

# Tracking the lithium isotopic evolution of the mantle using carbonatites

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## Abstract

Carbonatites are mantle-derived, intraplate magmas that provide a means of documenting isotopic variations of the Earth's mantle through time. To investigate the secular Li isotopic evolution of the mantle and to test whether Li isotopes document systematic recycling of material processed at or near the Earth's surface into the mantle, we analyzed the Li isotopic compositions of carbonatites and spatially associated mafic silicate rocks. The Li isotopic compositions of Archean (2.7 Ga) to Recent carbonatites ( $\delta^7\text{Li}=4.1\pm 1.3$  ( $n=23$ ,  $1\sigma$ )) overlap the range typical for modern mantle-derived rocks, and do not change with time, despite ongoing crustal recycling. Thus, the average Li isotopic composition of recycled crustal components has not deviated greatly from the mantle value ( $\sim+4$ ) and/or Li diffusion is sufficiently fast to attenuate significant heterogeneities over timescales of  $10^8$  years. Modeling of Li diffusion at mantle temperatures suggests that limited  $\delta^7\text{Li}$  variation in the mantle through time reflects the more effective homogenization of Li in the mantle compared to radiogenic isotope systems. The real (but limited) variations in  $\delta^7\text{Li}$  that exist in modern mantle-derived magmas as well as carbonatites studied here may reflect isotopic fractionation associated with shallow-level processes, such as crustal assimilation and diffusive isotopic fractionation in magmatic systems, with some of the scatter possibly related to low-temperature alteration.

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## 1. Introduction

Lithium (Li) is an incompatible element that is typically enriched 10 to 50-fold in crustal rocks ( $\sim 35$  ppm for upper continental crust) (Teng et al., 2004) compared to

mantle samples (1–2 ppm) (Jagoutz et al., 1979; Ottolini et al., 2004). Subducted sediments and metamorphosed basaltic rocks have high Li contents (up to 80 ppm) and diverse Li isotopic compositions ( $\delta^7\text{Li}=-12$  to  $+21$ ) (Bouman et al., 2004; Chan et al., 2002; Chan et al., 2006; Zack et al., 2003). These findings have fueled speculation that the mantle, as sampled by diverse families of basalts, may record a secular change in its Li isotopic composition as progressively more Li is recycled through subduction zones (Elliott et al., 2004). Modeling the mantle's Li

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isotopic composition through time on the basis of the riverine flux of Li into the oceans, Elliott et al. (2004) found that significant changes in  $\delta^7\text{Li}$  of restricted mantle regions may be expected if subducted material is not efficiently mixed into the mantle. Indeed, Li isotope evidence for recycling of subduction-modified mantle into the source of mid-ocean ridge basalts (MORBs) has been suggested locally (Elliott et al., 2006), although there is a notable lack of correlation between Li isotopes and other geochemical tracers in MORBs on a global scale (Tomascak et al., in press).

Carbonatitic magmatism occurs over a wide span of geologic time and is considered to originate in mantle source regions comparable to those of intraplate and ocean island basalts (OIB) (e.g., Nelson et al., 1988). Carbonatites have been previously used to monitor the Sr, Nd and Pb isotopic evolution of the mantle through time (Bell and Blenkinsop, 1987; Bell and Blenkinsop, 1989; Bell and Tilton, 2002). A number of carbonatites, including the so-called “Reference carbonatites” (Bell and Tilton, 2002) and those from East Africa, contain a HIMU (high  $\mu$  = high  $^{238}\text{U}/^{204}\text{Pb}$ ) isotopic component, which is commonly interpreted to reflect recycling of oceanic lithosphere (Hofmann, 2003; Sun and McDonough, 1989). Hence, these carbonatites may also be useful for tracing crustal recycling. Advantages of using carbonatites over silicate rocks to monitor mantle isotopic evolution are their extremely low viscosities, low temperatures and low densities compared to those of silicate melts (e.g., Genge et al., 1995; Krafft and Keller, 1989). This favors their rapid rise to the surface and hence reduces interaction with continental crust (Bell and Tilton, 2002). Moreover, carbonatite melts can separate from mantle sections as thick as 100 km (McKenzie, 1985). Therefore, carbonatitic melts will sample a sufficiently large region of mantle to homogenize any small-scale Li isotopic heterogeneities that may exist, such as those observed in peridotite xenoliths and massif peridotites (Lundstrom et al., 2005; Nishio et al., 2004; Rudnick and Ionov, 2007). Carbonatites thus provide a robust average mantle composition.

In this study, we investigate carbonatites and spatially associated primitive mafic rocks with ages ranging from the Archean (2.7 Ga) to the present in order to track the Li isotopic evolution of the Earth’s mantle. We find that Li isotopic compositions of carbonatites remain constant through time, suggesting that subduction processes and crustal recycling have not significantly influenced the mantle’s Li isotopic composition.

## 2. Samples

Most of the samples analyzed in this study were previously characterized in a variety of petrological, geochemical and isotopic studies. Sample locations and descriptions as well as new and published major and trace element data can be found in the Supplementary material. The oldest samples (2.7 Ga) are Archean carbonatites from the Dolodau and Lac Shortt occurrences in Canada (Tilton and Bell, 1994). Proterozoic samples (1.3–1.2 Ga) comprise silico-carbonatites from the 1.87 Ga old Borden complex (Canada) (Bell et al., 1987), and carbonatites, mafic dikes and basaltic lavas from the Gardar Province, South Greenland (Halama et al., 2003, 2004, 2005). Phanerozoic samples include a ~366 Ma old carbonatite from Sokli (Finland), Tertiary carbonatites from Fuerteventura (Canary Islands, Spain) (Demény et al., 1998), and alkaline silicate rocks and carbonatites from the Kaiserstuhl complex (Germany) (Schleicher et al., 1990). Moreover, various carbonatites from East Africa, spanning an age range from 1040 Ma to the present day (Bell and Tilton, 2001), were analyzed. Samples from Oldoinyo Lengai (Tanzania), the world’s only active carbonatite volcano, for which Li isotope data have previously been presented by Halama et al. (2007), are included in the data set.

## 3. Analytical methods

Methods used for the determination of major and trace element concentrations are outlined in the Supplementary material. Analytical procedures for C and O isotopic

Table 1  
Lithium isotopic compositions of solution and rock standards measured

Sample	Material	$\delta^7\text{Li}$ (this study) <sup>a</sup>	<i>n</i>	<i>n<sub>r</sub></i>	$\delta^7\text{Li}$ (published values)	References
IRMM-016	Standard solution	+0.3±0.9	44		-0.1±0.2	1–3
UMD-1	Standard solution	+54.8±1.0	44		+54.7±1.0	2,3
BHVO-1	Basalt	+4.4±0.7	7	2	+4.3±1.0 to +5.8±1.9	2–6
STM-1	Nepheline syenite	+4.1±1.1	13	3		

<sup>a</sup>Uncertainty is  $2\sigma$  standard deviation; *n*=number of analyses, *n<sub>r</sub>*=number of replicate sample preparations; published values represent averages along with  $2\sigma$  standard deviations; References: 1 = Qi et al. (1997), 2 = Rudnick et al. (2004), 3 = Teng et al. (2004), 4 = James and Palmer (2000), 5 = Chan and Frey (2003), 6 = Bouman et al. (2004).

Table 2  
Li concentration and Li–O–C–Nd isotope data of the sample suite

Sample	Locality	Rock type	Material	Age (Ma)	Li (ppm)	$\delta^7\text{Li}$	$\delta^{18}\text{O}$ WR	$\delta^{13}\text{C}$ WR	$\varepsilon_{\text{Nd}}$ (T)	References
<i>Canada</i>										
DOD 77	Dolodau	Calcite carbonatite	WR	2680	5.8	4.7	9.7	−3.7	2.6	1
DOD 77 repl.	Dolodau	Calcite carbonatite	WR	2680	5.5	5.6 / 5.7				1
DOD 91	Dolodau	Silico-carbonatite	WR	2680	0.7	4.8	9.0	−3.9	2.4	1
LSC 20	Lac Shorrt	Calcite carbonatite	WR	2680	7.0	1.5	11.4	−6.0	2.0	1
LSC 20 repl.	Lac Shorrt	Calcite carbonatite	WR	2680	6.2	2.1				1
LSC 108	Lac Shorrt	Calcite carbonatite	WR	2680	7.3	3.6	11.8	−5.4	4.3	1
BO 202	Borden	Silico-carbonatite	Biotite	1872	3.1	4.2	7.8 <sup>a</sup>	−4.0 <sup>a</sup>	2.8	2
BO 204	Borden	Silico-carbonatite	Biotite	1872	14	6.2	8.2 <sup>a</sup>	−4.4 <sup>a</sup>	2.8	2
<i>Gardar Province, Greenland</i>										
GR 46	Grønnedal-Ika	Calcite carbonatite	WR	1299	2.0	3.0	7.1	−5.0	2.7	3
GR 70	Grønnedal-Ika	Calcite carbonatite	Calcite	1299	0.08		8.6	−4.3		3
GR 73	Grønnedal-Ika	Calcite carbonatite	WR	1299	0.6	3.4	8.4	−4.3	2.8	3
GR 73	Grønnedal-Ika	Calcite carbonatite	Calcite	1299	0.09		8.3	−4.4		3
GR 74	Grønnedal-Ika	Calcite carbonatite	WR	1299	0.7	4.3	6.6	−4.7	2.4	3
EF 024	Eriksfjord basalts	Basalt	WR	1200	9.6	2.8	4.3		−3.2	4,5
EF 039	Eriksfjord basalts	Basalt	WR	1200	10.2	2.5			−2.2	4,5
EF 072	Eriksfjord basalts	Basalt	WR	1200	7.6	5.3	5.5		−1.2	4,5
EF 168	Eriksfjord basalts	Trachybasalt	WR	1200	43	0.2 / −0.5	3.8		−0.1	4,5
GM 1684	Isortoq dike swarm	Larvikite	WR	1190	10	5.3 / 4.6	7.2		−10.7	6
GM 1684	Isortoq dike swarm	Larvikite	Cpx	1190	10	2.9 / 2.6			−10.7	6
GM 1735	Isortoq dike swarm	Olivine gabbro	WR	1190	8.9	3.2 / 4.0			−3.7	6
GM 1735	Isortoq dike swarm	Olivine gabbro	Cpx	1190	13	5.5 / 4.4			−3.7	6
GM 1760	Isortoq dike swarm	Olivine gabbro	WR	1190	9.9	1.8 / 1.7			−1.8	6
GM 1760	Isortoq dike swarm	Olivine gabbro	Cpx	1190	8.7	4.6 / 3.5			−1.8	6
GM 1803	Isortoq dike swarm	Olivine gabbro	WR	1190	13	3.9	6.2		0.3	6
GM 1803 repl.	Isortoq dike swarm	Olivine gabbro	WR	1190	15	4.0 / 3.8				6
GM 1803	Isortoq dike swarm	Olivine gabbro	Cpx	1190	7.8	7.8 / 8.6			0.3	6
GM 1803 repl.	Isortoq dike swarm	Olivine gabbro	Cpx	1190	7.8	8.0				6
<i>East African Rift</i>										
VS 377	Ngualla	Calcite carbonatite	WR	1040	1.2	5.7	7.8	−4.7	0.4	7
N 1295	Chilwa	Calcite carbonatite	WR	138	1.3	−0.3 / −0.1	12.4	−2.7	4.1	8
PH 212	Panda Hill	Calcite carbonatite	WR	116	1.2	3.3	7.8	−4.7	0.4	9
PH 212 repl.	Panda Hill	Calcite carbonatite	WR	116	1.3	2.9				9
PH 213	Panda Hill	Calcite carbonatite	WR	116	0.6	2.9	8.1	−4.7	0.3	9
SU 103	Sukulu	Calcite carbonatite	WR	40	0.7	5.2	7.9	−3.0	3.9	9
DU 365	Toror	Ferrocarnatite	WR	40	10.7	0.0	15.6	−2.4	−0.7	9
HB	Homa Bay	Calcite carbonatite	WR	13	1.5	2.7	8.7	−2.5	−3.7	9
OL 123	Oldoinyo Lengai	Natrocarnatite	WR	0	211	4.8	8.6	−7.0	0.2 <sup>b</sup>	10,11
OL 148	Oldoinyo Lengai	Natrocarnatite	WR	0	292	4.4	7.4	−7.0	0.2 <sup>b</sup>	10,11
OL 148 repl.	Oldoinyo Lengai	Natrocarnatite	WR	0	283	4.8				10,11
OL 259	Oldoinyo Lengai	Natrocarnatite	WR	0	244	4.9	7.4	−6.9	0.2 <sup>b</sup>	10,11
OL 259 repl.	Oldoinyo Lengai	Natrocarnatite	WR	0	294	5.1				10,11
OL 2	Oldoinyo Lengai	Natrocarnatite	WR	0	282	3.6	9.2	−7.0	0.8	10,11
OL 7	Oldoinyo Lengai	Natrocarnatite	WR	0	255	3.3	9.3	−6.9	0.8	10,11
OL 352	Sinja Eledoi	Olivine melilitite	WR	0	21	3.5			2.5 <sup>c</sup>	11,12
OL 352 repl.	Sinja Eledoi	Olivine melilitite	WR	0	21	3.3				11,12
OL198	Dorobo cone	Olivine melilitite	WR	0	23	4.3			2.5	11,12
OL 343	Dorobo cone	Olivine melilitite	WR	0	14	2.4			2.5 <sup>c</sup>	11,12
OL 12/2 K	Amykon Hill	Olivine melilitite	WR	0	17	4.4			2.6	11,12
<i>Kaiserstuhl, Germany</i>										
K1	Föhrenberg/Ihringen	Olivine tephrite	WR	17	18	6.8 / 6.4	10.5		3.0	13
K1 repl.	Föhrenberg/Ihringen	Olivine tephrite	WR	17	17	5.1 / 6.0			3.0	13

Table 2 (continued)

Sample	Locality	Rock type	Material	Age (Ma)	Li (ppm)	$\delta^7\text{Li}$	$\delta^{18}\text{O}$ WR	$\delta^{13}\text{C}$ WR	$\epsilon_{\text{Nd}}$ (T)	References
<i>Kaiserstuhl, Germany</i>										
K1	Föhrenberg/Ihringen	Olivine tephrite	Cpx	17	13	0.3				13
K2	Lützelberg	Olivine nephelinite	WR	17	21	2.1	8.2		4.6	13
K3	Limberg	Limburgite	WR	17	14	3.3	7.2		4.6	13
K3	Limberg	Limburgite	Cpx	17	2.9	−6.0 / −6.1				13
K4	Limberg	Clinopyroxene megacryst	Cpx	17	1.4	3.5 / 2.9			5.4	13
K4 repl.	Limberg	Clinopyroxene megacryst	Cpx	17	1.6	3.3 / 3.0			5.4	13
K5	Badloch	Calcite carbonatite	WR	17	0.2	4.4	8.4	−6.0	3.4	13
<i>Fuerteventura, Canary Islands</i>										
96/31 bt	Punta del Peñon Blanco	Sheared carbonatite	biotite	23	119	7.1 / 6.2	6.5 <sup>a</sup>	−6.3 <sup>a</sup>	5.2 <sup>d</sup>	14,15
96/31 bt repl.	Punta del Peñon Blanco	Sheared carbonatite	biotite	23	118	6.6 / 6.9	6.5 <sup>a</sup>	−6.3 <sup>a</sup>	5.2 <sup>d</sup>	14,15
96/51 bt	Esquinzo complex	Calcite carbonatite	biotite	23	175	4.5 / 4.3	7.6 <sup>a</sup>	−4.7 <sup>a</sup>	5.2 <sup>d</sup>	14,15
97/3 bt	Caleta de la Cruz	Calcite carbonatite	biotite	23	78	0.9 / 1.8	7.3 <sup>a</sup>		5.2 <sup>d</sup>	14,15
<i>Kola Alkaline Province</i>										
SO	Sokli	Carbonatite	WR	366	31	4.4 / 4.9	11.3	−3.3	6.4 <sup>c</sup>	16

Age data,  $\epsilon_{\text{Nd}}$  values, and some of the C–O isotope data are from the literature sources given in the last column. Replicate analysis of samples that involve column chemistry using an aliquot of the stock solution, is reported as “repl.”. Two values for  $\delta^7\text{Li}$  refer to measurements of the same sample solutions on different days. References: 1 = Tilton and Bell (1994), 2 = Bell et al. (1987), 3 = Halama et al. (2005), 4 = Halama et al. (2003), 5 = Graser and Markl (2008), 6 = Halama et al. (2004), 7 = van Straaten (1989), 8 = Simonetti and Bell (1994), 9 = Bell and Tilton (2001), 10 = Bell and Simonetti (1996), 11 = Halama et al. (2007), 12 = Keller et al. (2006), 13 = Schleicher et al. (1990), 14 = Demény et al. (1998), 15 = Demény et al. (2004), 16 = Kramm et al. (1993). <sup>a</sup>=analyses of separated calcite, <sup>b</sup>= $\epsilon_{\text{Nd}}$  is an average of 9 natrocarbonatites from Bell and Simonetti (1996), <sup>c</sup>= $\epsilon_{\text{Nd}}$  is an average of 4 olivine mellilitites from Keller et al. (2006), <sup>d</sup>= $\epsilon_{\text{Nd}}$  is an average of 6 carbonatites analyzed by Hoernle and Tilton (1991). <sup>e</sup>= $\epsilon_{\text{Nd}}$  is an average of 3 analyses by Kramm et al. (1993).

analyses of carbonatite samples are described by Halama et al. (2007). C and O isotope compositions are reported in the standard  $\delta$ -notation relative to PDB and V-SMOW, respectively. Sample analyses are bracketed by several analyses of the NBS-19 carbonate standard, which gave  $\delta^{13}\text{C}_{\text{PDB}} = +2.73 \pm 0.14$  ( $2\sigma$ ,  $n = 7$ ) and  $\delta^{18}\text{O}_{\text{V-SMOW}} = +28.50 \pm 0.16$  ( $2\sigma$ ,  $n = 7$ ). Sample values were corrected for the offset from the accepted values ( $\delta^{13}\text{C}_{\text{PDB}} = +1.95$  and  $\delta^{18}\text{O}_{\text{V-SMOW}} = +28.6$ ). Oxygen isotope compositions of powdered silicate whole-rock samples were determined by a conventional method modified after Clayton and Mayeda (1963) and Vennemann and Smith (1990), using  $\text{BrF}_5$  as reagent and converting the liberated oxygen to  $\text{CO}_2$ . Mass spectrometric analyses were carried out on a Finnigan MAT 252 mass spectrometer at the University of Tübingen.

Preparation and digestion of whole rocks and separated minerals for Li isotopic analyses, as well as column chemistry methods, are described by Rudnick et al. (2004). Details of the instrumental analysis are given by Teng et al. (2004). Measurements were carried out at the University of Maryland using a Nu Plasma MC-ICP-MS. Each sample analysis is bracketed before and after by

measurements of the L-SVEC standard and the  $\delta^7\text{Li}$  value of the sample is calculated relative to the average of these two bracketing L-SVEC runs. Two standard solutions, IRMM-016 (Qi et al., 1997) and the in-house UMD-1 standard (a purified Li solution from Alfa Aesar<sup>®</sup>) were routinely analyzed during the course of an analytical session. Results for both and for international rocks standards measured during the course of this study are presented in Table 1. Li concentrations were determined by comparing signal intensities of sample solutions with a 50 ppb L-SVEC solution and then adjusting for sample weight. The accuracy of this method was established by Teng et al. (2004) as being  $\pm 5\%$  based on isotope dilution methods, and the precision is  $< \pm 10\%$  (Teng et al., 2006).

## 4. Results

### 4.1. Oxygen and carbon isotopes

$\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the carbonatites range from  $-7.0$  to  $-2.4$  and  $+6.5$  to  $+15.6$ , respectively (Table 2). Most samples fall into the range commonly assumed to reflect mantle C–O isotopic composi-

tions of primary magmatic carbonatites ( $\delta^{13}\text{C}=-8$  to  $-4$ ,  $\delta^{18}\text{O}=+5.5$  to  $+10$ ) (Keller and Zaitsev, 2006; Taylor et al., 1967). Three samples fall outside this range for both C and O isotopes (samples N 1295, DU 365, SO). Mafic silicate rocks have a relatively large spread in  $\delta^{18}\text{O}$  values between  $+3.8$  and  $+10.5$  (Table 2), when compared to typical  $\delta^{18}\text{O}$  values for mantle-derived basalts ( $+4.7$  to  $+6.1$ ) (Eiler et al., 1997; Eiler et al., 2000). This variability in  $\delta^{18}\text{O}$  is similar to whole-rock analyses of basaltic rocks from various intraplate settings, which has been demonstrated as being unlikely to reflect mantle values (Eiler et al., 1997).

#### 4.2. Lithium concentrations

Li concentrations of calcite carbonatites are generally low ( $<10$  ppm), whereas those of sodic carbonatites (natrocarbonatites) are high ( $>100$  ppm), comparable to Li concentrations reported by Simonetti et al. (1997) (Table 2). Our data and the compilation by Cooper et al. (1995) indicate that Li concentrations in carbonatites are highly variable, which is not surprising given the uneven distribution of Li-bearing phases in carbonatites. There is a relative enrichment of Li in some carbonatites compared to mantle-derived basalts, but no clear relation between Li content and age. Li contents in separated calcite from carbonatites are  $<0.1$  ppm, suggesting that Li is highly incompatible in calcite, and that this incompatibility controls the Li budget in calcite carbonatites. In silicate rocks, Li is a moderately incompatible element that typically shows enrichment in basaltic rocks over their sources by a factor of  $\sim 5$ , and higher concentrations in more differentiated silicic rocks. Most of the mafic silicate rocks analyzed in this study (East African Rift, Greenland and Germany) have Li contents between 7 and 21 ppm (Table 2).

The Li concentrations of biotites from carbonatites of the Canary Islands are high (78 to 175 ppm), whereas two biotites from silico-carbonatites of the Borden Complex are comparatively low (3–14 ppm). Clinopyroxenes from Gardar mafic dike rocks have Li contents (8–13 ppm) similar to their whole rocks. In contrast, clinopyroxenes from mafic lavas of the Kaiserstuhl complex have lower Li concentrations than their whole rocks. Clinopyroxene megacrysts from the Kaiserstuhl contain  $\sim 1.5$  ppm Li, typical of mantle clinopyroxenes (Ottolini et al., 2004).

#### 4.3. Lithium isotopic compositions

$\delta^7\text{Li}$  whole-rock values of carbonatites and spatially associated mafic igneous rocks range from 0 to  $+7$

(Table 2). Thirty-three of 36 samples fall into the compositional range typical of present day mantle-derived basalts ( $+2$  to  $+7$ ; Fig. 1) (Chan et al., 1992; Moriguti and Nakamura, 1998; Nishio et al., 2005; Tomascak, 2004; Tomascak et al., in press). The two carbonatites (samples N 1295 and DU 365) and one trachybasalt (sample EF 168) with lighter Li isotopic compositions ( $\delta^7\text{Li}\sim 0$ ) that fall outside this range also show deviations in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  from typical mantle values (see below). Biotite from carbonatites and silico-carbonatites has  $\delta^7\text{Li}$  values that vary from  $+1$  to  $+7$ . In contrast, clinopyroxene from mafic lavas shows a much larger spread in  $\delta^7\text{Li}$  from  $-6$  to  $+8$ .

The Li isotopic compositions of carbonatites are, on average, indistinguishable from each other (Table 3). Whole rocks give an average  $\delta^7\text{Li}$  of  $4.0\pm 1.1$  ( $n=18$ ,  $1\sigma$ ), and the global average including the biotites is  $\delta^7\text{Li}=4.1\pm 1.3$  ( $n=23$ ,  $1\sigma$ ). There is no systematic change in  $\delta^7\text{Li}$  of carbonatites as a function of age from Archean to present

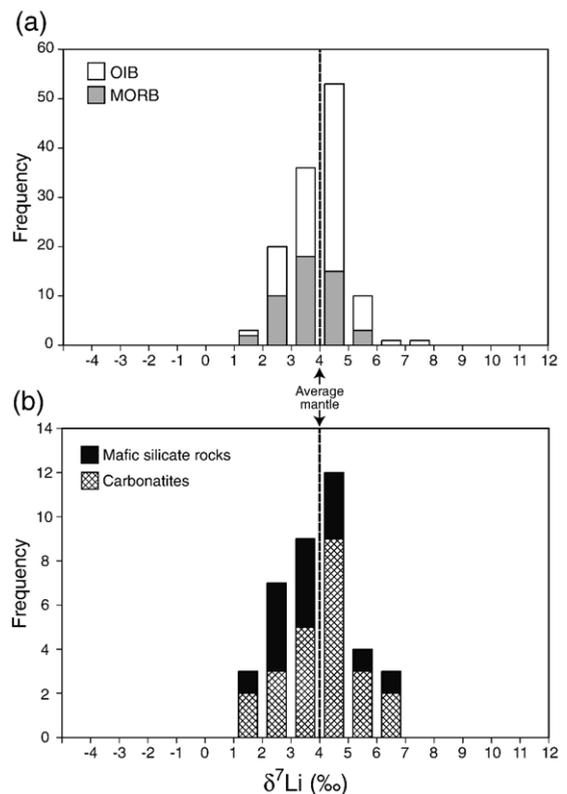


Fig. 1. Frequency distribution diagrams of  $\delta^7\text{Li}$  values for a) MORB (Elliott et al., 2006; Nishio et al., 2007; Tomascak et al., in press) and OIB (Chan and Frey, 2003; Nishio et al., 2005; Tomascak et al., 1999) and b) carbonatites and mafic silicate rocks from this study (three samples with low  $\delta^7\text{Li}$  and petrographic and C–O isotopic evidence for near-surface alteration are excluded from the plot — see text for discussion). The dashed line indicates the average mantle value of  $\sim +4$ .

Table 3

Average Li isotopic compositions of carbonatites and associated alkaline silicate rocks

	Average	$\pm$	n
	$\delta^7\text{Li}$	(1 $\sigma$ )	
<i>Carbonatites</i>			
Archean (>2500 Ma)	3.9	1.5	4
Proterozoic (545–2500 Ma)	4.5	1.3	6
Mesozoic (65–248 Ma)	3.0	0.1	2
Tertiary (1.8–65 Ma)	4.1	1.9	6
Quaternary (<1.8 Ma)	4.3	0.8	5
Global carbonatites	4.1	1.3	23
<i>Carbonatites and silicate rocks</i>			
Canada Archean (2680 Ma)	3.9	1.5	4
Canada Proterozoic (1870 Ma)	5.2	1.4	2
Greenland carbonatites (1299 Ma)	3.6	0.7	3
Greenland basaltic lavas (1200 Ma)	3.5	1.5	3
Greenland mafic dikes (1190 Ma)	3.6	1.3	4
Canary Islands (23 Ma)	4.1	2.7	3
Kaiserstuhl (17 Ma)	4.0	1.7	4
EAR carbonatites (1040–0 Ma)	4.1	1.1	10
EAR olivine melilitites (0 Ma)	3.6	0.9	4

EAR=East African Rift.

(Fig. 2). The average  $\delta^7\text{Li}$  values of mafic silicate rocks overlap those of the spatially associated carbonatites.

## 5. Discussion

In order to use the measured  $\delta^7\text{Li}$  of carbonatites to probe the composition of their mantle source regions,

the differences between phenocrysts and whole rocks need to be interpreted. In addition, the degree to which the whole-rock  $\delta^7\text{Li}$  values have been affected by shallow processes such as weathering/alteration or magmatic differentiation and crustal assimilation must be established. We address each of these topics, in turn.

### 5.1. Phenocrysts versus whole rock

Analyses of phenocrysts are often used to characterize magmatic stable isotope signatures because phenocrysts are less sensitive to low-temperature alteration and secondary water uptake than bulk rocks (Eiler et al., 1997). However, several recent studies have shown that the  $\delta^7\text{Li}$  values of igneous olivines and clinopyroxenes are highly variable, generally isotopically light relative to the whole rocks, and they show significant zonation due to the effects of Li diffusion during cooling (Beck et al., 2006; Halama et al., 2007; Jeffcoate et al., 2007; Parkinson et al., 2007). Thus, olivine and pyroxene phenocrysts may not be reliable tracers of magmatic  $\delta^7\text{Li}$ , and kinetic Li isotope fractionation by diffusion is a likely explanation for the large spread in  $\delta^7\text{Li}$  of the clinopyroxenes analyzed here. We therefore use only the whole-rock data for the mafic silicate rocks in further discussion.

In calcite carbonatites, there is a broad positive correlation between Li and  $\text{K}_2\text{O}$  (Fig. 3), which is consistent with silicate minerals (mica and/or amphibole) being the main carriers of Li in these rocks. Given the high Li contents of biotites (up to 175 ppm), particularly

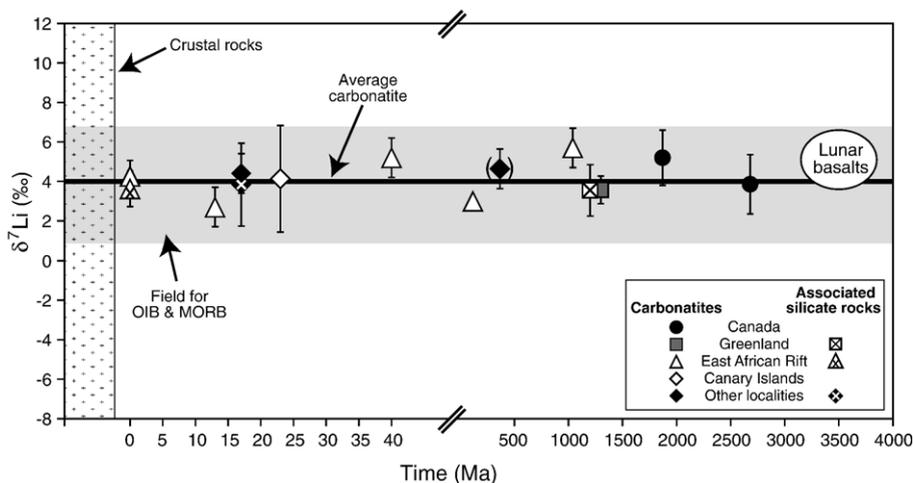


Fig. 2. Plot of time vs.  $\delta^7\text{Li}$ . The symbols represent averages for the respective localities with one standard deviation as error bars. The thick black line is the average of the carbonatite whole-rock data ( $\delta^7\text{Li}=+4.0$ ). Lithium isotopic compositions of OIB and MORB (data from Chan et al., 1992; Chan and Frey, 2003; Moriguti and Nakamura, 1998; Nishio et al., 2005; Tomascak, 2004 and crustal rocks (data from Teng et al., 2004, in review) are shown for comparison without any time implication. The total range in  $\delta^7\text{Li}$  for crustal rocks is  $-18$  to  $+20$ . Also shown are data for lunar basalts (Magna et al., 2006; Seitz et al., 2006). Note that sample SO (in parentheses) plots within the normal mantle range, despite elevated C- and O isotopic compositions.

compared to calcite ( $<0.1$  ppm Li), magmatic biotite is most likely to reflect the Li isotopic composition of the host rock. We thus use both biotite and whole-rock data as representative of the  $\delta^7\text{Li}$  of calcite carbonatites.

## 5.2. Alteration

We evaluate whether the  $\delta^7\text{Li}$  of our samples have been affected by alteration by examining the freshness of the samples, their Sr isotopic compositions and the behavior of other stable isotope systems.

The effects of alteration and weathering on the Li isotopic composition of magmatic rocks have been explored in both field-based and experimental studies (e.g., Huh et al., 2004; Pistiner and Henderson, 2003; Rudnick et al., 2004). In the absence of secondary mineral formation, congruent weathering of primary minerals does not change the  $\delta^7\text{Li}$  values of basalts (Pistiner and Henderson, 2003). Preferential incorporation of  $^6\text{Li}$  into clay or oxide-rich alteration products may produce an isotopically light rock during intense weathering in wet regions (e.g., development of laterites; Rudnick et al., 2004), whereas in arid regions, heavy Li may be added to the developing soil in the form of marine aerosols (Huh et al., 2004). All sample localities, except for Fuerteventura, are on continents, so the influence of marine aerosols on whole-rock  $\delta^7\text{Li}$  does not appear to be a factor here. The carbonatite samples are fresh, they retain their primary igneous mineralogy and they do not contain clay minerals. Only two samples, both from eastern Africa, have petrographic features that may indicate late-stage alteration of their isotopic composition. Sample N 1295 ( $\delta^7\text{Li} = -0.2$ ) shows alteration in the form of ankerite-rich veins (Simonetti and Bell, 1994), and sample DU 365 ( $\delta^7\text{Li} = 0$ ) is a ferrocarnatite, suggesting

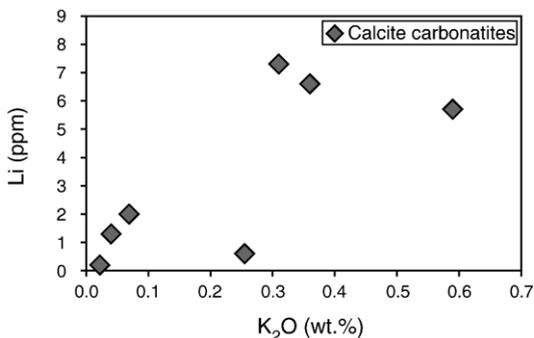


Fig. 3. Plot of Li vs.  $\text{K}_2\text{O}$  contents in calcite carbonatites. A rough positive correlation suggests incorporation of Li in K-bearing phases such as mica, the primary host for K in these rocks.

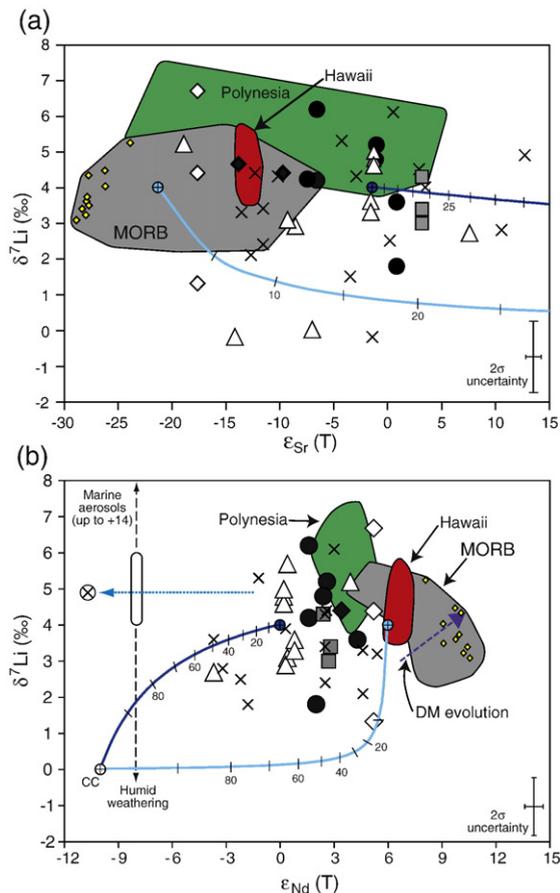


Fig. 4. Radiogenic isotope compositions of carbonatites plotted vs.  $\delta^7\text{Li}$ . Symbols are as in Fig. 2, except for silicate rocks, which are all shown as  $\times$ . The Sr isotopic composition is expressed as  $\epsilon_{\text{Sr}}$ , calculated using  $(^{87}\text{Rb}/^{86}\text{Sr})_{\text{BSE today}} = 0.0827$  and  $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{BSE today}} = 0.7045$ . Data sources: MORB: Elliott et al. (2006); Nishio et al. (2007); Tomascak et al. (in press), and references therein; Hawaii: Bryce et al. (2005); Chan and Frey (2003); Polynesia: Nishio et al. (2005); see Table 3 for data sources of other Nd isotopic data and sample description section (Supplementary material) for Sr isotope data sources. Data from Elliott et al. (2006) are shown as small yellow diamonds. Effects of humid weathering and the addition of marine aerosols in b) are schematically drawn (Huh et al., 2004), assuming no influence of these processes on the Nd isotopic composition. The dashed gray arrow indicates the evolution of the depleted mantle during the last 1.5 Ga based on models from Elliott et al. (2004) for  $\delta^7\text{Li}$  and Goldstein et al. (1984) for  $\epsilon_{\text{Nd}}$ . The most crustally contaminated mafic rock sample from Greenland (GM 1684), marked with a circle, was used to indicate an empirical crustal contamination trend (stippled arrow). Note that the  $\delta^7\text{Li}$  value of this sample is indistinguishable from normal mantle values. The blue lines in a) and b) show modeled mixing trends between carbonatite magma (light blue: calcite carbonatite; dark blue: natrocarbonatite) and continental crust (CC), tick marks reflect 5% (a) and 10% (b) intervals, respectively. Parameters used in the calculations are as follows: Calcite carbonatite: 2000 ppm Sr,  $\epsilon_{\text{Sr}} = -21.3$  ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.703$ ), 100 ppm Nd,  $\epsilon_{\text{Nd}} = +6$ , 2 ppm Li,  $\delta^7\text{Li} = +4$ ; natrocarbonatite: 9000 ppm Sr,  $\epsilon_{\text{Sr}} = -1.4$  ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7044$ ), 50 ppm Nd,  $\epsilon_{\text{Nd}} = 0$ , 200 ppm Li,  $\delta^7\text{Li} = +4$ ; continental crust: 300 ppm Sr,  $\epsilon_{\text{Sr}} = -646$  ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.750$ ), 30 ppm Nd,  $\epsilon_{\text{Nd}} = -10$ , 35 ppm Li,  $\delta^7\text{Li} = +0$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a possible genetic relationship to hydrothermal activity (Simonetti et al., 1995). Thus, based upon the general lack of alteration features, it would appear that weathering has had little effect on Li in these rocks, except samples N 1295 and DU 365, both of which are isotopically light.

Initial Sr isotopic compositions are consistently within the range of typical mantle-derived lavas (Fig. 4a). There is thus no evidence for Rb and/or Sr

mobility, and the mantle-like initial Sr isotopes suggest that these mobile elements have not been significantly affected by weathering or alteration.

The carbon and oxygen isotope compositions of carbonatites show considerable heterogeneity and it needs to be evaluated how these data relate to Li and, in particular, whether the measured Li isotopic compositions reflect mantle values.

The C–O isotopic compositions of primary, mantle-derived carbonatites have been defined based on measurements of natural samples (Keller and Zaitsev, 2006; Taylor et al., 1967). The elevated  $\delta^{18}\text{O}$  values of most carbonatites compared to “normal” mantle ( $\delta^{18}\text{O} = +5.5$ ) is due to a large fractionation (2.2‰) between carbonate magma and mantle olivine at 1000 °C (Rosenbaum et al., 1994). Carbonate melts in equilibrium with “normal” mantle

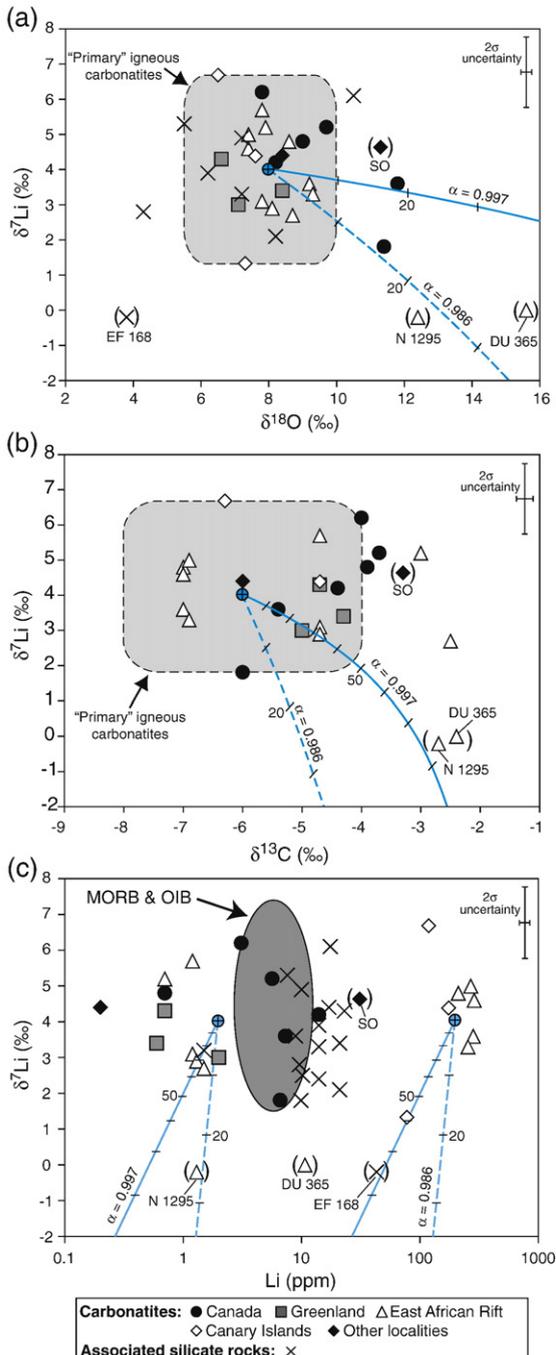


Fig. 5. Lithium vs. a) oxygen and b) carbon isotopic compositions of carbonatites and spatially associated silicate rocks. The light gray field encompasses the composition of “primary” igneous carbonatites, combining published  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values (Keller and Zaitsev, 2006; Taylor et al., 1967) with  $\delta^7\text{Li}$  values from this study (The term “primary” refers to magmatic crystallization as opposed to “secondary” alteration and replacement exchange). Symbols in parentheses denote samples that show evidence of by alteration based on petrography and by having C and O isotopic compositions outside the field of typical mantle values. Note, however, that mantle-derived carbonatite magmas may show significant variations in C and O isotopic compositions and plot outside this field due to fractional crystallization processes (Deines, 1989; Ray and Ramesh, 2000) (see text for discussion). Blue curves are low-temperature alteration models based on the equilibrium fractionation factor between  $\text{CaCO}_3$  and  $\text{H}_2\text{O}$  for O isotopes (+28.6‰; O’Neil et al. 1969) and equilibration with a carbonate with a C isotopic composition of -2‰. Model curves are shown for two different rock-fluid Li isotope fractionation factors, reflecting two extreme values. Solid lines represent calculations using an empirically derived value for  $D_{\text{rock-fluid}}^{\text{Li}}$  of 0.997 (Rudnick et al., 2004), dashed lines use an experimentally derived value of  $D_{\text{rock-fluid}}^{\text{Li}} = 0.986$  (Pistiner and Henderson, 2003). For simplicity, the relative amount of Li lost during the alteration process was equated with the percentage of C and O isotopic equilibration (note that these processes may proceed at different rates). Tick marks show 10% increments, indicating progressive C–O isotopic equilibration between magmatic calcite and water and progressively decreasing amounts of Li left in the rock. c) Lithium concentrations plotted vs. Li isotopic compositions. Note the logarithmic scale on the x-axis. Average values are plotted for samples where replicate analyses were carried out. The field for ocean island basalt (OIB) and mid-ocean ridge basalt (MORB) is based on published data (Chan et al., 1992; Chan and Frey, 2003; Moriguti and Nakamura, 1998; Nishio et al., 2005; Tomascak, 2004). Parentheses mark samples that have both C and O isotopic compositions outside the field of typical mantle values (see text). Blue lines show alteration models for natrocarbonatite (dark blue) and calcicarbonatite (light blue), respectively, using  $D_{\text{rock-fluid}}^{\text{Li}} = 0.997$  (solid lines; Rudnick et al., 2004), dashed lines use an experimentally derived value of  $D_{\text{rock-fluid}}^{\text{Li}} = 0.986$  (Pistiner and Henderson, 2003). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

would thus have  $\delta^{18}\text{O}$  in the range +6 to +9 (Ray and Ramesh, 2000), in agreement with the range defined by natural carbonatites. Alteration and hydrothermal activity usually lead to an increase in  $\delta^{18}\text{O}$  (Demény et al., 1998, Simonetti et al. 1995).

Of the carbonatites investigated here, the vast majority has  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  that fall within the mantle range (Fig. 5), but a few possess heavier  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . Variability in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in carbonatites may be related to source heterogeneity and regional differences (Deines, 1989; Nelson et al., 1988). Moreover, significant variation in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  can be produced by magmatic fractionation (Deines, 1989; Ray and Ramesh, 2000). During fractional crystallization, calcite carbonatite magmas may reach values of +11 to +14 for  $\delta^{18}\text{O}$  and –3 to –1 for  $\delta^{13}\text{C}$  (Ray and Ramesh, 2000). Thus,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values that are heavier than the field of primary igneous carbonatites may reflect crystal fractionation or low-temperature alteration.

We calculated the evolution of the C and O isotope systems during low-T alteration using equilibrium fractionation factors between  $\text{CaCO}_3$  and  $\text{H}_2\text{O}$  (Fig. 5). The equilibrium O isotopic composition of the carbonate depends on temperature and on the origin of the water with which it is equilibrates (magmatic vs. meteoric). Hence, alteration trends can follow different trajectories. For this calculation we chose an equilibration temperature of 25 °C to reflect weathering conditions and a water  $\delta^{18}\text{O}$  of 0, which may represent seawater, or a mixture of magmatic and meteoric waters. The isotopic composition of calcite in equilibrium with this water at 25 °C is  $\delta^{18}\text{O}=28.6$  (O’Neil et al., 1969). For C isotopes, an equilibration value of  $\delta^{13}\text{C}=-2$  is chosen, which is the mid-point between the means of marine and freshwater carbonates (Keith and Weber, 1964) and can be considered as representative for low-T carbonates. The modeled increase in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  is in good agreement with natural observations produced by carbonatite alteration (Keller and Zaitsev, 2006).

Decreasing  $\delta^7\text{Li}$  values during weathering, coupled to decreasing Li concentrations, can be explained by a Rayleigh distillation process (Rudnick et al., 2004). Rock-fluid Li isotope fractionation factors ( $\alpha=(^7\text{Li}/^6\text{Li})_{\text{rock}}/(^7\text{Li}/^6\text{Li})_{\text{H}_2\text{O}}$ ) for terrestrial weathering processes are somewhat variable and range from 0.986 to 0.997 (Pistiner and Henderson, 2003; Rudnick et al., 2004), reflecting the preference of  $^7\text{Li}$  for water over rock. Alteration trends were modeled using both extreme values to cover a reasonable range of possible alteration trends. The lower the fractionation factor, the more rapid the decrease in  $\delta^7\text{Li}$  for a given amount of Li lost to the fluid. For simplicity, the modeled curves assume that the

percentage of Li lost is equal to the percentage of C–O isotope equilibration, i.e. 20% C–O isotope exchange corresponds to 20% Li loss.

The alteration model curves define a negative correlation of  $\delta^7\text{Li}$  with both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . However, the data do not exhibit trends that suggest a decrease in  $\delta^7\text{Li}$  coupled to an increase in  $\delta^{18}\text{O}$  or  $\delta^{13}\text{C}$ . In contrast, a positive  $\delta^7\text{Li}$ – $\delta^{13}\text{C}$  correlation is seen for the Canadian carbonatites, which can therefore not be related to low-T alteration. The models indicate that, relative to analytical uncertainty, low-T alteration will have greater effects on O isotopes compared to Li. Small amounts (<10%) of alteration, however, would be difficult to discern isotopically due to scatter in the data. Nevertheless, the two East African carbonatites that show petrographic evidence for alteration (N 1295 and DU 365), also show the largest degree of isotopic alteration, consistent with petrographic observations. The modeled alteration trends in the  $\delta^7\text{Li}$ – $\delta^{13}\text{C}$  and  $\delta^7\text{Li}$ –[Li] diagrams also suggest that significant low-T isotope exchange (>20%) is required to cause significant variations in  $\delta^7\text{Li}$ , in particular if the Li isotope fractionation factor ( $\alpha$ ) is close to 1. This amount of alteration should then be observed petrographically, as is the case for samples N 1295 and DU 365.

In summary, the lack of petrographic evidence for alteration in all but two low- $\delta^7\text{Li}$  carbonatites, the indication from modeling that significant low-temperature alteration is necessary to alter  $\delta^7\text{Li}$  values, the lack of any trends in the data set consistent with the alteration models, and the fact that nearly all of the petrographically “fresh” samples have mantle-like O or C isotopic compositions leads us to conclude that the effects of low-temperature alteration on Li isotopic compositions of the carbonatites have been minimal. Nevertheless, we adopt a conservative approach and eliminate from further consideration all carbonatites where both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values fall outside the range of primary igneous carbonatites (samples in parentheses in Fig. 1: N 1295 and DU 365 from East Africa and SO from the Kola Alkaline Province), although this may lead to the elimination of purely mantle-derived samples.

A few of the mafic silicate rocks also show signs of incipient alteration (see sample description in the Supplementary material), which may have contributed to the variability in O isotopic compositions. However, only one sample (EF 168 from Greenland) is characterized by an unusually low  $\delta^7\text{Li}$  combined with an elevated Li concentration (43 ppm), which is considerably higher than those of chemically similar rocks. These features suggest secondary Li-uptake and perturbation of the Li isotope system, and this sample has therefore been eliminated from further discussion. For the other samples,

Sr isotopic compositions and Li concentrations consistent with a mantle derivation indicate that the Li isotope system was not significantly disturbed, although a minor influence of weathering cannot be fully excluded.

### 5.3. Magmatic differentiation, crustal assimilation and diffusional fractionation

In contrast to C and O isotopes, Li isotope fractionation is absent at the high temperatures of mantle melting and basalt differentiation (Chan and Frey, 2003; Tomascak et al., 1999). For temperatures down to ~500 °C, Halama et al. (2007) showed that  $\delta^7\text{Li}$  remains constant during differentiation in sodic carbonatite systems. Moreover, Foustoukos et al. (2004) found no Li isotope fractionation during supercritical phase separation. Since the separation of carbonate melt and Na-rich (and probably Li-rich), hydrous fluids occurs at high, magmatic temperatures of 700–900 °C (Veksler and Keppler, 2000), equilibrium Li isotope fractionation is expected to have little effect on  $\delta^7\text{Li}$  values. This is in agreement with experimental studies demonstrating that liquid-vapor phase separation at 400 °C causes negligible Li isotope fractionation of  $\leq 0.5\%$  (Liebscher et al., 2007). Thus,  $\delta^7\text{Li}$  values of carbonatites and associated silicate rocks are unlikely to have been affected by magmatic differentiation processes or syn-crystallization fenitization processes.

Relative to the mantle, the continental crust appears to be isotopically light ( $\delta^7\text{Li} \sim 0$ , Teng et al. 2004). Thus, mantle-derived magmas that assimilate continental crust should evolve toward lighter  $\delta^7\text{Li}$  values, although this shift might be rather limited given that the isotopic differences between crust and mantle are not large. To evaluate this process we calculated mixing curves between upper continental crust and carbonatite magmas (Fig. 4, see caption for mixing parameters). For Li-rich natrocarbonatite magmas, even large amounts (~50%) of mixing with crustal material do not change  $\delta^7\text{Li}$  values outside the analytical uncertainty ( $\pm 1\%$ ). The spread of 2‰ in  $\delta^7\text{Li}$  in the natrocarbonatites would require some 80% of crustal assimilation, which is inconsistent with the major element composition of these lavas. However, taken at face value, the low apparent Li contents of calcicarbonatites mean that significant changes in  $\delta^7\text{Li}$  would occur for moderate degrees (~10%) crustal assimilation in Li-poor calcicarbonatite magma. For example, using the observed Li, Sr and Nd contents of calcicarbonatites, about 10% crustal addition would lower  $\delta^7\text{Li}$  by 2‰, but would cause only minor changes in  $\epsilon_{\text{Sr}}$  and  $\epsilon_{\text{Nd}}$ . Both radiogenic isotope compositions would still fall within the range of “normal” mantle-derived carbonatites. However, primary mantle-

derived carbonatite melts are likely to have high Li contents due to the preference of Li for melt compared to clinopyroxene and olivine (Blundy and Dalton, 2000). Thus, the Li-poor character of the calcicarbonatites is unlikely to be a primary feature of the melt, but related to the cumulate nature of carbonatites and/or Li loss due to fenitization (Cooper et al., 1995). Preferential loss of Li compared to heavier elements of similar incompatibility is also indicated by the low primitive mantle-normalized Li/Y ratios of calcicarbonatites (~0.02–0.1). If the calcicarbonatite magmas originally were more Li-rich, effects of crustal contamination during ascent would be largely buffered.

Although the above modeling shows that crustal assimilation can, in theory, affect  $\delta^7\text{Li}$  values of calcicarbonatites, several physical features of carbonatite magmas, which distinguish them from basaltic magmas, mitigate against their assimilation of crust. These include their low viscosities and consequent rapid ascent to the surface (Genge et al., 1995), which reduces the time for the melt to react with crust. The low magmatic temperatures of carbonatite magmas, 490–540 °C measured in natrocarbonatite lavas (Krafft and Keller, 1989) and 700–950 °C estimated for calcicarbonatites based on oxygen isotope thermometry (Haynes et al., 2003; Demény et al., 2004), significantly inhibit assimilation of crust.

In summary, the  $\delta^7\text{Li}$  values of carbonatites are not likely to have been significantly changed by crustal assimilation because of their distinct physical properties and the likelihood that primary carbonatite magmas are Li-rich. The overlap in  $\delta^7\text{Li}$  of carbonatites with the mantle range is consistent with limited crustal assimilation.

Recent work has demonstrated that diffusion can fractionate Li isotopes at magmatic temperatures in the presence of a concentration or thermal gradient because  $^6\text{Li}$  diffuses up to 3% faster than  $^7\text{Li}$  (e.g., Beck et al., 2006; Lundstrom et al., 2005; Richter et al., 2003; Teng et al., 2006; Jeffcoate et al., 2007; Rudnick and Ionov, 2007). If we consider a batch of ascending carbonatite magma, two scenarios are possible: an initially Li-rich magma would preferentially lose  $^6\text{Li}$  from the melt conduit into the country rock, and erupt with a slightly heavier isotopic composition than that of the initial melt. On the other hand, a Li-poor carbonatite magma may selectively gain  $^6\text{Li}$  by diffusion from the wall rock and hence acquire a lighter  $\delta^7\text{Li}$ . Given that the  $\delta^7\text{Li}$  variations in the carbonatites investigated do not correlate with radiogenic isotopes (indicators of source heterogeneity), then it is possible that this variation is related to diffusion-driven fractionation. Nevertheless, the limited variation in

$\delta^7\text{Li}$  of carbonatites is comparable to that in OIB and MORB, further emphasizing that, like crustal assimilation, diffusional processes have not had large effects on  $\delta^7\text{Li}$  of these carbonatites.

The above observations suggest that the whole-rock carbonatites and associated mafic magmas investigated here record the  $\delta^7\text{Li}$  of their mantle sources, with possible limited ( $\pm 2\%$ ) fractionation associated with crustal assimilation and/or diffusion-related fractionation associated with melt migration (Tomascak et al., in press). We now explore the implications of these data for the evolution of Li in the mantle.

#### 5.4. Recycling of subducted material

It has been suggested that recycling of oceanic lithosphere, particularly the oceanic crustal portion, may change the mantle composition through time (Elliott et al., 2004). Li is partly liberated from the slab during subduction due to dehydration, but a significant amount of Li ( $\sim 45\%$ ) likely remains in the slab to be subducted deeper into the mantle (Marschall et al., 2007a). The Li isotopic composition of subducted material is affected by the relative contributions of different slab components and modifications during the subduction process. Both altered oceanic crust (AOC) and marine sediments are highly variable in their  $\delta^7\text{Li}$  values, spanning a range from  $-2$  to  $+14$  and  $-4$  to  $+15$ , respectively (Chan et al., 1992; Chan et al., 2006). The weighted average for AOC ( $\delta^7\text{Li} = +11$ ; Elliott et al., 2006) is distinct from fresh MORB ( $\delta^7\text{Li} \sim +4$ ), but the global mass-weighted mean for marine sediment ( $\delta^7\text{Li} = +3$ ; Chan et al., 2006) is very similar. During subduction, dehydration reactions may decrease  $\delta^7\text{Li}$  values of the slab, although the extent of such fractionation is currently a matter of debate (Zack et al., 2003; Marschall et al. 2007b), and isotopically heavy, slab-derived fluids may equilibrate with and be absorbed by the mantle wedge (Tomascak et al., 2002), which can be dragged downward by convection and add isotopic heterogeneity to the mantle's Li budget (Elliott et al., 2006). These complexities of Li cycling contribute to the general difficulties of tracking slab components using Li isotopes in arc lavas (Tomascak et al., 2002) or precisely determining which components contributed to magma generation. On a global scale, the compositions of MORB, island arc basalt (IAB) and OIB show a large overlap in  $\delta^7\text{Li}$ , which could possibly mean that there is little compositional contrast between slab input and the mantle (Tomascak, 2004; Chan et al., 2006).

The effects of subduction on the Li isotopic composition of the mantle has been modeled based on the riverine Li flux into the oceans by Elliott et al. (2004),

assuming Li homogenization via mixing during mantle convection. The effects of recycling such a Li flux on the mantle's  $\delta^7\text{Li}$  value would be to increase it by less than  $0.5\%$  for whole-mantle convection or by about  $1.2\%$  for upper mantle convection over 1.5 billion years. The calculated average  $\delta^7\text{Li}$  values from the various localities investigated here (Table 3) are in good agreement with whole-mantle convection scenario, as there is no systematic increase of  $\delta^7\text{Li}$  with decreasing age (Fig. 2). However, isotopic heterogeneities in the mantle might be more easily preserved if mixing is inefficient. For example, a correlation of  $\epsilon_{\text{Nd}}$  values and Li isotopes in basalts at one MOR locality has been interpreted to reflect variable incorporation of subduction-modified mantle into the magma source (Elliott et al., 2006). More commonly, however, any clear correlation between Li isotopes and radiogenic isotope tracers is lacking in individual mantle-derived basalt suites (Chan and Frey, 2003; Nishio et al., 2007; Tomascak et al., in press).

Our data for carbonatites show that neither Nd nor Sr isotopic compositions correlate with  $\delta^7\text{Li}$  (Fig. 4), suggesting the absence of global systematic trends related to the incorporation of recycled material. A distinction between various mantle components, as identified in ocean island basalts (Hofmann, 2003) as well as in carbonatites (Bell and Tilton, 2001; Bell and Tilton, 2002) on the basis of radiogenic isotopes, is also not seen in the  $\delta^7\text{Li}$  values. The lack of a distinct isotopic signature of the depleted MORB mantle (DMM) in the carbonatite mantle source (Bell and Tilton, 2002) suggests that the extraction of continental crust, which is most commonly assumed to have predominantly affected DMM, is unlikely to be reflected in the  $\delta^7\text{Li}$  values of the carbonatites. However, there is real variation in  $\delta^7\text{Li}$  both within the sample set of a particular location as well as between different localities. For example, samples from Fuerteventura show a large spread in  $\delta^7\text{Li}$  ( $+1$  to  $+7$ ), but  $\epsilon_{\text{Nd}}$  values that are nearly constant at  $+5$  (Hoernle and Tilton, 1991). Similar observations were made by Chan and Frey (2003), who found a considerable range for  $\delta^7\text{Li}$  within a very narrow range of Nd and Sr isotopic compositions for OIB from Hawaii (Fig. 4). Thus, it is unlikely that the spread in  $\delta^7\text{Li}$  values reflects specific contributions from subducted components, a conclusion that is also bolstered by the absence of support in other geochemical parameters.

#### 5.5. Li isotope variability in time and space

A first order conclusion gained from these data is that there is no apparent change in the average Li isotopic composition of the mantle with time (Fig. 2). In fact, the

range in the carbonatites from Archean to present ( $\delta^7\text{Li} = +1.3$  to  $+6.7$ ) is almost identical to the range seen in fresh MORB ( $+1.5$  to  $+6.8$ ) and OIB ( $+2.5$  to  $+7.4$ ) (see Chan and Frey, 2003; Elliott et al., 2006; Nishio et al., 2005; Nishio et al. 2007; Tomascak, 2004; Tomascak et al., in press). Moreover, the results for carbonatites and associated mafic silicate rocks demonstrate that the average Li isotopic composition of their mantle sources in Proterozoic and Archean times was similar to the other inner solar system mantle reservoirs (3.15–3.85 Ga old lunar basalts:  $+3.4$  to  $+6.4$ , Mars:  $+3.6$  to  $+6.6$ ; Magna et al., 2006; Seitz et al., 2006). These results imply that recycled Li was effectively homogenized and/or that the average  $\delta^7\text{Li}$  of recycled Li is similar to that of the upper mantle. Thus, the presence of crust and hydrosphere on the Earth apparently has not changed the average Li isotope composition of the Earth's mantle through recycling since the Archean, as evidenced by carbonatites.

In spite of the small variations in average  $\delta^7\text{Li}$  values of carbonatites for the various localities (Table 3), there is a real variability in the Li isotopic composition of mantle-derived melts of all ages, demonstrated by the fact that the range of  $+1$  to  $+7$  for individual carbonatite samples (see also Tomascak (2004) for a review on OIB and MORB data) is greater than analytical uncertainty (typically  $\pm 1\%$ ). This variability is difficult to explain by intrinsic mantle heterogeneities due to the lack of correlation between  $\delta^7\text{Li}$  with other geochemical tracers (the East Pacific MORB data being a possible exception; Elliott et al., 2006). We therefore suggest that this range is produced by Li isotopic fractionation resulting from diffusion during melt transfer and magma storage, as proposed by Tomascak et al. (in press) and discussed in Section 5.3. Indeed, carbonatites may be a sensitive tracer of diffusion processes because of a relatively low melt/rock ratio, whereas diffusion processes in settings with a high ratio of melt to rock such as MORs may be more muted. A natural example of this process has been described in a melt channel within an ophiolite (Lundstrom et al., 2005).

### 5.6. Obliteration of Li heterogeneities via solid-state diffusion at mantle temperatures

Li is one of the fastest diffusing elements in melts (Richter et al., 2003) and mantle minerals (Coogan et al., 2005), so any Li isotopic heterogeneity in the mantle is likely to be erased over relatively short time periods. This property of Li should produce a relatively uniform  $\delta^7\text{Li}$  in mantle-derived rocks, whereas diffusion of radiogenic isotope tracers (e.g., Sr, Nd, Pb) is orders of magnitude slower and those are thus more

likely to record source heterogeneities. To evaluate the preservation of Li heterogeneities at mantle temperatures, diffusion of Li out of a sphere was modeled using equation 6.18 from Crank (1975):

$$\frac{C - C_1}{C_0 - C_1} = 1 + \frac{2\alpha}{\pi r} \cdot \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \cdot \sin \frac{n\pi r}{a} \cdot e^{-\frac{Dn^2\pi^2 t}{a^2}}$$

where  $a$  is the radius of the sphere (representing the introduced Li heterogeneity),  $t$  is the time,  $r$  is the distance from the center of the sphere,  $C_1$  is the initially uniform concentration in the sphere and  $C_0$  is the concentration at the sphere's surface (i.e., in the surrounding mantle). In this model,  $C_0$  is kept constant at 1.5 ppm Li, reflecting the average Li concentration of the mantle (Jagoutz et al., 1979) and  $C_1$  was chosen to be 8 ppm, reflecting the average Li concentration in subducted oceanic crust (Chan et al., 2002). A sphere was chosen in order to represent a heterogeneous blob within the mantle and to take into account radial diffusion, which is not considered by diffusion in a plane sheet. Values for the diffusion coefficient  $D$  are from Coogan et al. (2005) based on diffusion coefficients for Li in clinopyroxene determined experimentally. The rate of lithium diffusion in olivine is uncertain, but most studies suggest it is slower than in clinopyroxene (Jeffcoate et al., 2007; Parkinson et al., 2007; Spandler and O'Neill, 2006; Rudnick and Ionov 2007). For this reason we adopt the Li diffusivity in clinopyroxene (Coogan et al., 2005) for our modeling, and explore how different bulk diffusion coefficients may affect our calculations. The ratio between the diffusion coefficients for  $^7\text{Li}$  and  $^6\text{Li}$  is expressed as  $D_7/D_6 = (m_6/m_7)^\beta$ , where  $m_6$  and  $m_7$  are the atomic masses of  $^6\text{Li}$  and  $^7\text{Li}$ , respectively, and  $\beta$  is an empirical parameter reflecting the isotopic fractionation. Using a value for  $\beta$  of 0.215 as determined for Li diffusion in silicate melts (Richter et al., 2003),  $D_7$  equals 0.967 times  $D_6$ . For the purpose of modeling Li concentration profiles, this small difference between  $D_7$  and  $D_6$  is negligible. Thus, the time in which compositional differences are compensated also gives a good estimate of how long isotopic variations may persist. At a temperature of 1100 °C,  $D$  is  $4.6 \times 10^{-12} \text{ m}^2/\text{s}$  (Coogan et al., 2005), and for higher temperatures, values for  $D$  are calculated by extrapolating the Arrhenius expression given by Coogan et al. (2005):

$$D = 0.029 \cdot e^{\frac{-258000}{RT}},$$

where  $R$  is the gas constant [J/mol K] and  $T$  the temperature [K].  $D$  at 1400 °C is  $2.55 \times 10^{-10} \text{ m}^2/\text{s}$ .

Two diffusion profiles for spheres with radii of 50 and 1000 m, respectively, are shown in Fig. 6. The model assumes that Li is efficiently transported away in the surrounding mantle by convection. Calculations were performed for times of 1 Ma and 100 Ma, respectively, at temperatures ranging from 1100 °C to 1400 °C. The latter value reflects a likely value for the potential temperature of the convecting upper mantle and is a conservative estimate compared to recent temperature determinations for MORB mantle (1453–1475 °C) and mantle plumes (1637–1688 °C) (Putirka, 2005), thereby taking into account that temperatures in the subducted material may be colder than in the surrounding mantle. For the 50 m sphere, the Li concentration differences disappear after 1 Ma at temperatures as low as 1300 °C. In Fig. 6a, the red line traces potential variation at a distance of 25 m from the center of the sphere ( $r/a=0.5$ ), significant gradients in Li concentration are only maintained at temperatures below  $\sim 1250$  °C after 1 Ma. Therefore, at mantle temperatures of approximately 1400 °C, it is unlikely that Li heterogeneities on the scale of  $\sim 50$  m are preserved for more than a couple of million years. Moreover, rates of thermal diffusion are considerably faster (on the order of  $10^{-6}$  m<sup>2</sup>/s; Stacey, 1992), which leads to faster thermal equilibration of subducted material with the surrounding mantle, and in turn to a rapid attenuation of compositional and isotopic gradients.

For the 2 km wide sphere, the diffusion profile is fully equilibrated in less than 100 Ma at mantle temperatures  $>1350$  °C. Thus, it will be difficult for Li heterogeneities on these scales to survive at time-scales relevant for mantle convection, especially in the lower mantle, where temperatures exceed 1400 °C. Moreover, coupled Li and radiogenic isotopic correlations are unlikely to survive given their different rates of diffusivities. Mantle heterogeneities in Li can only be maintained for long periods (circa 100 Ma or more) under low-temperature conditions ( $<1300$  °C) or if very large ( $>2$  km in diameter) bodies remain intact and are not thinned and stirred into the mantle.

The high diffusivity of Li under mantle conditions and the likelihood that diffusion and advection achieve an equilibrium Li distribution may explain why crustal recycling does not appear to show up in  $\delta^7\text{Li}$  of the carbonatite samples. The possibility that recycled Li is effectively sequestered in the mantle and not sampled again by magmatism seems to be unlikely because of the geophysical and geochemical evidence for mantle convection, mass exchange and recycling (e.g., Hofmann, 2003). An implication of these data is that the net flux of subducted Li has approximately

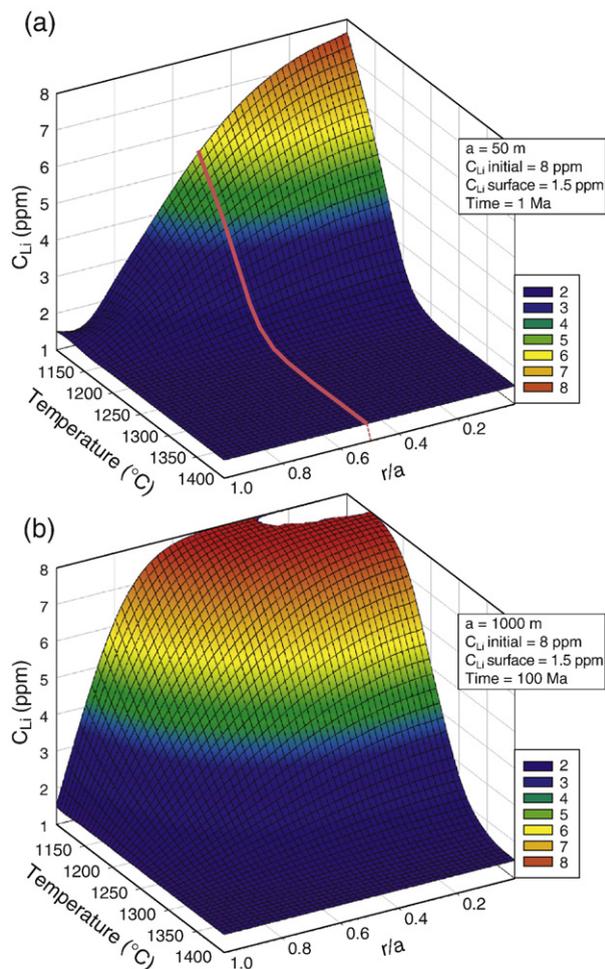


Fig. 6. Diffusion models for 2 spheres (radii of 50 m and 1000 m) with an initial Li concentration of 8 ppm and a constant surface concentration of 1.5 ppm using equation 6.18 from Crank (1975) (see text for discussion). The diffusion surfaces were determined by calculating the Li concentrations in 50 °C intervals from 1100–1400 °C. The  $r/a$  value is a dimensionless parameter based on the sphere's radius  $a$  and the distance from the sphere's center  $r$ , i.e. the surface of the sphere corresponds to a value of 1. The red line exemplifies the Li concentrations for a constant value of  $r/a$  of 0.5 at variable temperatures after 1 million years. The color scale indicates the approximate Li concentrations, from initially 8 ppm (red colors) to 1.5 ppm (dark blue colors). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mantle-like isotopic compositions, even though the potential components that are subducted (dehydrated basaltic crust and sediments) have a wide range in  $\delta^7\text{Li}$  ( $-12$  to  $+15$ ). (Bouman et al., 2004; Chan et al., 2006; Zack et al., 2003). It is plausible that the weighted average  $\delta^7\text{Li}$  of these materials is in the mantle range.

## 6. Conclusions

1. Carbonatites reflect the average Li isotopic composition of their mantle source and their  $\delta^7\text{Li}$  values overlap with those of present day, mantle-derived oceanic basalts.
2. In individual carbonatite complexes, the  $\delta^7\text{Li}$  values of carbonatites and associated mafic silicate rocks are indistinguishable.
3. During the last 2.7 Ga, there have been no major, large-scale variations in the Li isotopic composition of the Earth's mantle as sampled by carbonatites and associated intracontinental mafic silicate rocks. This global selection of 23 carbonatites has an average  $\delta^7\text{Li}$  value of  $+4.1 \pm 1.3$  ( $1\sigma$ ).
4. The relatively constant  $\delta^7\text{Li}$  value of mantle-derived rocks through time implies that the bulk composition of subducted material does not deviate greatly from the mantle value ( $\delta^7\text{Li} \sim +4 \pm 2$ ) and that Li diffusion is sufficiently fast at mantle temperatures to obliterate isotopic heterogeneities over geologically short time periods over meter to kilometer length scales.
5. Modeling of Li diffusion at appropriate mantle temperatures shows that Li heterogeneities are likely to be rehomogenized for bodies  $< 100$  m in size after a few million years and after approximately 100 million years for bodies up to 2 km in diameter. Lithium is much more effectively homogenized in the mantle than most other elements, including radiogenic isotopes, which may also explain why there is little overall deviation in  $\delta^7\text{Li}$  values of mantle-derived material from the average mantle value of  $+4 \pm 2$ .
6. Real variability exists in  $\delta^7\text{Li}$  values of mantle-derived carbonatites. Averages range from  $+3.0$  to  $+5.7$  for individual complexes, and individual samples have values ranging from  $+1.3$  to  $+6.7$ . This variability most likely reflects limited Li isotope fractionation due to crustal assimilation and diffusion during melt transfer and magma storage.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.epsl.2007.11.007](https://doi.org/10.1016/j.epsl.2007.11.007).

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