Lithium isotopic signatures of peridotite xenoliths and isotopic fractionation at high temperature between olivine and pyroxenes

Hans-Michael Seitz[*], Gerhard P. Brey, Yann Lahaye, Soodabeh Durali, Stefan Weyer

Institut für Mineralogie, Universität Frankfurt, Senckenberganlage 28, 60054 Frankfurt, Germany

Abstract

We determined the Li isotopic composition of coexisting olivine, clinopyroxene, and orthopyroxene from spinel- and garnet-bearing peridotite xenoliths from San Carlos (Arizona), Vitim (Siberia), Dreiser Weiher (Eifel, Germany), and Kapfenstein (Austria). These samples represent the upper mantle that experienced varying degrees of partial melting followed by different metamorphic and metasomatic histories. Ultrasonic cleaning of handpicked mineral separates with Milli-Q water (18 MΩ cm) removed significant amounts (10–30%) of the lithium from unwashed separates and resulted in systematically heavier lithium isotopic compositions in the washed minerals. δ^7Li values for washed minerals range from +1.4‰ to +4.5‰ in olivines, from −1.0‰ to +3.9‰ in orthopyroxenes, and from −2.4‰ to +3.0‰ in clinopyroxenes, $\delta^7Li=[(^7Li/^6Li)_{sample}/(^7Li/^6Li)_{L\text{-}SVEC\ standard}−1]\times1000$. Olivines in mildly depleted lherzolites (Eifel, Vitim, San Carlos) are isotopically the heaviest (δ^7Li +3.4–+4.5‰). A metasomatised, amphibole-bearing lherzolite from the Eifel gave the lightest value (+1.4‰). Olivines have similar δ^7Li values to that of MORB, while the pyroxenes are isotopically lighter. In all but one sample, the δ^7Li changes systematically between the minerals; olivine has the heaviest δ^7Li value followed by orthopyroxene, and clinopyroxene has the lightest values. The degree of intramineral fractionation ($\Delta\delta^7Li=[\delta^7Li^{ol}−(\delta^{7cpx})]$) correlates negatively with equilibration temperature. $\Delta\delta^7Li$ is about 3.5 for low-temperature (~950 °C) xenoliths and 1.5 for high-temperature (~1150 °C) xenoliths. We therefore suggest Li isotope fractionation may occur at high, magmatic temperatures.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Lithium; Isotopes; Upper mantle; Peridotite; Isotope fractionation

1. Introduction

Lithium and its isotope ratios have been shown to be useful tracers of mantle, subduction, and surficial processes (e.g., Sywall, 1996; Hoefs and Sywall, 1997; Huh et al., 1998; Seitz and Woodland, 2000; Woodland et al., 2002; Tomascak et al., 2002; Chan et al., 2002a,b; Decitre et al., 2002; Zack et al., 2003, Seitz et al., 2003; Pistiner and Henderson, 2003). The natural isotopic variation of Li is about +60‰. Fresh N-MORB has δ^7Li values between +1.5‰ and +6.5‰ (Chan et al., 1992; Moriguti and Nakamura, 1998;

---

* Corresponding author. Tel.: +49 69 798 22547; fax: +49 069 798 28066.

E-mail address: h.m.seitz@em.uni-frankfurt.de (H.-M. Seitz).

Tomascak and Langmuir, 1999), the C1 chondrite Orgueil has +3.9‰ (James and Palmer, 2000a), other hydrous and nonhydrous chondrites have values ranging between +3‰ and −3.5‰ (McDonough et al., 2003), seawater has +32.3‰ (Chan and Edmond, 1988), marine pore waters vary between +11.1‰ and +41‰ (James and Palmer, 2000b), and river waters between +6‰ and +32‰ (Huh et al., 1998). Isotopically lighter δ^7Li values are reported from granites, serpentine, continental clays, loess, shales, eclogites, and mantle clinopyroxenes, ranging between +5.2‰ and −17.1‰ (Sywall, 1996; James and Palmer, 2000a; Zack et al., 2003; Nishio et al., 2004; Teng et al., in press).

Chan et al. (2002b) showed that low temperature alteration of the basaltic oceanic crust leads to enrichment of Li (5.6–27.3 ppm) and a shift to heavier isotopic composition (δ^7Li +6.6‰ to +20.8‰) relative to fresh MORB, and that deeper sections remain MORB-like, although the isotopic variation is significant (−1.7‰ to +7.9‰). Decitre et al. (2002) studied serpentinised peridotites of the SW Indian Ridge with Li concentrations of 0.6–8.2 ppm and a range of δ^7Li of +2.9‰ to +14‰. δ^7Li values of Central American volcanic arc lavas (Chan et al., 2002a) are similar to fresh MORB and arc lavas elsewhere (Kuriles, Sunda, Aleutians; Tomascak et al., 2002) and range between +2.1‰ to +5.1‰. This is surprising considering that Li is a fluid mobile element, and Li isotope fractionation may occur during dehydration of subducting material (Zack et al., 2001). Tomascak et al. (2002) suggested that isotopically heavy Li leaves the slab and is being introduced and masked by dilution in the overlying mantle wedge. Fractionated lithium can therefore be reintroduced into the mantle. The extremely high Li concentrations in ferropericlase and Ca–Si–perovskite inclusions in diamond suggest such lithium may even make it into the lower mantle (Seitz et al., 2003).

Thus, there are multiple ways to create or destroy heterogeneities in Li abundances and isotopic composition in the Earth's mantle. Evidence from isotopic signatures of OIB and MORB points to large, homogeneous reservoirs in the mantle with δ^7Li around +4‰. Kobayashi et al. (this volume), however, report isotopic variations from +8.4‰ to −10‰ in glass inclusions from Hawaiian volcanics

and suggest that these heterogeneities indicate involvement of recycled material. Direct measurements of mantle samples are scarce and have mostly been performed on serpentinised and hydrothermally altered samples. Decitre et al. (2002) measured δ^7Li in supposedly relict olivine, orthopyroxene, and clinopyroxene in the serpentinised peridotites of the SW Indian Ridge by Secondary Ion Mass Spectrometry (SIMS) and obtained δ^7Li values between −4‰ and +27‰. They believe these values reflect interaction with hydrothermal fluids. Their δ^7Li data for Zabargad peridotites and pyroxenites gave +5.1‰ for olivine, −3.3‰ for orthopyroxene, −4.6‰ for clinopyroxene (the latter two from a pyroxenite), and +9.6‰ for a further cpx (Decitre et al., 2002). Additional Zabargad data are provided by Brooker et al. (2000, this volume), who report δ^7Li values between +4.4 to +7.2 for anhydrous whole rock peridotites, +9.8‰ for an amphibole peridotite and more variable δ^7Li of −4.1 to +11.8 for pyroxenites. They interpret this isotopic heterogeneity to reflect the influence of slab-derived lithium in this region, which experienced pan-African subduction. Recently, Nishio et al. (2004) measured clinopyroxene separates from peridotite xenoliths from Australia, Japan, and Far Eastern Russia. Four samples from Bullenmerri, SE Australia, gave δ^7Li values between +5‰ and +6‰, two from Ichinomegata (Japan) also gave values around +5‰, while all others have negative values from −3‰ to the extreme value of −17‰. These negative δ^7Li values are accompanied by very high Li contents in the clinopyroxenes.

Here, we report the Li content and δ^7Li values of olivine, orthopyroxene, and clinopyroxene separates from previously well-documented mantle xenoliths from worldwide localities in order to

(1) characterise the mantle by analysing relatively primitive to highly depleted peridotites;
(2) test for internal mineral equilibrium;
(3) consider the effects of partial melting by looking at a xenolith suite from the Eifel, which ranges from lherzolite to harzburgite; and
(4) investigate the effects of metasomatism by analysing modally metasomatised, amphibole-bearing spinel peridotites.

2. Analytical methods

Minerals were handpicked from crushed and sieved rocks (100–500 μm) under a binocular microscope. Because lithium is water-soluble, most minerals were washed for 60 min in Milli-Q water in order to remove surface contamination. To evaluate the effects of this washing procedure, three mineral separates from a single sample (Vi 313-10) were also run without Milli-Q washing.

2.1. Chemistry and chromatography

For column separation, we modified the procedures of Tomascak et al. (1999) and Bouman (2004) using a single column pass. Mineral separates or powdered rock samples (25–35 mg) are digested in a mixture of 1 ml conc. HNO_3 and 1 ml conc. HF on a hot plate (140 °C) for several days. The digested solution is evaporated at around 170 °C and redissolved in 1 ml 6 M HCl (at 140 °C for 24 h). Evaporation and digestion in conc. HNO_3 is repeated twice (24 h each), followed by uptake in 1 ml 6 M HCl. This solution is dried and redissolved in 1 ml 6 M HNO_3. The clear solution is then dried carefully and dissolved in 0.18 ml 5 M HNO_3. Prior to column separation, 0.72 ml 100% methanol (ana-

lytical grade) is added. The water is deionised with a resistivity of 18.2 MΩ cm (Milli-Q), and all acids are double-distilled.

We use small 1.4-ml exchange columns with a resin height of 6 cm to minimise the amount of acid and methanol needed for chromatography and consequently to minimise the blank. The columns are filled with BioRad AG50W-X8 (200–400 mesh). Geometry and small column size allow a maximum sample size of 50 mg (20 mg is used routinely), and collection of 10 ml elution is sufficient to recover all lithium.

Fig. 1 shows the elution curves for basalt standard JB-2 for an olivine and a clinopyroxene. Lithium and sodium are clearly separated, and all lithium is collected in the 10 ml fraction (shaded area) for the very different sample chemistries. We routinely analysed aliquots from each purified unknown sample or the various standards for all elements by single collector ICP-MS (Element 2, ThermoElectron) to check for potential impurities. The separation of Li and Na was always excellent so that no matrix effect should influence the isotopic measurements. The only exception is Ti, which passes through the column without delay and overlaps with Li. Isotope measurements on JB-2 and the Ti-rich standards JGB-1 and SRM 688 give values in agreement with literature
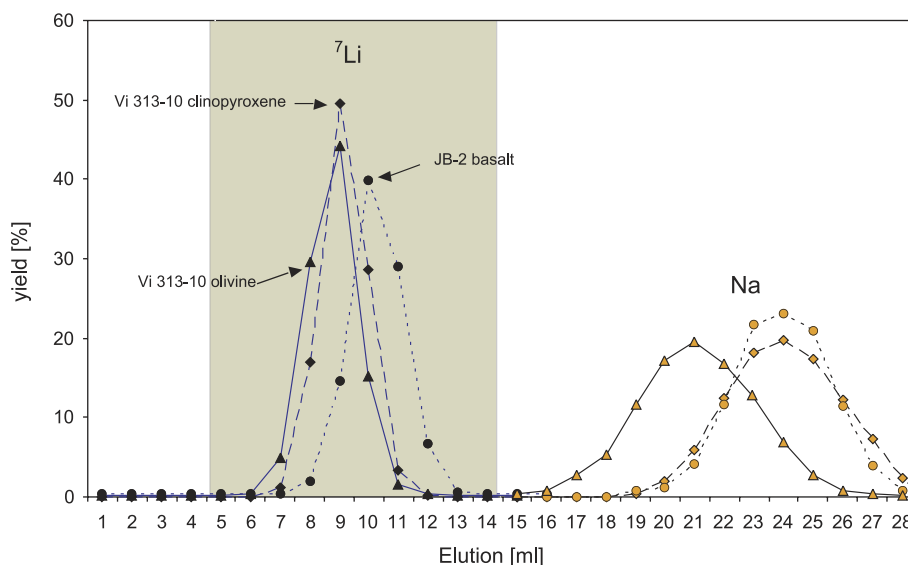

Fig. 1. Elution curve of Li and Na in basalt standard JB-2 (a) and Vi 313-10 olivine (b), using a 1.4-ml column and AG 50W-X8 resin. A 10 ml fraction (shaded area) was collected for quantitative recovery of Li.

values (Table 1), so that a matrix effect from Ti is not indicated. Organic material, which might be introduced into the sample through chromatography, is eliminated with a few drops of conc. HNO_3. Samples are then dried and finally taken up in 2% HNO_3 (10 ppb solution) for measurement by MC-ICP-MS. For the blank correction, each set of samples is accompanied by an 'analytical blank' that represents the total contribution of Li from the chemical agents used during dissolution and chromatography. These blanks always proved to be negligible, and the blank corrected analyses agreed with the uncorrected analyses within uncertainty (± 0.6‰, 2 S.D.).

2.2. Mass spectrometry

The Multi-Collector Inductively Coupled Plasma Mass Spectrometer Neptune (ThermoElectron) allows simultaneous measurement of both Li isotopes. Solutions are run through an Cetac Aridus® nebuliser fitted with a PFA spray chamber and an ESI micro-concentric nebuliser with an uptake rate of 20 μl/s. The sample gas is dried at 70 °C before being introduced into the plasma. With the ThermoElectron standard cones (H-Cones), an intensity of 40–50 pA, 10^{11} Ω resistor (4–5 V) for ^{7}Li at a 10 ppb concentration level is achieved. The high ion yields guarantee a sufficiently high signal even for 20 mg sample weights with less than 1 ppm Li. Intensities of 13–15 mV ^{7}Li are obtained for the analytical blank. Sample analysis is carried out sequentially by

'bracketing' the sample with the L-SVEC standard (Flesch et al., 1973) followed by a blank-measurement. A single analysis consists of a baseline measurement (on 5.9, 6.1 and 6.9, 7.1) followed by 3 blocks of 10 cycles with an acquisition time of 8 s for the Li isotope measurement. Isotopic compositions of the samples are given in delta values relative to the NIST L-SVEC standard solution (10 ppb).

2.3. Standards

The internal precision and long-term external reproducibility were tested by measuring the basalt standards JB-2 and SRM 688 and the gabbro standard JGb-1 over several months. A partly serpentinised peridotite, standard PCC-1, was also measured for the first time. Internal precision is typically between 0.2‰ and 0.6‰ (2 S.E.). The results are compiled in Table 1. Twenty-three measurements on JB-2 basalt standard over a period of 3 months gave a δ^7Li value of +5.2‰±1.2 (2 S.D.), which is a measure of the long-term reproducibility. On the basis of 23 measurements, the absolute value for JB-2 is therefore determined to be +5.20‰±0.25 (2 S.E.) relative to L-SVEC. Our value compares well with the values given by Tomascak et al. (1999), Moriguti and Nakamura (1998), Chan et al. (2002a), and Zack et al. (2003). Their value is slightly higher than those reported by Pistiner and Henderson (2003) and Nishio and Nakai (2002) and lower than that reported by James and Palmer (2000a). The latter authors also

Table 1
Measurements of international standards

Sample	Li (μg/g)	δ^7Li (mean) L-SVEC	2σ	n	Reference
JB-2 basalt	8	6.8[a]	0.4	3	James and Palmer (2000)
JB-2 basalt	6.7	3.9	0.4	n.g.	Pistiner and Henderson (2003)
JB-2 basalt	8.34	4.3	0.4	5	Nishio and Nakai (2002)
JB-2 basalt		5.1	1.2	13	Tomascak et al. (1999)
JB-2 basalt	8.05	4.9	n.g.	n.g.	Moriguti and Nakamura (1998)
JB-2 basalt		5.1[a]	0.4	7	Chan et al. (2002a,b)
JB-2 basalt		4.7	1.0	n.g.	Zack et al. (2003)
JB-2 basalt		5.2	1.2	23	This study
JGb-1 gabbro	4.2	6.1	2.4	3	James and Palmer (2000a)
JGb-1 gabbro		4.5	1.0	4	This study
SRM-688 basalt	4.9	2.8	2.6	4	Tomascak et al. (1999)
SRM-688 basalt		2.9	1.6	5	This study
PCC-1 peridotite		8.9	0.2	4	This study

n = numbers of measurements.
[a] TIMS measurements. n.g.: Not given. Uncertainty is the 2σ standard deviation.

report a slightly higher value for gabbro JGb-1 compared to our measurement. For basalt SRM 688, there is very good agreement between our value and that given by Tomascak et al. (1999). A δ^7Li value of +8.9‰ for PCC-1 is within the range of serpentinised peridotites given by Decitre et al. (2002).

3. Samples

Altogether, 31 mineral separates and one bulk sample from 12 mantle peridotite xenoliths were analysed. All samples are well characterised for their major, minor, and trace elements, their Sr, Nd, and some also for their Pb isotopes. We have chosen two samples that represent relatively primitive mantle based on their major element and isotopic compositions: spinel lherzolite SC-1 from San Carlos, Arizona (Jagoutz et al., 1979), and garnet lherzolite Vi 313-10 from Vitim (near Lake Baikal, Siberia; Ionov et al., 1993). Both samples are fertile peridotites that fall close to Bulk Silicate Earth (BSE) in a Nd–Sr diagram. A third fertile spinel lherzolite, Ib/8 from Dreiser Weiher, Germany (Stosch, 1987), plots in the MORB field, close to depleted mantle (DM).

A second set of spinel lherzolites and harzburgites (samples Ib/3, Ib/24, Ib/K1, Ib/58, Ia/171, and Ia/211; Stosch, 1987) from Dreiser Weiher (Eifel, Germany) and Ka 167 from Kapfenstein, Austria (Kurat et al., 1980), was selected to document the isotopic signature of variously depleted and metasomatised mantle.

The low-temperature Ia xenoliths are amphibole-bearing and show strong reenrichment of incompatible elements. In contrast, high-temperature, amphibole-free Ib samples are also refractory but are only mildly affected by metasomatism.

4. Results

4.1. Sample purity, surface contamination

It is known since the early days of detailed isotope investigations on mantle xenoliths that their mineral surfaces, cracks, and cleavages are covered by a contaminant with high incompatible trace element concentrations and which can have very different radiogenic isotope compositions (Basu and Murthy, 1977). Weak acids can readily remove this contaminant. Accordingly, Nishio et al. (2004) leached their handpicked clinopyroxenes with dilute acid (5% HNO_3) in their study of Li isotopes from mantle xenoliths. We intended to determine Li isotopes in all three main mineral phases in mantle xenoliths and were concerned especially about the stability of olivine with such a treatment. We therefore adopted the procedure of Zack et al. (2003), who cleaned their clinopyroxenes ultrasonically in Milli-Q water. To determine whether a leachable contaminant is present and, if so, its isotopic composition, we analysed washed and unwashed aliquots of the same samples. The results for Li contents and isotopes are given in Table 2 and shown in Fig. 2a, b.

Table 2
Surface contamination

Sample	Li (μg/g) not cleaned	2σ	Li (μg/g) cleaned	2σ	Li (μg/g) SIMS	2σ	δ^7Li not cleaned	n	δ^7Li cleaned	n
Vi 313-10 ol	2.19	0.34	1.55	0.51	1.28	0.04	2.1	11	4.2	13
Vi 313-10 opx			1.08	0.02	0.65	0.02			2.2	3
Vi 313-10 cpx	1.20	0.02	1.04	0.02	0.75	0.02	−1.7	7	2.5	5
Ib/8 ol	1.85	0.13	1.65	0.05			2.7	3	4.5	5
SC-1 ol			1.73	0.07	1.58	0.08			3.4	5
SC-1 opx			1.47	0.05	1.08	0.04			−0.2	7
SC-1 cpx			1.86	0.15	1.00	0.06			−0.8	3
SC-1 bulk	1.99	0.34					−1.1	3		
SC ol-1[a]	1.81	0.05					2.2	7		

n: Number of measurements on a given solution or repeated dissolutions (see Table 3 for more detail). Uncertainty is the 2σ standard deviation.
[a] Single olivines of 1×1.1×1.15 cm in size. Data from SIMS are taken from Seitz and Woodland (2000).
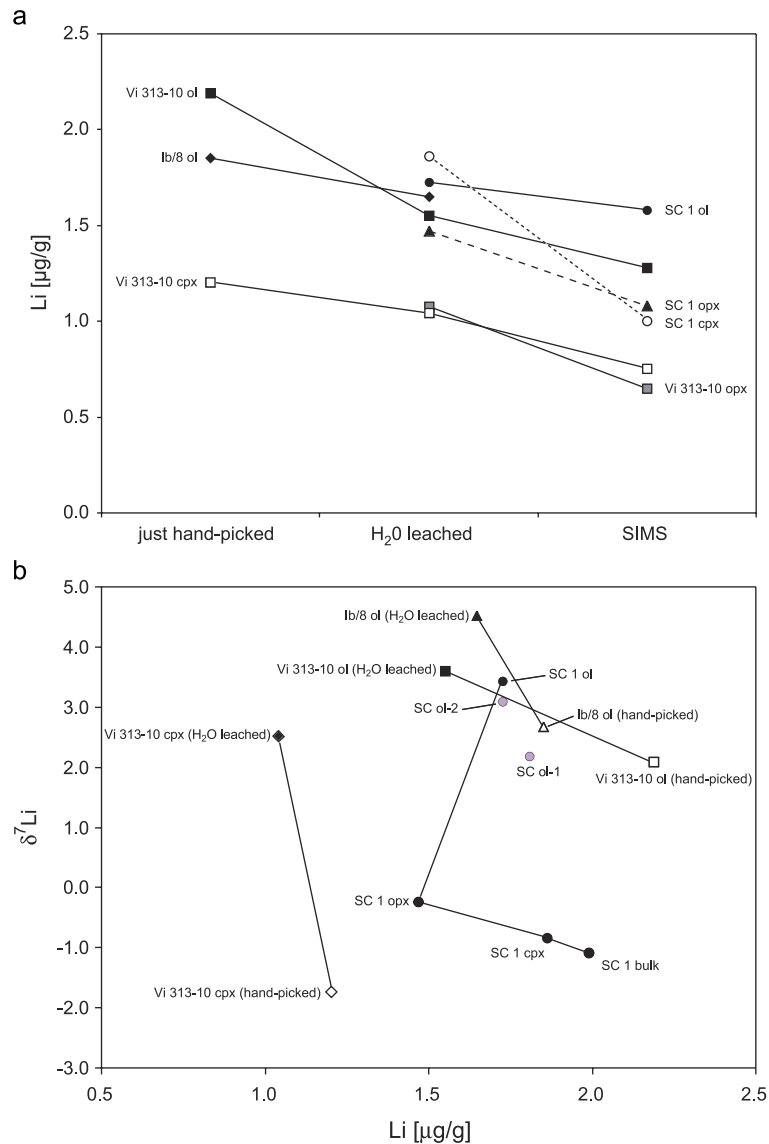
a

b

Fig. 2. Comparison of different sample treatments. (a) The Li concentration in handpicked samples (each grain was carefully examined under the binocular microscope for surface contamination) and in samples that were additionally cleaned ultrasonically in Milli-Q water for 60 min. Also shown are SIMS in situ measurements of the same samples (Seitz and Woodland, 2000). (b) The influence of different sample preparation techniques on δ^7Li and Li concentration.

4.1.1. Vitim 313-10

Olivines and clinopyroxenes were handpicked from the crushed sample, but not much care was taken to avoid surface contamination before grinding and dissolving. A second aliquot was handpicked, and each grain was carefully examined under the binocular microscope for surface contamination. These, plus an orthopyroxene separate, were cleaned ultrasonically for 60 min in Milli-Q water before chemical dissolution and column separation. The "dirty" separates contain significantly higher Li contents, and their δ^7Li is shifted to lighter isotope

ratios compared to the purified samples (Table 2 and Fig. 2a, b). For the ultrasonically cleaned samples, olivine is isotopically heavier than coexisting opx and cpx.

4.1.2. Olivine Ib/8

An aliquot of carefully handpicked olivine of anhydrous lherzolite Ib/8 was crushed and put through the chemical procedure without being ultra-

Table 3
Lithium concentrations and isotopic compositions of mineral separates from mantle xenoliths

Sample	Run	Mode (%)	Mg#	Li (µg/g)	2σ	D_{Li} ol/cpx	T (°C; BK, SS)	δ^7Li	2σ	n
SC ol-1	21, 24		90.6	1.8	0.05			2.2	1.2	7
SC ol-2	17, 20, 22		91.1	1.7	0.43			3.1	1.4	6
SC-1 ol	30	47.0	89.7	1.7	0.07			3.4	1.0	5
SC-1 opx	31	32.0		1.5	0.05	0.93	1052	−0.2	0.7	7
SC-1 cpx	31	18.0		1.9	0.15			−0.8	1.0	3
SC-1 bulk (measured)	32			2.0	0.34			−1.1	0.7	3
Vi 313-10 ol	28	64.5	90.3	1.6	0.51			4.2	1.1	13*
Vi 313-10 opx	28	19.5		1.1	0.01	1.49	1050	2.2	0.1	3
Vi 313-10 cpx	28	7.1		1.0	0.02			2.5	1.0	5
Vi 313-10 bulk (calc)								3.8		
Ka 167 ol	27	83.4	90.6	1.8	0.19			3.2	0.7	5
Ka 167 opx	27	13.7		1.1	0.21	1.64	1040	2.8	0.8	3
Ka 167 cpx	27	2.2		1.1	0.09			1.5	0.8	5
Ka 167 bulk (calc)								3.1		
Ia/171 ol	29	79.7	91.5	1.3	0.04			3.1	0.4	5
Ia/171 opx	30	13.4		0.9	0.05	1.75	842	1.3	1.3	4
Ia/171 cpx	29	3.6		0.8	0.03			0.4	1.5	6
Ia/171 bulk (calc)								2.9		
Ia/211 ol	30	70.1	91.1	1.8	0.07			1.4	1.1	5
Ia/211 opx	30	19.3		0.9	0.10	1.82	969	−1.0	0.9	3
Ia/211 cpx	30	6.2		1.0	0.20			−2.4	1.0	3
Ia/211 bulk (calc)								0.9		
Ib/3 ol	29	69.2	90.9	1.4	0.05			3.0	1.0	5
Ib/3 opx	29	25.5		0.7	0.03	1.83	1185	1.6	0.2	3
Ib/3 cpx	29	4.3		0.8	0.07			1.3	0.3	3
Ib/3 bulk (calc)								2.7		
Ib/8 ol	28	49.0	89.7	1.6	0.05			4.5	0.7	5
Ib/8 opx	27	29.1		1.1	0.01	1.60	1190	3.9	0.5	3
Ib/8 cpx	27	21.1		1.0	0.10			2.8	1.0	3
Ib/8 bulk (calc)								4.1		
Ib/24 ol	32	82.4	91.0	1.2	0.03			3.9	1.2	5
Ib/24 opx	32	15.0		0.8	0.14	1.61	1152	3.6	1.1	3
Ib/24 cpx	32	2.2		0.8	0.04			3.0	0.6	3
Ib/24 bulk (calc)								3.8		
Ib/K1 ol	31	68.8	91.3	1.0	0.03			2.4	1.1	6
Ib/K1 opx	31	20.1		0.8	0.07	1.21	1121	0.0	1.3	5
Ib/K1 cpx	31	10.3		0.9	0.06			2.3	0.4	3
Ib/K1 bulk (calc)								2.0		
Ib/58 ol	32	68.6	91.3	1.3	0.09			2.1	1.2	5

All samples were washed in Milli-Q water. Temperatures after Brey and Köhler (1990) and Sachtleben and Seck (1981) are taken from Stosch (1980) and Seitz et al. (1999). Mineral modes and Mg# are taken from Jagoutz et al. (1979), Stosch (1987), and Kurat et al. (1980). Corresponding to 'Run' numbers 'n' represents the number of measurements on a given solution or on repeated dissolutions (* indicates measurements from multiple analytical sessions). The bulk δ^7Li is calculated from Li concentrations and mineral modes. Uncertainty is the 2σ standard deviation.

sonically purified in Milli-Q water. It gave a lighter δ^7Li value than the purified aliquot (+2.5‰ vs. +4.5‰) and higher Li contents (see Table 2 and Fig. 2a, b).

4.1.3. San Carlos SC-1

Sample SC-1 is a fairly primitive spinel lherzolite that has been studied in detail for its major and trace element chemistry and its isotopic composition by Jagoutz et al. (1979) and later work. Because of this, the xenolith has been handpicked extensively, and only small amounts of pyroxenes are left. This makes the preparation of clean pyroxene separates difficult. Olivine is still available in ample quantity and a clean, handpicked separate was prepared and ultrasonically

purified. Ortho- and clinopyroxene had to be taken more or less as is and were ultrasonically purified in Milli-Q water. They give much higher Li contents compared to in situ measurements by SIMS (Seitz and Woodland, 2000) and negative δ^7Li values, while the olivine gives Li contents within the error of the SIMS value and a positive δ^7Li of +3.4‰ (see Table 2 and Fig. 2a, b).

4.1.4. Olivines SC-ol1 and SC-ol2

These are two large, clear, single crystals (about $1\times1\times1.5$ and $1.5\times1.5\times2$ cm, respectively) of homogeneous composition ($Fo_{90.6}$ and $Fo_{91.1}$, respectively) from San Carlos with few large cracks and some small spinel inclusions. They were gently
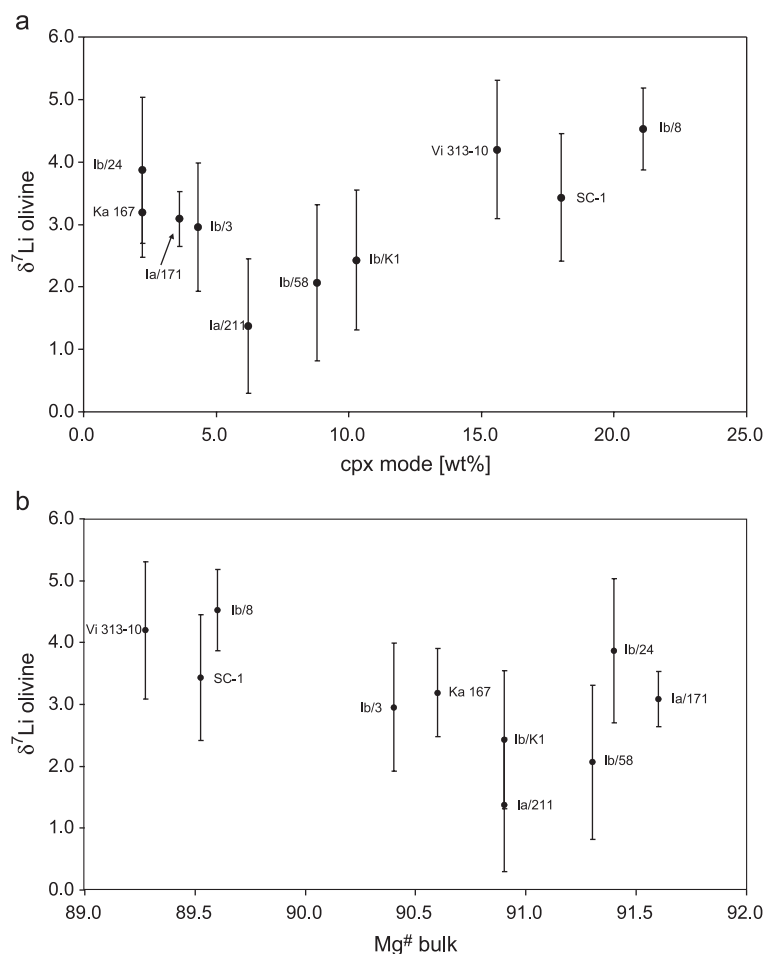

Fig. 3. (a and b) δ^7Li values are plotted against modal amount of cpx and Mg values of the bulk rock as a measure of fertility. Fertile lherzolites have high modal clinopyroxene corresponding to low Mg# bulk. Error bars are 2σ (mean).

crushed, and clear splinters without any obvious sign of inclusions or cracks taken from the interior. These splinters were chemically processed with no further cleaning. They yield positive δ^7Li values similar to olivine from SC-1 (Table 2 and Fig. 2a, b). We assume that these values are not affected by contamination, and the agreement with SC-1 olivine makes us confident that our separation and cleaning procedure is the basis to obtain δ^7Li values inherent to the individual mineral.

4.2. Purified mineral separates

The δ^7Li and lithium concentrations of purified and Milli-Q-washed mineral separates are given in Table 3. The δ^7Li values for olivines range from +1.4‰ to +4.5‰, for orthopyroxenes from −1.0‰ to +3.9‰, and for clinopyroxenes from −2.4‰ to +3.0‰. The olivines are within the range of MORB, while the pyroxenes are lighter. For individual samples, olivines always give the heaviest δ^7Li, orthopyroxenes lighter values with clinopyroxenes having similar or slightly lower δ^7Li than the orthopyroxenes. An exception is sample Ib/K1, where the δ^7Li of olivine and clinopyroxene are very similar, whereas δ^7Li of orthopyroxene is significantly lower. The olivines from the fertile lherzolites Ib/8, Vi 313-10, and SC-1 plot towards the heavier end of the δ^7Li range, while one of the two amphibole-bearing lherzolites (Ia/211) from the Eifel area gives the lightest value (Fig. 3a, b).

Li concentrations of the Dreiser Weiher samples are in good agreement with results obtained by Ottolini et al. (submitted and personal communication) by SIMS. Li concentrations for other samples are systematically higher than the values obtained by Seitz and Woodland (2000) (see Table 2 and Fig. 2a for comparison). The calculated partitioning of Li between ol/cpx and ol/opx, however, is similar to that derived by Seitz and Woodland (2000) except for Ib/K1. They found K_D to be independent of pressure and temperature. From this agreement and the agreement with the SIMS data Ottolini et al. (submitted and personal communication), we deduce that our values are not corrupted by surface contamination of the mineral separates and, by inference, that the measured δ^7Li values are inherent to the minerals.

5. Discussion

5.1. Correlation with other chemical or isotopic parameters?

δ^7Li values of olivines are representative of the bulk rocks, which are lighter on average by 0.3‰ when concentrations and modal abundances of cpx and opx are considered (see Table 3). In the following, only olivine values are discussed in relation to other chemical and isotopic parameters. The possible meaning of the differing isotopic values of ortho- and clinopyroxenes is discussed below.

It can be seen from Fig. 3 that the more fertile lherzolites, with high modal clinopyroxene and low Mg values, have higher δ^7Li values at around +4.0‰, close to C1 chondrite Orgueil (James and Palmer, 2000a) and average MORB, which is taken as being representative of the depleted mantle (Nishio et al., 2004). This suggests that the BSE may have a δ^7Li value of around +4‰. It also suggests that partial melt removal has not significantly changed the Li isotope ratio of the mantle. The agreement with Orgueil also indicates that the solar system has the same value. However, work by McDonough et al. (2003) on other hydrous and nonhydrous chondrites shows that Orgueil may have been affected by hydrous alteration, and that the solar system value may be close to zero. Our refractory samples (as indicated by higher Mg values and lower modal cpx) tend to have lower δ^7Li values although overlap with the more fertile samples occurs (Fig. 3). These lower δ^7Li values may be due to metasomatic overprinting of lithium, to lithium isotope fractionation during partial melting, or they may reflect primordial heterogeneity of the Earth's mantle.

The two amphibole-bearing xenoliths, Ia/171 and Ia/211, are among the most depleted samples, but, like other refractory peridotites (Frey and Green, 1974), they are also most enriched in incompatible elements. This is shown in Fig. 4 by high (La/Sm)$_N$ ratios in their clinopyroxenes. Clinopyroxenes are representative of the bulk composition, because they are the almost exclusive carriers of REE in spinel lherzolites (e.g., Frey and Green, 1974; Eggins et al., 1998). A (La/Sm)$_N$ ratio of one corresponds to a chondritic earth mantle; higher values reflect metasomatically enriched mantle, and lower values
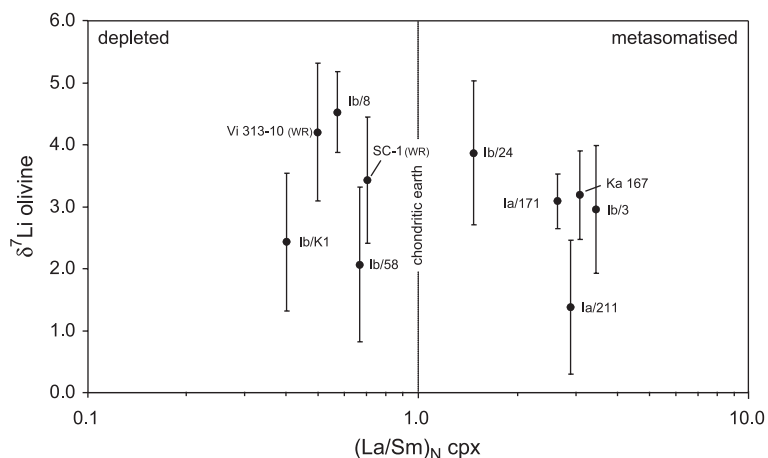
Fig. 4. $(La/Sm)_N$ ratios in clinopyroxenes versus δ^7Li values in olivine as indicator of depletion and metasomatism. Clinopyroxenes are the almost exclusive carriers of REE in spinel lherzolites, and their composition reflects the bulk composition. REE data for all other samples are taken from Stosch (1980), Stosch and Seck (1980), from Jagoutz et al. (1979) and Kurat et al. (1980).

reflect a depleted mantle. The most fertile lherzolites in our collection have a slightly depleted LREE pattern and plot somewhat below 1 and at the highest δ^7Li values. More refractory peridotites have lower δ^7Li values but are also metasomatically overprinted. Thus, the light Li isotopic composition of the latter may have formed as a result of mantle metasomatism. It is not clear however whether Li is enriched during metasomatism and if it is, which of the various kinds of metasomatising agents is a

carrier of lithium. Seitz et al. (2003) found an inverse relationship of Li and forsterite content in olivines from spinel and garnet peridotites and from inclusions in diamonds. They suggested that the Li content in olivines from garnet peridotites is a proxy for the degree of partial melt removal and that lithium was not reintroduced into these peridotites during metasomatic overprinting. Their data plot around a simple batch melting trend and this line are reproduced in Fig. 5. Most of our samples
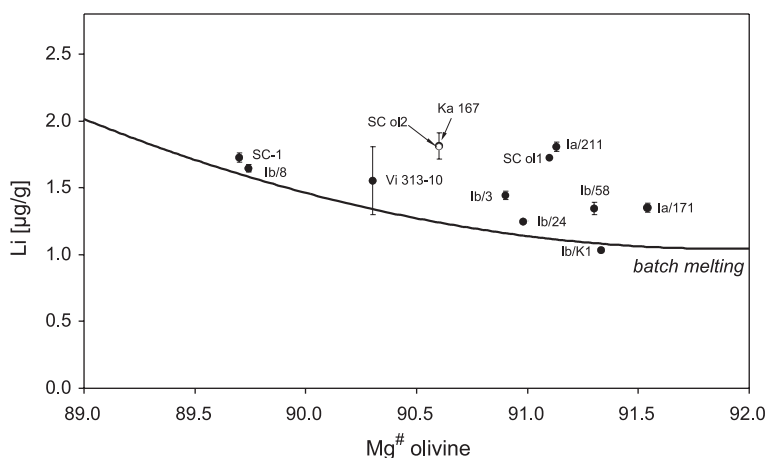

Fig. 5. Li in olivine versus Mg# in olivine from spinel and garnet peridotites. Lithium decreases with increasing Mg#, reflecting simple partial melting, similar to Mg#. Reference line for batch melting is taken from Seitz et al. (2003). Error bars are 2σ(mean).

plot close to this line except for San Carlos samples, SC-ol1 and Sc-ol2, Ka 167 from Austria, and an amphibole-bearing sample Ia/211 from the Eifel, which have olivine with elevated Li contents. The other amphibole-bearing peridotite (Ia/171) and the rest of the metasomatised samples (Ib/24 and Ib3) plot near the line and show no evidence for metasomatic addition of lithium. Thus, metasomatism, both modal and cryptic, does not correlate with addition of lithium. Not taking into consideration that D values for fluid/mineral may be »1,

we suggest that the variable Li isotopic compositions we have measured reflect small heterogeneities in the mantle that are not clearly related to metasomatic overprinting.

The δ^7Li values of olivines also do not correlate with the Nd and Sr isotopic composition of coexisting clinopyroxenes (Fig. 6). Amphibole-free, high-temperature Ib-Eifel peridotites plot within or close to the MORB field on a Nd–Sr isotope variation diagram, except for the strongly metasomatised sample Ib/3, which plots close to the amphibole-
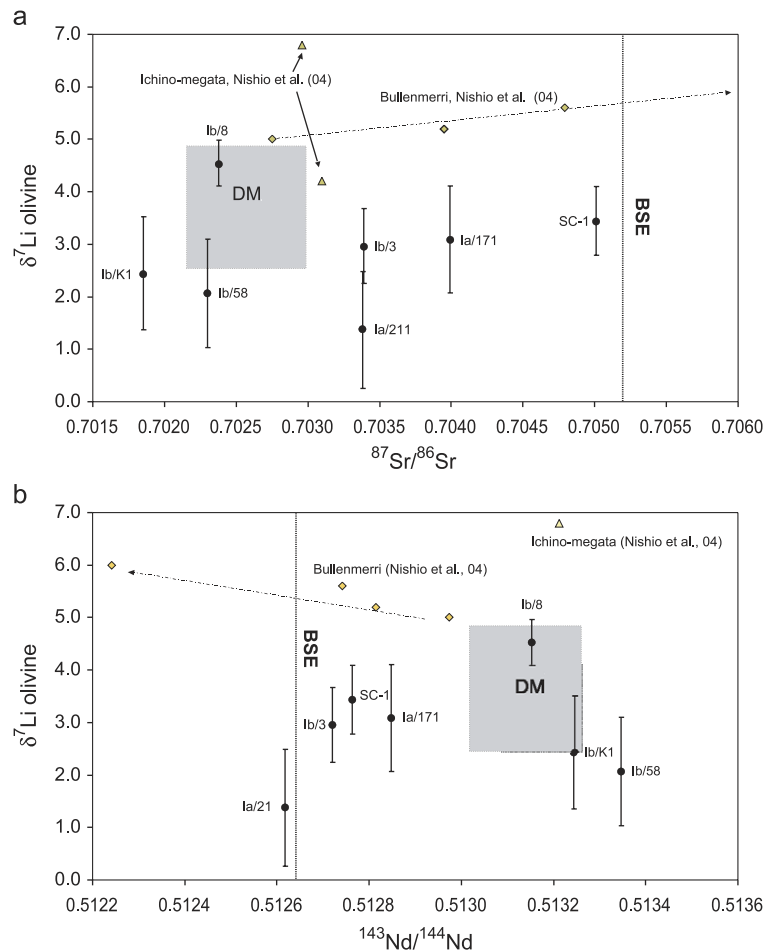

Fig. 6. (a and b) δ^7Li values of olivines are plotted as a function of the Nd and Sr isotopic compositions of clinopyroxenes from the same xenoliths. Clinopyroxene data are taken from Stosch (1980), Stosch et al. (1980), Stosch and Lugmair (1986), and Jagoutz et al. (1980). Also shown are the Li, Nd, and Sr isotopic data given by Nishio et al. (2004) for clinopyroxenes from spinel peridotite xenoliths from Bullenmerri, Australia, except one sample with very high ^{87}Sr/^{86}Sr of 0.70982 and low ^{143}Nd/^{144}Nd of 0.512241 and from Ichino-megata (NE Japan). Not shown are their peridotites from SW Japan and Far Eastern Russia with extremely light δ^7Li values down to −17‰. BSE: bulk silicate Earth; DM: depleted mantle.

bearing, low-temperature Eifel peridotites (Ia group). The latter form a mixing array between EM1 and HIMU on the Sr vs. Nd isotope diagram and are thus shifted to lower $^{87}Sr/^{86}Sr$ values compared to the Eifel lava field (Witt-Eickschen et al., 2003; Stosch, 1980; Stosch and Lugmair, 1986). In contrast to Sr and Nd, the δ^7Li values of all but two of the Eifel peridotites are similar to DM (as defined by Nishio et al., 2004).

Nishio et al. (2004) suggested that EM2 may be characterised by a positive δ^7Li value, and EM1 extremely negative δ^7Li values, based on comparisons between Sr–Nd and Li isotopes in clinopyroxene from mantle xenoliths from SE Australia (Bullenmerri) and NE Japan (Ichinomegata), both of which have EM2 characteristics, and Far East Russia and SW Japan, both of which have EM1 characteristics (Fig. 6). In comparison, the mantle below the Eifel is MORB-like in terms of lithium and slightly lower in δ^7Li than underneath Eastern Australia and NW Japan and considerably higher in δ^7Li than that is found beneath Far East Russia and SW Japan. Three samples, Ib/3, Ia/171, and Ia/211, plot towards more radiogenic Sr and less radiogenic Nd outside the MORB field, but only Ia/211 also has lighter δ^7Li. The fairly primitive sample SC-1, with a slightly more radiogenic Nd isotope ratio

than bulk silicate earth (BSE), lies in the middle of the range of δ^7Li values for N-MORBs. BSE should then have a similar Li isotopic composition to MORB.

5.2. Preferential surface contamination, isotope disequilibrium or isotope fractionation at high temperature?

In Fig. 2, we show that mineral surface contamination is a serious problem in the analysis of Li isotopes of mantle xenoliths, but we have also shown that this surface contamination can be successfully removed by gentle ultrasonic cleaning in Mill-Q water. We have also shown in Fig. 7 that there is a systematic difference of δ^7Li values between olivines and pyroxenes. This may reflect incomplete removal of surface contamination in the pyroxene, which may reside on cleavage plains, which are absent in olivines. Cleavage planes may not be as easily accessible to our gentle cleaning procedure, and more surface contamination may be retained in the pyroxenes. However, we consider this unlikely because (i) if contamination were the cause of the offsets, we would expect the deviations to be more erratic and not as systematic as seen in Fig. 7; and, (ii) the measured partitioning of Li
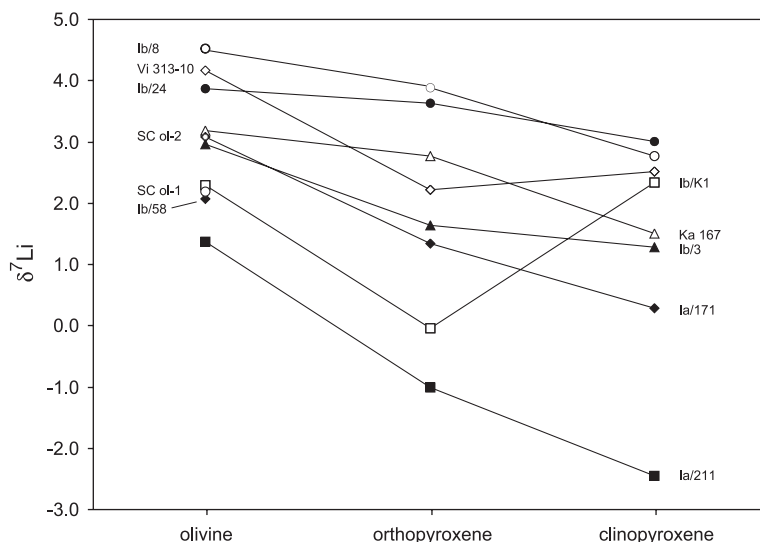

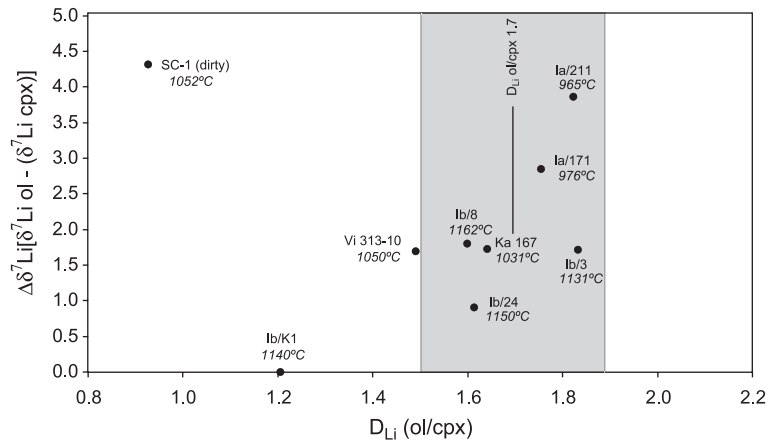Fig. 7. Systematic differences of δ^7Li values between olivines, ortho-, and clinopyroxenes.

Fig. 8. Differences in the isotopic ratios of olivine and clinopyroxene expressed as $\Delta\delta^7Li=(\delta^7Li^{ol}-\delta^7Li^{cpx})$ plotted against $D_{Li}^{ol/cpx}$. Shaded area outlines $D_{Li}^{ol/cpx}$ of 1.7 ± 0.2 from Seitz and Woodland (2000), which is believed to represent equilibrium partitioning of Li between these two phases. Temperature estimates for spinel and garnet peridotites are taken from Seitz et al. (1999) and Sachtleben (1980).

between olivine and clinopyroxene $D_{Li}^{ol/cpx}$ is very similar to the value of 1.7 ± 0.2 obtained by SIMS (Seitz and Woodland, 2000). Seitz and Woodland (2000) considered lithium partitioning to be independent of pressure and temperature but to be very sensitive to mineral-dependent metasomatic overprinting. Samples following the partition coefficient should therefore be in internal mineral equilibrium. Fig. 8 plots the difference between the isotopic ratios of olivine and clinopyroxene ($\Delta\delta^7Li=\delta^7Li^{ol}-\delta^7Li^{cpx}$) vs. $D_{Li}^{ol/cpx}$. Sample SC-1 has $D_{Li}^{ol/cpx}$ too low to represent mineral–mineral equilibrium. This is likely due to surface contamination in the cpx. Thus, its $\Delta\delta^7Li^{ol/cpx}$ is not considered to be inherent to the rock. Sample Ib/K1 is the only one that shows no difference in isotopic ratios between olivines and clinopyroxenes, but it also has a low $D_{Li}^{ol/cpx}$. All other samples have partition coefficients $D_{Li}^{ol/cpx}$ consistent with the equilibrium value given by Seitz and Woodland (2000). It is rather conspicuous that the two xenoliths equilibrated at low temperature (around 950 °C) have the largest difference in $\Delta\delta^7Li^{ol/cpx}$ of around 3.5, whereas those equilibrated at high temperatures (around 1150 °C) have significantly lower values of $\Delta\delta^7Li^{ol/cpx}$ around 1.5 (Fig. 8). We therefore suggest that equilibrium Li isotope fractionation at high temperature is the cause for the systematic difference in isotope ratios between olivine and clinopyroxene. We are currently in the process of testing this

hypothesis by varying cleaning procedures and isotopic analysis of both cleaned minerals and leaching solutions. We exclude isotopic disequilibrium between the minerals because of overall elemental equilibrium.

6. Conclusions

Systematic temperature-dependent differences in δ^7Li-values exist between olivine, orthopyroxene, and clinopyroxene, which suggests that δ^7Li may be an effective geothermometer below 1000 °C in silicate systems. In contrast to the very light δ^7Li values measured in Li-rich clinopyroxene separates by Nishio et al. (2004), our fertile, depleted, and metasomatised samples show only relatively small variations in δ^7Li, similar to or lighter than the presently assumed value for BSE. The Li contents of Nishio et al.'s clinopyroxenes with extremely light δ^7Li are higher by a factor of 10 to 20 compared to our clinopyroxenes and also their own clinopyroxenes having δ^7Li near BSE. Both these latter samples of Nishio et al. (2004) and our samples derive from continental rifting environments, whereas their isotopically light samples derive from a setting with previous arc volcanism. Metasomatic agents in such an environment must be fundamentally different to those in a continental lithosphere both in terms of Li abundances and isotope ratios.

Acknowledgements

References

Basu, A.R., Murthy, V.R., 1977. Ancient lithospheric lherzolite xenoliths in alkali basalts from Baja California. Earth Planet. Sci. Lett. 35, 239–245.

Bouman, C., 2004. Lithium isotope systematics at subduction zones. PhD thesis, Vrije Universiteit Amsterdam, Netherlands.

Brey, G.P., Köhler, T., 1990. Geothermobarometry in four-phase lherzolites: II. New thermometers and practical assessment of existing thermometers. J. Petrol. 31, 1353–1378.

Brooker, R.A., James, R.H., Blundy, J.D., 2000. Subduction-related mantle pyroxenites at Zabargad Island, Red Sea: evidence from Li isotopes and trace element geochemistry. 10th Annual V.M. Goldschmidt Conference, Oxford, J. Conf. Abstr., vol. 5, p. 249.

Chan, L.H., Edmond, J.M., 1988. Variation of lithium isotope composition in the marine environment: a preliminary report. Geochim. Cosmochim. Acta 52, 1711–1717.

Chan, L.H., Edmond, J.M., Thompson, G., Gillis, K., 1992. Lithium isotopic composition of submarine basalts: implications for the lithium cycle in the oceans. Earth Planet. Sci. Lett. 108, 151–160.

Chan, L.H., Leeman, W.P., You, C.-F., 2002a. Lithium isotopic composition of Central American volcanic arc lavas: implications for modification of subarc mantle by slab-derived fluids: corrections. Chem. Geol. 182, 293–300.

Chan, L.-H., Alt, J.C., Teagle, D.A.H., 2002b. Lithium and lithium isotope profiles through the upper oceanic crust: a study of seawater-basalt exchange at ODP Sites 504B and 896A. Earth Planet. Sci. Lett. 201 (1), 187–201.

Decitre, S., Deloule, E., Reisberg, L., James, R., Agrinier, P., Mevel, C., 2002. Behaviour of Li and its isotopes during serpentinisation of oceanic peridotites. Geochem. Geophys. Geosystems 3 (1), 1–20.

Eggins, S.M., Rudnick, R.L., McDonough, W.F., 1998. The composition of peridotites and their minerals: a laser-ablation ICP-MS study. Earth Planet. Sci. Lett. 154, 53–71.

Flesch, G., Anderson, A.R., Svec, H.J., 1973. A secondary isotopic standard for $^6Li/^7Li$ determinations. Int. J. Mass Spectrom. Ion Phys. 12, 265–272.

Hoefs, J., Sywall, M., 1997. Lithium isotope composition of Quaternary and Tertiary biogen carbonates and global lithium isotope balance. Geochim. Cosmochim. Acta 61 (13), 2679–2690.

Huh, Y., Chan, L.-H., Zhang, L., Edmond, J.M., 1998. Lithium and its isotopes in major world rivers: implications for weathering and the oceanic budget. Geochim. Cosmochim. Acta 62, 2039–2051.

Ionov, D.A., Ashchepkov, I.V., Stosch, H.-G., Witt-Eickschen, G., Seck, H.A., 1993. Garnet peridotite xenoliths from the Vitim volcanic field, Baikal region: the nature of the garnet-spinel peridotite transition zone in the continental mantle. J. Petrol. 34, 1141–1175.

Jagoutz, E., Palme, H., Baddenhausen, H., Blum, K., Cendales, M., Dreibus, G., Spettel, B., Lorenz, V., Wänke, H., 1979. The abundances of major, minor and trace elements in the earth's mantle as derived from primitive ultramafic nodules. Proc. Lunar Planet. Sci. Conf. 10th, 2031–2050.

Jagoutz, E., Carlson, R.W., Lugmair, G.W., 1980. Equilibrated Nd-unequilibrated Sr isotopes in mantle xenoliths. Nature 286, 708–710.

James, R.H., Palmer, M.R., 2000a. The lithium isotope composition of international rock standards. Chem. Geol. 166, 319–326.

James, R.H., Palmer, M.R., 2000b. Marine geochemical cycles of the alkali elements and boron: the role of sediments. Geochim. Cosmochim. Acta 64, 3111–3122.

Kurat, G., Palme, H., Spettel, B., Baddenhausen, H., Hofmeister, H., Palme, C., Wänke, H., 1980. Geochemistry of ultramafic xenoliths from Kapfenstein, Austria: evidence for a variety of upper mantle processes. Geochim. Cosmochim. Acta 44, 45–60.

Kobayashi, K., Tanaka, R., Moriguti, T., Shimizu, K., Nakamura, E., this volume. Lithium, Boron and Lead isotope systematics of glass inclusions from Hawaiian lavas: implications for the involvement of recycled material in the Hawaiian plume. Chemical Geology.

McDonough, W.F., Teng, F.-Z., Tomascak, P.B., Ash, R.D., Grossman, J.N., Rudnick, R.L., 2003. Lithium isotopic composition of chondritic meteorites. Lunar Planet. Sci. XXXIV 1931 pp.

Moriguti, T., Nakamura, E., 1998. Across-arc variation of Li isotopes in lavas and implications for crust/mantle recycling at subduction zones. Earth Planet. Sci. Lett. 163, 167–174.

Nishio, Y., Nakai, S., 2002. Accurate and precise lithium isotopic determinations of igneous rock samples using multi-collector inductively coupled plasma mass spectrometry. Anal. Chim. Acta 456, 271–281.

Nishio, Y., Nakai, S., Yamaoto, J., Sumino, H., Matsumoto, T., Prikhod'ko, V.S., Arai, S., 2004. Lithium isotopic systematics of the mantle-derived ultramafic xenoliths: implications for EM1 origin. Earth Planet. Sci. Lett. 217, 245–261.

Ottolini, L., Le Fēure, B., Vannucci, R., Direct assessment of mantle Boron and Lithium contents and distribution by SIMS analyses of peridotite minerals (re-submitted to EPSL).

Pistiner, J.S., Henderson, G.M., 2003. Lithium-isotope fractionation during continental weathering processes. Earth Planet. Sci. Lett. 214, 327–339.

Sachtleben, T., 1980. Petrologie ultrabasischer Auswürflinge aus der Westeifel: Diss. Univ. Köln. 201 pp.

Sachtleben, T., Seck, H.A., 1981. Chemical control of Al-solubility in orthopyroxene and its implications on pyroxene geothermometry. Contrib. Mineral. Petrol. 78, 157–165.

Seitz, H.-M., Woodland, A.B., 2000. The distribution of lithium in peridotitic and pyroxenitic mantle lithologies—an indicator of magmatic and metasomatic processes. Chem. Geol. 166, 47–64.

Seitz, H.-M., Altherr, R., Ludwig, T., 1999. Partitioning of transition metals between orthopyroxene and clinopyroxene in peridotitic and pyroxenitic xenoliths: empirical trace element geothermometers. Geochim. Cosmochim. Acta 63, 3967–3982.

Seitz, H.-M., Brey, G.P., Stachel, T., Harris, J.W., 2003. Li abundances in inclusions in diamonds from the upper and lower mantle. Chem. Geol. 201, 307–318.

Stosch, H.-G., 1980. Zur Geochemie der ultrabasischen Auswürflinge des Dreiser Weihers in der Westeifel: Hinweise auf die Evolution des kontinentalen oberen Erdmantels: Dissertation, Universität Köln, pp. 232.

Stosch, H.-G., 1987. Constitution and evolution of subcontinental upper mantle and lower crust in areas of young volcanism: Differences and similarities between the Eifel (F.R. Germany) and Tariat depression (central Mongolia) as evidence by peridotite and granulite xenoliths. Fortschr. Mineral. 65, 49–86.

Stosch, H.-G., Lugmair, G.W., 1986. Trace element and Sr and Nd isotope geochemistry of peridotite xenoliths from Eifel (West Germany) and their bearing on the evolution of the subcontinental lithosphere. Earth Planet. Sci. Lett. 80, 281–298.

Stosch, H.-G., Carlson, R.W., Lugmair, G.W., 1980. Episodic mantle differentiation: Nd and Sr isotopic evidence. Earth Planet. Sci. Lett. 41, 263–271.

Sywall, M.A., 1996. Variation der lithium-isotopenzusammensetzung in der natur: Konsequenzen für den globalen lithium-kreislauf. Papierflieger, Clausthal-Zellerfeld. 97 pp.

Teng, F.-Z., McDonough, W.F., Rudnick, R.L., Dalpé, C., Tomascak, P.B., Chappell, B.W., Gao, S., 2004. Lithium isotopic composition and concentration of the upper continental crust. Geochim. Cosmochim. Acta (in press).

Tomascak, P.B., Langmuir, C.H., 1999. Lithium isotope variability in MORB. EOS 80, F1086–F1087.

Tomascak, P.B., Carlson, R.W., Shirey, S.B., 1999. Accurate and precise determination of Li isotopic compositions by multi-collector sector ICP-MS. Chem. Geol. 158, 145–154.

Tomascak, P.B., Widom, E., Benton, L.D., Goldstein, L.D., Ryan, J.G., 2002. The control of lithium budgets in island arcs. Earth Planet. Sci. Lett. 196 (3–4), 227–238.

Woodland, A.B., Seitz, H.-M., Altherr, R., Marschall, H., Olker, B., Ludwig, T., 2002. Li abundances in eclogite minerals: a clue to a crustal or mantle origin? Contrib. Mineral. Petrol. 143, 587–601.

Witt-Eickschen, G., Seck, H.A., Mezger, K., Eggins, S.M., Altherr, R., 2003. Lithospheric mantle evolution beneath the Eifel (Germany): constraints from Sr–Nd–Pb isotopes and trace element abundances in spinel peridotite and pyroxenite xenoliths. J. Petrol. 44, 1077–1095.

Zack, T., Tomascak, P.B., Rudnick, R.L., McDonough, W.F., 2001. Li isotope fractionation during slab dehydration? Implications from studies of subduction-related eclogites and associated garnet mica shists. Eleventh Annual Goldschmidt Conference, LPI Contribution 1088 (CD-Rom). Lunar and Planetary Institute, Houston, TX, pp. 3768.

Zack, T., Tomascak, P.B., Rudnick, R.L., Dalpe, C., McDonough, W.F., 2003. Extremely light Li in orogenic eclogites: the role of isotope fractionation during dehydration in subducted oceanic crust. Earth Planet. Sci. Lett. 208 (3–4), 279–290.