formation of charged hydrated ions. Quantitative relationships are unknown, particularly for fluids at subduction zone conditions. Our experiments with both weakly basic OH- and neutral Cl-bearing fluids revealed that the extent of fractionation at a given temperature is not sensitive to fluid composition at pressures of 2.0 GPa. This implies that the Li coordination in our Cl- and OH-bearing aqueous fluids was not significantly different. It is striking that the Li isotopic fractionation between hot spring water at 350°C and altered basalt (Chan et al. 1993) is in agreement with our experimentally determined T-dependence at higher temperatures. Because tremolitic amphibole and chlorite are the major Li-bearing minerals in altered basalts and because Li is six-fold coordinated in both phases, this could mean that (1) Li had the same structural state in the fluid at 350°C than at high P and T, provided that any possible Li isotope fractionation between clinopyroxene and amphibole (and chlorite) is minor, or (2) there is fractionation between the solids, which is compensated by structural changes of Li in the fluid. Similar arguments may hold for altered basalt–seawater fractionation at 2°C . Seitz et al. (2004) indeed suggested a small but significant equilibrium Li isotope fractionation at high temperatures between olivine and clinopyroxene, where Li is octahedrally coordinated in both minerals. This would indicate that small differences in the geometry and energetics of the $[\text{LiO}_6]$ octahedra between olivine and clinopyroxene might also induce isotopic fractionation, and that second-order effects cannot be ruled out. This is supported by our experiments on the fractionation of Li isotopes between synthetic Li-bearing mica [lepidolite, $\text{K}(\text{AlLi}_2)\text{Si}_4\text{O}_{10}(\text{OH})_2$] and fluid at similar conditions as for the system spodumene–fluid. Preliminary data indicate that ^7Li fractionates preferentially into the fluid. The fractionation, however, is slightly less compared to the Li isotopic fractionation between spodumene and fluid.

Our experiments confirm earlier assumptions drawn from the Li isotopic record of dehydrated metamorphic rocks (Zack et al. 2003) and from basalt–seawater fractionations (Chan and Edmond 1988; Tomascek 2004; and references therein) that fluids are enriched in ^7Li relative to silicates. This is in sharp contrast to experimental results of Li isotope exchange between quartz, muscovite, and saline fluids at $400\text{--}500^\circ\text{C}$, $50\text{--}100$ MPa (Lynton et al. 2005). These results suggest that fluids were strongly lighter than quartz and muscovite, and that fractionation would increase with increasing temperature, so that $\Delta^7\text{Li}_{\text{qtz-fluid}} \approx +5 \pm 1\text{‰}$ at 400°C ; $+10 \pm 2\text{‰}$ at 500°C , and $\Delta^7\text{Li}_{\text{ms-fluid}} \approx +18$ to $+20\text{‰}$ at 500°C . The obvious discrepancies might be due to the fact that Lynton et al. (2005) used diffusion experiments under hydrothermal conditions, introducing Li of

known isotopic composition from saline fluid into quartz and muscovite. The major drawback of that work is that the incorporation mechanism of Li into quartz (at the 20-ppm level) and into muscovite (200–350 ppm) was not investigated and the crystal-chemical constraints remain unclear. It is therefore ambiguous which mechanism was responsible for their measured isotopic fractionation. It would seem that using experiments with well-understood incorporation mechanisms of the respective elements into solids was the better approach. It is also possible that Li isotopic fractionation during their diffusion experiments was transport-controlled, with different diffusivities for ^7Li and ^6Li in the quartz and muscovite lattice (see Richter et al. 2003; Lundstrom et al. 2005; for the same effect in melts). If so, the values would not represent equilibrium fractionations.

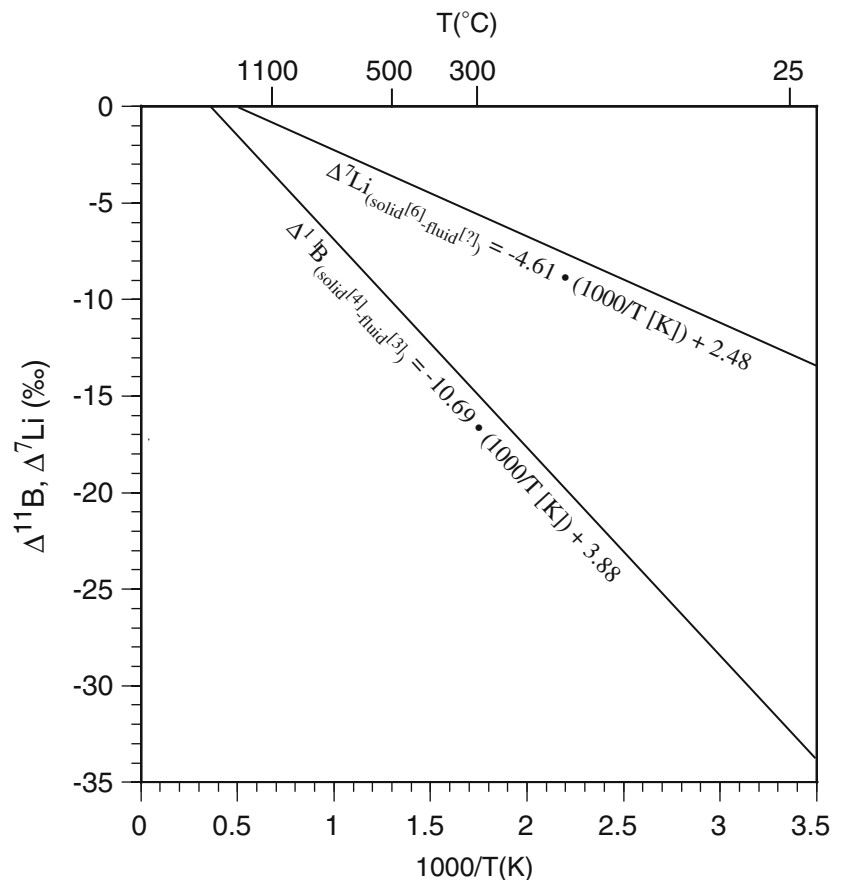
Fig. 4 shows our $\Delta^7\text{Li}_{\text{spd-fluid}}$ fractionations versus temperature along with the experimentally determined $\Delta^{11}\text{B}_{\text{mineral-fluid}}$ equilibrium fractionation curve of Wunder et al. (2005), the latter being valid for minerals with B in tetrahedral coordination and slightly acidic to neutral fluids in the temperature range from 25 to 1,000°C. The fractionation behaviour is similar in that for both the light elements, the heavier isotope, ^7Li and ^{11}B , is enriched in the fluid. Fractionation increases with decreasing temperature in both the cases. In terms of the

Δ -notation, the fractionation effect for Li is about half as large as that for B at a given temperature.

Lithium isotope ratios in subduction settings

In numerous studies, the Li isotope characteristics of rocks and minerals have been used to trace mass transfer in the subduction cycle (for a review see Tomascak 2004). There is overall agreement that altered oceanic crust is enriched in Li and ^7Li relative to MORB due to the uptake of isotopically heavy seawater Li during weathering (e.g., Bouman et al. 2004). Subduction and concomitant dehydration expel fluids enriched in Li and ^7Li into the fore-arc and fore-arc mantle. This is because Li preferentially partitions into fluids over minerals at metamorphic conditions (Brenan et al. 1998). Depending on the P–T path, the main dehydration occurs by the continuous and discontinuous reactions from 200°C, where a fully hydrated oceanic crust may contain 8 wt.% of water, up to about 600–650°C, where some tenths of per cent of water remain in the rock, mainly present in phengitic mica (Schmidt and Poli 2004). The Li isotopic fractionation is most pronounced during the initial stages of dehydration, because fractionation is more effective at lower temperatures. Consequently,

Fig. 4 Comparison of the temperature-dependence of the $\Delta^{11}\text{B}_{\text{mineral-fluid}}$ (Wunder et al. 2005) and $\Delta^7\text{Li}_{\text{spd-fluid}}$ (this study) equilibrium fractionation, both determined experimentally. The coordination shell of lithium in a high P–T fluid is unknown. See text for further explanations



heavy Li is preferentially transported into the fore-arc mantle. Assuming a Rayleigh distillation process, the ongoing dehydration along the P–T path depletes the slab in ^7Li , and the fluids released later are lighter than the earlier ones. Moreover, fractionation decreases with increasing temperature so that at 500°C $\Delta^7\text{Li}_{\text{mineral–fluid}}$ is only about -3.5% and at 650°C it is -2.5% . This implies that the slab and fluids released late may attain $\delta^7\text{Li}$ -values that are both lower than unaltered MORB and average mantle when the slab reaches locations underneath the volcanic front. Zack et al. (2003) earlier hypothesized on such behaviour, which is now verified by our experimental data. They also attempted to roughly model a Li isotope mass balance for slab dehydration using constant values for $\Delta^7\text{Li}_{\text{mineral–fluid}}$ of -15% and a Li partition coefficient between whole rock and fluid of 0.05. While values for temperature-dependent Li isotopic fractionations are now available, a sound mass balance would require mineral–fluid partition coefficients of Li for the involved metamorphic minerals including their temperature dependence. These are, unfortunately, not available.

The heterogeneity of lithium isotopes in rocks from subduction settings shown in Fig. 1 is produced by the hydration–dehydration cycle and concomitant Li isotopic fractionations between minerals and fluids. In that, the light elements Li and B behave similarly, at least with respect to their concentrations and isotopic ratios in slab rocks. Both elements fractionate into the fluid during continuous dehydration with the heavier isotope enriched in the fluid. The main difference is that the boron isotopic signature of the slab fluid is still seen in volcanic arc rocks, whereas that of Li is generally not (e.g., Ishikawa and Nakamura 1994; Ishikawa and Tera 1997; Tomascak et al. 2000, 2002; Ishikawa et al. 2001; Rosner et al. 2003; Tomascak 2004; Wunder et al. 2005). In volcanic arc rocks, $\delta^{11}\text{B}$ systematically decreases across the arc with increasing distance from the trench, recording the dehydration history and the thermal structure of the slab. By contrast, $\delta^7\text{Li}$ values are similar to MORB and show no cross-arc variations. The different behaviour of B and Li is due to two reasons: (1) the memory of arc magmas of the slab fluid source is weaker for $\delta^7\text{Li}$ than for $\delta^{11}\text{B}$, simply because the mineral–fluid isotopic fractionation at a given temperature is lower. (2) B is incorporated into mantle minerals only at the sub-ppm level (e.g., Paquin et al. 2004), whereas Li is incorporated up to several parts per million mainly in olivine and clinopyroxene (e.g., Seitz et al. 2004; Woodland et al. 2004). Thus, boron isotopic ratios of fluids percolating through the arc mantle may remain unaltered up to the site of magma generation. For Li, the arc mantle acts as a chromatographic column, where Li from the fluid is redistributed among mantle minerals with temperature-dependent isotopic fractionations as given above. Varying Li isotope ratios in the metasomatized mantle is easily explained by such a process (see also Tomascak et al. 2000; Tomascak 2004). The slab fluid source is seen in Li isotopic heterogeneities in

mantle rocks, whereas boron isotopic heterogeneities are recorded in arc melts.

Conclusions

The Li isotopic fractionation between clinopyroxene and Cl- and OH-bearing fluids was determined between 500 and 900°C and 2.0 GPa. The major conclusions obtained in this study are:

^7Li is always preferentially partitioned into the fluid. The isotopic exchange between the fluid and solid was effective and rapid; isotopic equilibrium fractionation was achieved in the experiments. No Li loss occurred during the experiments.

Using weakly basic and acidic fluids in the experiments revealed that the amount of fractionation is not sensitive to the fluid composition. This implies that the coordination of lithium of the experimentally used Cl- and OH-bearing aqueous fluids is not significantly different.

Lithium isotopic fractionation is temperature-dependent and approximated by the equation $\Delta^7\text{Li}_{\text{(cpx–fluid)}} = -4.61 \times (1,000/T [\text{K}]) + 2.48$; $R^2 = 0.86$. The Li isotopic fractionation between hot spring water and altered basalt is in good agreement with the experimentally determined T-dependence at high temperatures. The equation might be roughly applicable for quantification of fluid–rock interaction where Li in minerals resides in octahedral coordination (pyroxene, amphibole, mica, and chlorite).

Fluids expelled from a dehydrating slab are enriched in ^7Li . Due to the large affinity of lithium to mantle phases, Li and Li isotopes are redistributed among wedge minerals as slab fluids travel across the wedge columns into regions of arc magma production. Such a process modifies the Li isotopic characteristics of slab-derived fluids, erasing their source memory. This explains the general absence of cross-arc variations of Li isotopes in arc basalts.

Heterogeneity of lithium isotopes in subduction settings is mainly produced by the hydration–dehydration cycle. It may result from the combination of different processes: isotopic fractionation between seawater and oceanic crust; between slab and fluid, enriched in ^7Li , and wedge minerals; intramineral isotopic fractionation between mantle phases; isotopic Li fractionation by diffusion during mantle melting; and incorporation of slab restites, depleted in ^7Li , into the mantle.

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