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Lithium isotopic composition and concentration of the deep continental crust

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ABSTRACT

Samples from Archean high-grade metamorphic terranes in China and granulite-facies xenoliths from Australia (Chudleigh and McBride suites) and China (Hannuoba suite) have been analyzed to assess the Li concentrations and isotopic compositions of the middle and lower continental crust, respectively. Thirty composite samples from metamorphic terranes, including tonalite–trondjhemite–granodiorite (TTG) gneisses, amphibolites and felsic to mafic granulites, show a large variation in Li concentrations (5–33 ppm) but a relatively narrow range in δ^7Li values, from +1.7 to +7.5 with a mean of +4.0±1.4 (1σ). These results suggest that the middle continental crust is relatively homogenous in Li isotopic composition and indistinguishable from the upper mantle. This may be a primary feature or may reflect homogenization of Li isotopes during exhumation of the metamorphic terranes. In contrast, Li isotopic compositions of granulite xenoliths from the lower crust vary significantly, with δ^7Li ranging from −17.9 to +15.7. δ^7Li of minerals also shows a very large spread from −17.6 to +16.7 for plagioclases and −14.6 to +12.7 for pyroxenes. Large Li isotopic variations exist between plagioclase and pyroxene, with pyroxenes (13 out of 14) isotopically equal to or lighter than coexisting plagioclases. Lithium concentrations of granulite xenoliths also vary widely (0.5 to 21 ppm) and are, on average, lower than those of terranes (5±4 vs. 13±6 ppm respectively, 1σ), consistent with a higher proportion of mafic lithologies and a higher metamorphic grade for the xenoliths. Pyroxene separates from granulite xenoliths have equal or significantly greater Li than coexisting plagioclase.

These large Li isotopic variations between minerals and in whole-rock granulite xenoliths mostly reflect diffusion-driven kinetic isotopic fractionation during the interactions of xenoliths with host magma. Only those xenoliths that reach inter-mineral isotopic equilibria are likely to preserve the initial Li isotopic signatures of the lower crust. Eight such equilibrated samples have δ^7Li from −14 to +14.3, with a concentration weighted average of +2.5, which is our best estimate of the average δ^7Li of the lower continental crust. The substantial isotopic heterogeneity of the lower crust may reflect the combined effects of isotopic fractionation during granulite-facies metamorphism, diffusion-driven isotopic fractionation during igneous intrusion and variable protolith compositions. Consistent with previous B elemental and O isotopic studies, the Li isotopic heterogeneity in the lower crust indicates that pervasive fluid migration and equilibration have not occurred.

Using all data for granulite xenoliths, the Li concentration of the lower crust is estimated to be ~8 ppm. Together with previous estimates of Li concentration in the upper and middle crust, the average Li concentration of the bulk continental crust is estimated to be 18 ppm, which is similar to previous estimates. The average Li isotopic composition of the continental crust is estimated to be +1.2, which is isotopically lighter than upper mantle and may reflect the loss of isotopically heavy Li from the continents during weathering and metamorphic dehydration.

1. Introduction

Although the continental crust comprises only ~0.5% by mass of the silicate Earth, it is estimated to contain more than 5% of the Earth's Li, with the upper crust having one to two times as much Li as the deep crust (middle and lower crust) (Teng et al., 2004). Knowledge of the composition of the continental crust is therefore important in mass-balance calculations of the Li budget in the silicate Earth, as well as in

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using Li isotopes to trace crustal recycling in the mantle. Based on studies of shale, loess, granite and upper crustal composites, the upper continental crust appears to have a lighter Li isotopic composition than the mantle, which may result from isotopic fractionation associated with weathering and water–rock interactions. During these processes, heavy Li (^{7}Li) preferentially partitions into water relative to rocks, causing a shift in the present upper continental crust towards a lighter Li isotopic composition (Teng et al., 2004).

In contrast to the upper continental crust, very little is known about Li in the deep continental crust, and there has been no comprehensive examination of Li isotopes in deep crustal rocks. In order to characterize this region, we have undertaken a systematic study of 30 composite samples from eight Archean high-grade terranes from eastern China and three suites (44 whole-rock samples +29 mineral separates) of granulite-facies xenoliths from Queensland, Australia and Hannuoba, China. Studies of these high-grade metamorphic rocks help us to evaluate the effects of different processes on Li concentrations and isotopic compositions of high-grade metamorphic rocks, estimate the Li concentration and isotopic composition of the deep continental crust and, in combination with previous studies of the upper crust, assess the bulk composition of the continental crust.

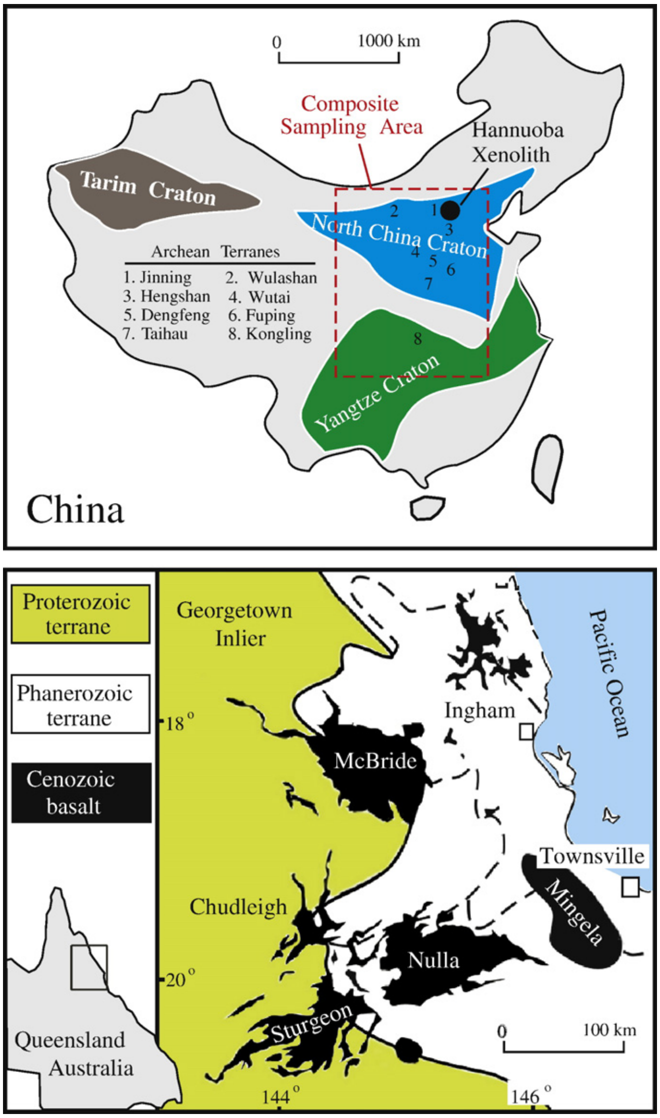

Fig. 1. Upper: Cratons of eastern China with composite sampling area outlined (dashed line box), numbers correspond to the eight Archean terranes and three Archean cratons as well as the location of Hannuoba xenoliths. Bottom: locations of McBride and Chudleigh volcanic fields, North Queensland, Australia. Latitudes and longitudes of each xenolith locality are provided in the footnote of the data tables. Modified from Rudnick et al. (1986) and Gao et al. (1998a).

2. Samples and geological background

Seismological studies indicate that the deep continental crust (below ~10–15 km depth) can be divided into two heterogeneous layers: the middle crust and lower crust (Holbrook et al., 1992; Christensen and Mooney, 1995; Rudnick and Fountain, 1995). The middle crust lies between ~10–15 and 20–25 km depth and is dominated by amphibolite-facies to lower granulite-facies metamorphic rocks having relatively evolved compositions (Christensen and Mooney, 1995; Rudnick and Fountain, 1995; Gao et al., 1998a). The lower crust, below ~20–25 km depth, mainly consists of granulite-facies rocks with more mafic compositions (Rudnick and Presper, 1990; Rudnick, 1992; Christensen and Mooney, 1995; Rudnick and Fountain, 1995). In general, two types of samples have been used to determine the composition of the deep crust: high-grade metamorphic terranes and lower crustal xenoliths carried in volcanic pipes. The former are often considered representative of the middle crust and/or the uppermost lower crust (Bohlen and Mezger, 1989) and the latter representative of the lower crust (see review of Rudnick and Gao, 2003).

Both types of samples, including whole rocks and mineral separates, have been investigated here (Fig. 1): granulite xenoliths from Damaping, Hannuoba, eastern China (Liu et al., 2001, 2004), McBride and Chudleigh, North Queensland, Australia (Rudnick et al., 1986; Rudnick and Taylor, 1987) and high-grade metamorphic rocks from eight different Archean metamorphic terranes in eastern China, including tonalite–trondhjemite–granodiorite (TTG) gneisses, amphibolites and felsic to mafic granulites (Gao et al., 1998a). All these samples were used to study the composition of the deep continental crust in previous investigations. Granulite xenoliths from Hannuoba and North Queensland are dominated by mafic compositions and match the estimated composition of lower continental crust very well (Saal et al., 1998; Liu et al., 2001). In contrast, the metamorphic terrane samples represent various lithologies of Archean-aged high-grade crust from eastern China (Gao et al., 1998a), but are dominated by felsic bulk compositions. Although such evolved compositions are unlike the lowermost crust in most regions of the world, they may be representative of the upper part of the lower crust beneath eastern China, which has a thinner and more evolved crust composition relative to global averages (Gao et al., 1998b) and middle crust compositions elsewhere (Rudnick and Fountain, 1995).

2.1. High-grade metamorphic rocks from Archean terranes

These samples derive from eight different high-grade metamorphic terranes in the two largest Archean cratons in China (Fig. 1). Seven of these terranes are from the North China Craton, including Wutai and Dengfeng amphibolite-facies terranes, Fuping, Hengshan and Taihau amphibolite-granulite-facies terranes, Jinning and Wulashan granulite-facies terranes. The eighth terrane, the Kongling amphibolite-granulite-facies terrane, is from the Yangtze craton (Gao et al., 1999; Qiu and Gao, 2000). All samples from these terranes, including 13 TTG gneisses, five amphibolites, four felsic, four intermediate and four mafic granulites, are composites that were produced by mixing equal amounts of individual rock sample (n=1 to 15) having the same age and lithology and coming from the same tectonic unit. These composites are thus considered to be representative of most Archean units exposed in eastern China. These samples were collected along road cuts, riverbanks, or mountain valleys and are very fresh, as indicated by petrographic studies (Gao et al., 1998a). More details about these Archean terranes can be found in Gao et al. (1992, 1996, 1998a, 1999), Qiu and Gao (2000), and Zhao et al. (2001, 2005).

2.2. Granulite xenoliths from Damaping, Hannuoba, China

Lower crustal xenoliths from the Cenozoic Hannuoba basalts, situated in the central orogenic belt of the North China Craton (Fig. 1), occur mostly at two locations: Damaping and Zhouba. These xenoliths show a diversity of compositions, with Damaping dominated by mafic granulites and Zhouba dominated by felsic compositions (Gao et al., 2000; Chen et al., 2001; Liu et al., 2001; Zhou et al., 2002; Liu et al., 2004). Granulite xenoliths from Damaping are 4 to 20 cm in diameter and range in composition from pyroxenites, plagioclase-rich mafic granulites to intermediate granulites. Although all xenoliths here and from the north Queensland localities show some amount of grain boundary alteration, most have pristine mineral interiors. A few samples from Hannuboa, however, show more pervasive alteration within feldspars and pyroxenes (see photomicrographs provided in the on-line supplement) and these are designated as "altered" in the data table and in the figures. All these xenoliths equilibrated under high temperatures (800–950 °C), corresponding to depths of greater than 30 km (Chen et al., 2001; Liu et al., 2003). U–Pb zircon chronology on these granulite xenoliths indicates that basaltic magma intruded Precambrian lower crust at ~160–140 Ma and induced subsequent granulite-facies metamorphism (Liu et al., 2004). The large variations in Sr, Nd and Pb isotopic compositions of these xenoliths are interpreted to reflect mixing between preexisting Precambrian deep crust with the underplated basalts (Liu et al., 2001, 2004). Eighteen samples, which include both fresh and altered xenoliths and span the entire mineralogical and chemical compositional spectrum, have been analyzed in this study.

2.3. Granulite xenoliths from McBride, North Queensland, Australia

The late Cenozoic basalts from the McBride volcanic province, North Queensland, erupted through and onto Proterozoic crust of the Georgetown Inlier (Fig. 1), which is composed of greenschist to amphibolite-facies metamorphic rocks. Lower crustal granulite and upper mantle peridotite xenoliths are abundant. The granulite xenoliths are small (≤10 cm in diameter) and range from mafic through felsic bulk compositions, with many containing hydrous phases (e.g., biotite). Alteration is generally restricted to grain boundary zones or in development of kelyphite on garnet (see photomicrographs in the on-line supplement). Although mafic orthogneisses dominate, felsic to intermediate lithologies also make up a significant (~20%) proportion of the xenolith suite (Rudnick and Taylor, 1987). U–Pb zircon dating indicates that most protoliths formed at ~300 Ma, a time of extensive calc-alkaline igneous activity in this region, but several protoliths formed during the Proterozoic at ~1570 Ma (Rudnick and Williams, 1987). All xenoliths underwent granulite-facies metamorphism at 300 Ma, followed by slow cooling in the lower crust. The wide range of whole-rock $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ compositions follows a mixing trend at 300 Ma, suggesting that most of these rocks were formed via large scale mixing between mantle-derived basalts and preexisting crust at this time (Rudnick, 1990). Twelve granulite xenoliths ranging from felsic to mafic compositions were selected for this study.

2.4. Granulite xenoliths from Chudleigh, North Queensland, Australia

The Chudleigh volcanic province in North Queensland occurs ~180 km south of McBride (Fig. 1). Granulite xenoliths are abundant in recent alkali basalts that erupted on the boundary between the Proterozoic Georgetown Inlier and the Paleozoic Tasman fold belt of eastern Australia (Rudnick et al., 1986). These xenoliths are large (up to 50 cm in diameter), fresh, mafic (SiO_2 from 49 to 51 wt.%, Mg# from 40 to 81) and anhydrous. Two bulk compositions occur: plagioclase-rich (anorthositic) granulites and pyroxene-rich granulites. As with the McBride xenoliths, alteration is generally restricted to grain boundaries and in kelyphite replacing garnet (see photomicrographs in the on-line supplement). Despite nearly constant major-element compositions for the plagioclase-rich xenoliths, their mineralogy varies from olivine-bearing assemblages through the gabbro-granulite transition to plagioclase–garnet–clinopyroxene assemblages approaching eclogite, indicating a range of equilibration depths between 20 and >40 km and temperatures between 600 and 1000 °C (Rudnick et al., 1986; Rudnick and Taylor, 1991). Chemical and isotopic compositions (O, Sr, Nd, Hf, Pb and Os) of these xenoliths suggest that they are cogenetic crystal cumulates derived from mafic magmas that intruded and assimilated the preexisting lower crust and cooled <100 Ma ago (Rudnick et al., 1986; Rudnick, 1990; Rudnick and Goldstein, 1990; Kempton and Harmon, 1992; Saal et al., 1998; Vervoort et al., 2000). Fourteen granulites, spanning the observed compositional and mineralogical range, were chosen for this study.

3. Analytical methods

All whole-rock powders are the same as those used in previous studies (Rudnick et al., 1986; Rudnick and Taylor, 1987; Gao et al.,

Table 1
Lithium concentrations and isotopic compositions of samples from high-grade metamorphic terranes in East China

Sample	Terrane	n[a]	δ^7Li[b]	Li (ppm)[c]	Li (ppm)[d]	Mg#[d]	SiO_2 (wt.%)[d]
Tonalite gneisses							
D138	Dengfeng	1	+2.8	21.3	20.2	54.8	62.8
D141	Taihau	4	+3.2	16.9	15.6	51.2	61.4
14R109	Wutai	10	+5.2	22.2	19.3	56.2	62.7
14R110	Wutai	10	+2.6	19.4	20.0	61.4	70.8
14R118	Wutai	15	+5.6		14.2	48.2	61.0
14R117	Wutai	15	+5.2	11.5	12.0	41.8	61.3
Trondhjemite gneisses							
14R116	Wutai	15	+7.5		15.3	40.0	69.3
D142	Taihau	1	+3.9	9.8	10.7	31.9	72.5
D139	Dengfeng	3	+3.7	12.2	12.6	39.0	72.4
D147	Kongling	7	+2.9	16.2	15.2	51.5	67.6
Granite gneisses							
D143	Taihau	3	+4.0	6.6	5.2	19.3	72.0
D140	Dengfeng	2	+3.8	6.5	6.5	29.1	72.3
D148	Kongling	4	+2.7	17.5	16.0	41.9	71.8
Amphibolites							
D149	Dengfeng	10	+3.4		10.9	49.9	51.4
D153	Taihau	12	+6.8	5.8	5.2	45.4	50.8
14R162	Fuping	2	+3.9	8.7	10.5	58.4	47.1
14R167	Hengshan	8	+3.7		11.0	46.8	50.7
D171	Kongling	8	+6.2	8.2	8.1	49.5	49.5
Mafic granulites							
D154	Taihau	2	+4.4	8.3	8.3	43.1	50.1
14R161	Fuping	8	+4.7	8.9	6.7	40.3	50.7
14R168	Hengshan	1	+5.7		8.1	32.0	48.9
D368	Jinning	10	+3.4		7.3	46.5	45.7
Intermediate granulites							
15R281	Wulashan	10	+2.3	32.6	30.8	45.1	54.5
15R267	Wulashan	10	+5.1	12.5	10.3	54.6	61.6
15R278	Wulashan	10	+3.2		15.9	41.6	62.3
15R266	Wulashan	10	+2.4		20.9	35.9	62.8
Felsic granulites							
D366	Jinning	3	+2.8		8.4	46.2	59.0
15R277	Wulashan	10	+1.7		20.8	44.1	65.3
15R268	Wulashan	10	+3.1	8.7	8.6	42.6	65.5
15R263	Wulashan	10	+2.8	12.8	11.3	33.7	70.4

[a] n = number of individual samples comprising the composite.
[b] $\delta^7Li = [(^7Li/^6Li)_{Sample}/(^7Li/^6Li)_{LSVEC} - 1] \times 1000$.
[c] Lithium measured by voltage comparison with 50 or 100 ppb LSVEC.
[d] Data from Gao et al. (1998a).

Table 2
Lithium concentrations and isotopic compositions of granulite xenoliths from Hannuoba, East China

Sample	δ^7Li	Li (ppm)[a]	Li (ppm)[b]	Mg#[b]	SiO_2 (wt.%)[b]
Pyroxenite					
DMP-10	−4.2		4.1	76.1	49.0
Two-pyroxene mafic granulites					
DMP-03	+0.5	4.5	5.8	78.9	49.1
DMP-09	−1.9	5.2	4.9	77.9	49.5
DMP-11	−1.9	2.4	2.2	77.0	49.8
DMP-28[c]	−8.0	6.9	7.7	70.2	50.3
DMP-45	−9.6		7.4	74.3	50.7
DMP-66	−2.9	3.7	3.5	77.7	50.5
DMP-68	−3.3	5.4	5.6	77.6	49.7
Garnet-bearing mafic granulites					
DMP-08	+0.2	2.3	1.9	71.6	45.3
DMP-15	+4.3	4.4	4.1	70.2	44.2
Plagioclase-rich mafic granulites					
DMP-06[c]	+13.8	2.1	2.7	64.4	51.7
DMP-07	+2.2	4.2	4.6	61	45.7
DMP-62[c]	+6.7	2.0	1.9	72.2	52.9
DMP-75[c]	+1.3	3.3	3.4	55.6	52.4
Intermediate granulites					
DMP-01[c]	+12.1	0.6	0.5	71.5	60.3
DMP-27	−5.1	4.6	5.7	47.3	54.0
DMP-61[c]	+3.8	0.9	0.9	69.5	57.5
DMP-70	+7.1	1.4	1.2	65.4	56.8
Plagioclase[d]	+10.4	0.6			
Pyroxene	+10.7	1.9			

All samples were collected from Damaping, Hebei province. GPS data: N 40°58′67″, E 114°31′67″.

[a] Lithium measured by voltage comparison with 50 or 100 ppb LSVEC.

[b] Data from Liu et al. (2001).

[c] Altered samples (see photomicrographs in electronic supplement).

[d] Size of mineral = 180–300 µm.

1998a; Liu et al., 2001) and all analyses were performed at the Geochemistry Laboratory, University of Maryland, College Park.

Plagioclase and pyroxene (mostly clinopyroxene, but including some orthopyroxene) were first separated by using a Frantz® magnetic separator, then handpicked under a binocular microscope, and finally cleaned with Milli-Q water for 3 × 10 min in an ultrasonic bath and dried under a heat lamp. Plagioclase and most pyroxene were separated within the grain-size fraction of 180–300 µm. In some samples the 180–300 µm size fraction pyroxene contained impurities. In this type of sample, two different size fractions of pyroxene were separated: one is between 150 and 180 µm, pure and fresh, and the other one is between 180 and 300 µm, and includes both fresh pyroxene and altered grain boundary materials. The purity of mineral separates is estimated to be >99% for plagioclase and 150–180 µm size pyroxene separates and >90% for the 180–300 µm size pyroxene separates.

Detailed procedures for sample dissolution, column chemistry, and instrumental analyses are reported in Teng et al. (2006c). In brief, samples were dissolved in a combination of HF-HNO_3-HCl. Lithium was purified on a cation exchange resin (Bio-Rad AG50w-X12, 200–400 mesh) first in a HCl medium, followed by in a HCl-ethanol medium. Lithium concentrations and isotopic compositions were analyzed using the sample-standard-bracketing method on a Nu Plasma MC-ICPMS. The external precision of Li isotopic analyses, based on 2σ of repeat runs of pure Li standard solutions and rock solutions over a four-year period, is ≤±1.0‰ (Teng et al., 2004; 2007). The uncertainty in Li concentration measurements, determined by voltage comparison between sample solution and that measured for 50 or 100 ppb LSVEC standard solution and then adjusting for sample weight, is <±10% (1σ) (Teng et al., 2007).

4. Results

Table 1 reports data for metamorphic terrane samples, Table 2 for Hannuoba xenoliths, Table 3 for McBride xenoliths and Table 4 for Chudleigh xenoliths. Lithium concentrations and isotopic compositions of all whole-rock samples are plotted against SiO_2 concentrations in Fig. 2.

4.1. Whole rocks

Lithium concentrations are highly variable, ranging from 5 to 33 ppm in samples from the metamorphic terranes, 0.5 to 7.7 ppm in mafic and intermediate granulite xenoliths from Hannuoba, 2 to 21 ppm in mafic to felsic granulite xenoliths from McBride and 0.2 to 18 ppm in mafic granulite xenoliths from Chudleigh. Altered xenoliths from Hannuoba show a similar range in Li concentrations as fresh ones, but tend to have lower Li concentrations (Table 2, Fig. 2). On average, terrane composites have higher Li concentrations than xenoliths (13 ± 6 vs. 5 ± 4 ppm, 1σ), even when accounting for the more evolved bulk compositions of the terrane samples (Fig. 2).

The δ^7Li (see caption of Table 1 for the definition of δ^7Li) of TTG gneisses, amphibolites and granulites from Archean metamorphic

Table 3
Lithium concentrations and isotopic compositions of granulite xenoliths from McBride, North Queensland, Australia

Sample	δ^7Li	Li (ppm)[a]	Mg#[b]	SiO_2 (wt.%)[b]
Two-pyroxene mafic granulites				
85-100	−2.4	10.2	66.0	51.7
Replicate[c]	−1.9	10.2		
85-120	−4.6	9.5	63.4	52.4
Garnet-clinopyroxene granulites				
85-106	+5.8	16.7	62.8	46.3
Replicate[c]	+5.0	16.8		
85-107	+15.7	2.3	21.2	52.8
Plag[d]	+5.8	1.7		
pyr[d]	+7.1	2.3		
pyr[e]	+7.5			
85-114	−10.4	4.3	48.9	41.2
Replicate[c]	−10.6	4.7		
pyr[d]	−6.6	4.3		
83-159	−13.5	3.5	46.7	43.4
Replicate[c]	−13.1	4.2		
Two-pyroxene garnet mafic granulites				
85-108	0	5.3	54.9	48.9
Replicate[c]	−0.3	5.7		
plag[e]	−5.6	1.6		
plag[d]	−5.5	1.3		
pyr[d]	−4.2	5.1		
83-158	2.8	7.0	61.3	46.7
plag[d]	+6.0	3.8		
pyr[d]	+0.8	7.2		
Intermediate xenoliths				
85-101	−3.3	7.5	44.8	55.9
83-157	0	6.6	53.0	54.6
Replicate[c]	−1.8	7.2		
Felsic xenoliths				
83-160	+2.7	6.8	47.5	64.0
83-162	−3.1	7.5	41.2	66.9
Replicate[c]	−3.8	6.9		

All samples are collected from Hill 32, McBride. GPS data: S 18°15′11.14″, E 144°43′ 13.45″, estimated by using Google Earth.

[a] Lithium measured by voltage comparison with 50 or 100 ppb LSVEC.

[b] Data from Rudnick and Taylor (1987).

[c] Replicate = two times of column chemistry from the same stock solution.

[d] Size of mineral separate = 180–300 µm. pyr = pyroxene; plag = plagioclase.

[e] Different sample dissolution and column chemistry for the same size fraction of mineral separates.

Table 4
Lithium concentrations and isotopic compositions of granulite xenoliths from Chudleigh, North Queensland, Australia

Sample	δ^7Li	Li (ppm)[a]	Mg#[b]	SiO_2 (wt.%)[b]
Plagioclase-rich mafic granulites				
83-107	+1.1	3.6	66.9	49.6
plag	+5.4	0.5		
pyr	0	3.5		
83-112	+1.2	4.6	41.1	51.0
plag	+13.3	1.4		
plag[e]	+13.2	1.1		
pyr	+3.6	2.3		
83-114	+4.7	2.1	69.0	50.5
Replicate[c]	+3.3	2.0		
plag	+2.0	1.8		
pyr	0	2.4		
83-117	−12.0	4.6	76.4	49.8
83-125	−17.9	2.3	71.9	50.7
plag	−13.6	2.8		
plag[e]	−13.1	2.4		
pyr	−14.6	2.4		
83-126	−2.4	0.2	72.0	51.1
83-127	+5.1	1.3	72.2	50.1
Replicate[c]	+5.9	1.7		
83-131	−2.7	1.8	71.6	50.5
Replicate[c]	−1.3	1.7		
plag	−0.7	0.9		
Pyr	−1.7	1.5		
83-133	−16.3	2.6	69.3	50.0
plag	−15.2	0.5		
plag[e]	−17.6	0.4		
pyr	−12.6	2.4		
83-138	−5.5	4.4	72.7	49.7
83-140	−8.7	3.9	62.6	51.2
Replicate[c]	−9.1	3.6		
plag	+1.6	0.2		
plag[e]	+2.1	0.2		
pyr	−5.1	4.9		
BC	−1.3	3.3	80.6	49.7
Replicate[c]	−1.1			
plag	+1.0	2.5		
pyr	+0.4	3.0		
pyr[d]	−0.3	2.6		
Pyroxene-rich mafic granulites				
83-110	+6.1	6.2	73.4	50.8
Replicate[c]	+5.7	7.0		
plag	+16.7	2.5		
plag[e]	+14.8	1.7		
pyr	+12.7	6.2		
83-115	−3.9	18.0	77.8	50.9
Replicate[c]	−4.4			
plag	+8.9	3.0		
pyr	−6.7	22.9		
pyr[d]	−7.4	20.3		

Samples BC, 83-114, 83-115, 83-117, 83-121 were collected from Batchelor's crater: S 19°38′15″, E 144°07′39″. Samples 83-106, 83-107, 83-110, 83-112 were collected from Airstrip crater S 19°38′36.75″, E 144°08′33.13″. Remaining samples (83-126, 83-127, 83-131, 83-133, 83-138, 83-140) come from the nearby Sapphire Hill, for which no latitude and longitude are available. Latitude and longitude were estimated using Google Earth.

[a] Lithium measured by voltage comparison with 50 or 100 ppb LSVEC.

[b] Data from Rudnick et al. (1986).

[c] Replicate = two different column separations from the same stock solution.

[d] Size of pyroxene separate = 150–180 μm. All other mineral separates are larger (180–300 μm). pyr = pyroxene; plag = plagioclase.

[e] Different sample dissolution and column chemistry for the same size fraction of mineral separates.

terranes range from +1.7 to +7.5, with an average of +4 ± 1.4 (1σ) (Fig. 3), indistinguishable from the upper mantle, based on the isotopic compositions of oceanic basalts (Tomascak et al., 2008 and references therein) (Fig. 3) and mantle peridotites (Seitz et al., 2004; Magna et al., 2006; Jeffcoate et al., 2007). The δ^7Li values of granulite xenoliths, however, vary widely from −17.9 to +15.7, with the range bracketed by a plagioclase-rich mafic granulite from Chudleigh at the lower end and a garnet-clinopyroxene mafic granulite from McBride at the higher end (Fig. 3). Among the three suites of xenoliths, the 12 McBride xenoliths display the greatest variation in δ^7Li (−13.3 to +15.7), followed by 14 Chudleigh xenoliths (−17.9 to +5.9) and 18 Hannuoba xenoliths (−9.6 to +13.8). The δ^7Li values of altered Hannuoba xenoliths tend to be higher than those of their fresher counterparts (Figs. 2 and 3).

4.2. Mineral separates

Lithium concentrations in mineral separates correlate with those of whole rocks (Fig. 4). Pyroxene generally has higher Li concentration than coexisting plagioclase (1.5 to 22.9 vs. 0.2 to 3.8 ppm, respectively). The Li concentration ratios between pyroxene and plagioclase, $K^{pyr/plag}$ ($Li_{pyroxene}/Li_{plagioclase}$), in the 14 granulite xenoliths for which we have data, varies significantly from 0.9 to 24.5. This range is slightly

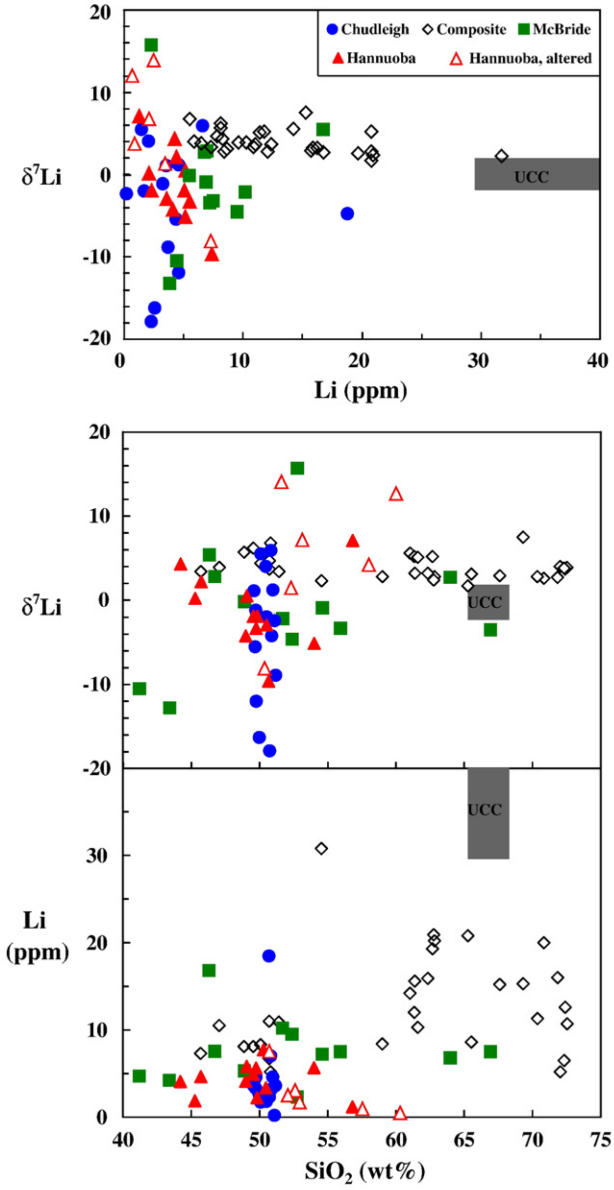

Fig. 2. Plots of Li concentrations and isotopic compositions vs. SiO_2 concentrations of whole-rock high-grade metamorphic rocks. The average Li concentration, isotopic composition and SiO_2 concentration of the upper continental crust (Li = 35 ± 5.5 ppm, δ^7Li = 0 ± 2‰ and SiO_2 = 66.6 ± 1.18%, 1σ, Teng et al., 2004; Rudnick and Gao 2003) are plotted for comparison as gray boxes. Data are from Tables 1–4.

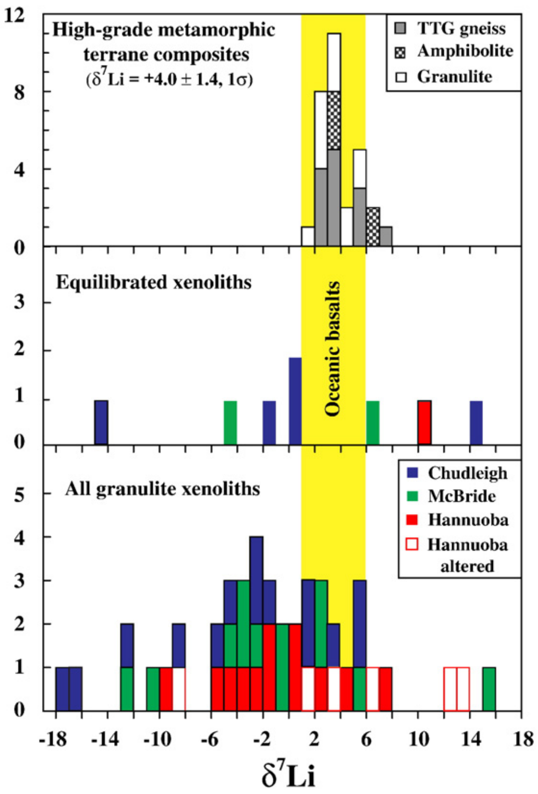

Fig. 3. Histograms of lithium isotopic compositions of Archean high-grade metamorphic terranes and granulite xenoliths. Equilibrated xenoliths represent those granulite xenoliths that exhibit Li isotopic equilibria between plagioclase and pyroxene (Types 1 and 2, as defined in the text). The yellow band represents the range in δ^7Li of oceanic basalts (Tomascak et al., 2008 and references therein). Data are from Tables 1–4.

greater than that determined experimentally for Li partitioning between cpx and plagioclase at 1 atm by Coogan et al. (2005), who found $K^{pyr/plag}$ varied systematically from 1.7 to 20 between temperatures of 1200 to 900 °C, respectively. Equilibration temperatures are not well determined for most of the xenoliths (e.g., Rudnick and Taylor, 1991), but for the Chudleigh suite, the systematic change in mineralogy can be used, along with experimentally determined phase stability fields and an assumed geotherm, to infer approximate equilibration temperatures (see Fig. 4 of Rudnick and Taylor, 1991). A linear correlation exists between ln ($K^{pyr/plag}$) and the estimated equilibration temperature for seven of the ten samples for which we have mineral pair data (Fig. 5). In contrast to the sharp decrease of $K^{pyr/plag}$ with temperature observed in laboratory experiments (Coogan et al., 2005, dashed line in Fig. 5), $K^{pyr/plag}$ in the granulite xenoliths changes more slowly with temperature. The reason for this difference is unknown. It may reflect the effects of pressure on $K^{pyr/plag}$ or the differences in mineral compositions between the granulite xenoliths and those in the experimental study. For example, both clinopyroxene and plagioclase become systematically more Na-rich with increasing derivation depth of the Chudleigh xenoliths (Rudnick and Taylor, 1991; Rudnick and Jackson, 1995).

The δ^7Li values of plagioclase and pyroxene are highly variable, with δ^7Li of pyroxene generally being similar to that of the whole rock (Fig. 4). δ^7Li ranges from −17.6 to +16.7 in plagioclase and from −14.6 to +12.7 in pyroxene. The inter-mineral isotopic fractionation factor, $\Delta^7Li_{pyr\text{-}plag}$ ($=\delta^7Li_{pyroxene}-\delta^7Li_{plagioclase}$), varies from +3.8 to −15.9, with most pyroxenes (13 out of 14) isotopically identical to or lighter than coexisting plagioclase (Fig. 4 and Table 5). Lithium concentrations and isotopic compositions of different grain-size pyroxenes (altered vs. fresh) from two xenoliths (plagioclase-rich granulite, BC, and pyroxene-rich granulite, 83-115) are within error of each other,

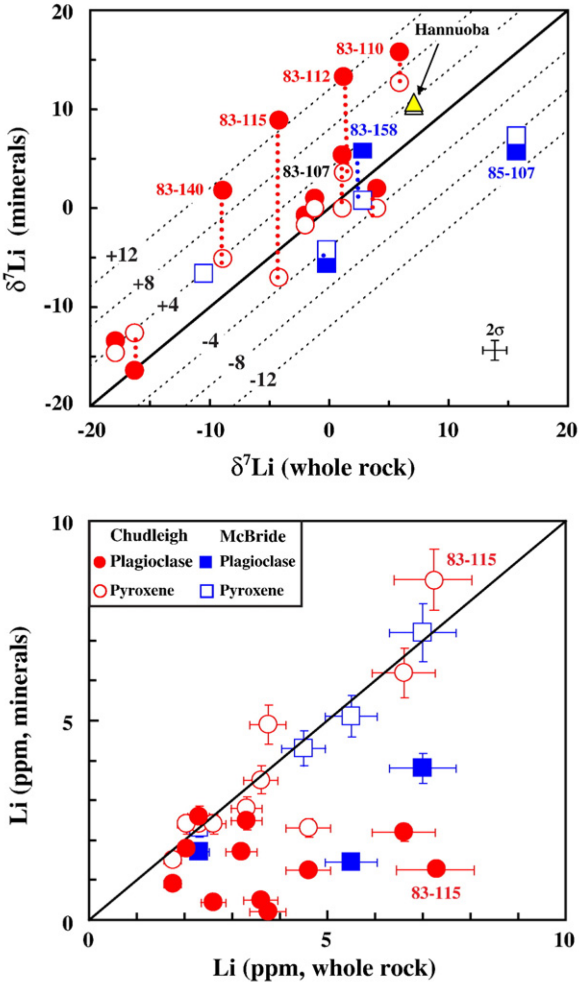

Fig. 4. Variations of δ^7Li and Li concentrations between whole rocks and mineral separates. Diagonal solid line marks a 1:1 correlation in both figures. Numbers on dashed lines in the upper figure represent $\Delta^7Li_{(minerals\text{-}wr)}=\delta^7Li_{minerals}-\delta^7Li_{whole\ rock}$. Lithium concentrations in both whole-rock and mineral separates of sample 83-115 in the lower figure are reduced by a factor of 2.5 to facilitate plotting. Data are from Tables 2–4.

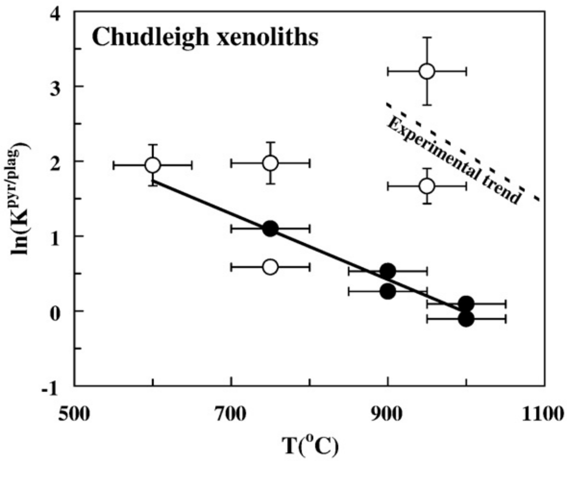

Fig. 5. Measured pyroxene–plagioclase partition coefficient ($K^{pyr/plag}$) vs. approximate equilibration temperature for Chudleigh xenoliths. Open circles are xenoliths that show isotopic disequilibria, closed circles are equilibrated samples. Equilibration temperatures are averages based on mineral assemblage and experimentally determined stability fields (see text and Rudnick and Taylor, 1991). Solid line is the best fit for all equilibrated samples ($y=-0.0044\times+4.4$). Dashed line is experimentally determined temperature dependence of the partitioning of Li between diopside and plagioclase at one atmosphere ($y=-0.0066\times+8.7$) (Coogan et al., 2005).

Table 5
Lithium concentration ($K^{pyr/plag}$) and isotopic difference ($\Delta^7Li_{pyr\text{-}plag}$) between pyroxene and plagioclase in granulite xenoliths

Sample	Granulite type	$K^{pyr/plag*}$	$\Delta^7Li_{pyr\text{-}plag}$*	Type
Hannuoba				
DMP-70	Intermediate	3.2	+0.3	2
McBride				
85-107	Garnet-clinopyroxene	1.4	+1.5	2
85-108	Two-pyroxene garnet	3.5	+1.4	2
83-158	Two-pyroxene garnet	1.9	−5.2	3
Chudleigh				
83-110	Pyroxene-rich	3.0	−3.1	2
83-115	Pyroxene-rich	12.7	−15.9	3
83-107	Plagioclase-rich	7.0	−5.4	3
83-112	Plagioclase-rich	1.8	−9.7	3
83-114	Plagioclase-rich	1.3	−2.0	2
83-125	Plagioclase-rich	0.9	−1.2	2
83-131	Plagioclase-rich	1.7	−1.0	1
83-133	Plagioclase-rich	5.3	+3.8	3
83-140	Plagioclase-rich	24.5	−7.0	3
BC	Plagioclase-rich	1.1	−1.0	1

*$\Delta^7Li_{pyr\text{-}plag} = \delta^7Li_{pyroxene} - \delta^7Li_{plagioclase}$; $K^{pyr/plag} = Li_{pyroxene}/Li_{plagioclase}$; both $K^{pyr/plag}$ and $\Delta^7Li_{pyr\text{-}plag}$ are calculated based on data from Tables 2, 3 and 4. See section 5.5 for designation of xenolith types.

which indicates that the alteration products in the xenoliths has either similar Li isotopic composition to the primary pyroxene or insignificant amounts of Li compared to fresh pyroxene.

5. Discussion

High-grade metamorphic rocks have complex thermal and fluid histories and may have experienced a multitude of processes that could affect their Li concentrations and isotopic compositions. Such processes include progressive metamorphism during burial (possibly accompanied by dehydration), interactions with magmas and derivative fluids in the deep crust and processes that acted during their return to the surface, either through long-term exhumation (in the case of metamorphic terranes) or rapid ascent within alkali basaltic magma (in the case of xenoliths). The effects of these processes on Li systematics are not well known. In the following sections, we discuss these factors, as well as protolith compositions, and evaluate their relative importance in dictating the Li composition of these metamorphic rocks. Finally, we estimate the Li concentration and isotopic composition of the deep continental crust.

5.1. Protolith composition

The protoliths of all but one of the metamorphic rocks investigated here are inferred to be igneous, with bulk compositions ranging from gabbro to granite and including mafic cumulates (both plagioclase-rich and pyroxene-rich), tonalites and trondhjemites. One granulite xenolith from the McBride locality has been interpreted to be a meta-graywacke (83-157, see Rudnick and Taylor 1987). Based upon data for δ^7Li in a wide variety of igneous rock types, the overall isotopic range in the igneous protoliths is expected to fall between −3 and +7 (excluding pegmatites, Tomascak, 2004, and references therein, Bryant et al., 2004; Teng et al., 2006c). Graywackes from Australia and China have similar δ^7Li, ranging from −3 to +5 (Teng et al., 2004). The highly variable δ^7Li (>30‰) of the metamorphic rocks investigated here ranges far beyond the likely values of their protoliths. In addition, due to its moderate incompatibility, Li concentrations in igneous rocks increase with progressive crystal fractionation from a few ppm in basalts to tens of ppm in granites and thousands of ppm in pegmatites (Ryan and Langmuir, 1987; Bryant et al., 2004; Teng et al., 2004, 2006c). However, Li concentrations of these metamorphic samples show no significant correlation with SiO_2 content (41–73%). This, together with the highly variable δ^7Li of the metamorphic rocks, suggests that metamorphism and subsequent processes have overprinted protolith Li signatures.

5.2. Weathering and alteration

Lithium isotopes can be fractionated during surface weathering and hydrothermal alteration, since Li is fluid-mobile and significant isotopic fractionation can occur at low temperatures (Chan et al., 1992; Pistiner and Henderson, 2003; Huh et al., 2004; Kisakurek et al., 2004; Rudnick et al., 2004). In general, subareal weathering and alteration lowers δ^7Li values of rocks, as ^7Li is partitioned preferentially into groundwater. However, sea-floor weathering increases the δ^7Li values of rocks by addition of isotopically heavy seawater Li into clays. The visibly altered granulite xenoliths from Hannuoba generally have low Li and high δ^7Li values, which is inconsistent with addition of heavy Li or preferential leaching of ^7Li (both of which would produce a positive correlation between Li and δ^7Li). It may be that the alteration has had little overall effect on whole rock Li and that the plagioclase-rich xenoliths (which have intrinsically lower Li) are simply more susceptible to alteration than the pyroxene-rich xenoliths. This possibility is supported by observations from the Queensland xenoliths, where larger size fraction pyroxene separates containing altered grain boundary material have Li and δ^7Li values that are indistinguishable from smaller size fractions in which altered material is absent (Table 3, sample 85-107; Table 4, samples BC and 83-115). At least in these cases, the presence of grain boundary alteration appears to have had little effect on Li. In addition, since weathered surfaces of granulite xenoliths were removed before rock crushing, the samples from terranes were collected along fresh exposures in road cuts, riverbanks, or mountain valleys, and petrographic examination reveals no clays in these samples (see the electronic supplement), the effects of weathering and alteration are expected to be negligible.

5.3. Prograde metamorphism

Most prograde metamorphic reactions release water, yielding lower water content in high-grade rocks than in their lower-grade equivalents (Spear, 1993). This progressive dehydration leads to the depletion of fluid-mobile elements (e.g., B, K, Rb, Sr, Cs, Ba and U) in high-grade metamorphic rocks (Rudnick et al., 1985; Leeman et al., 1992). Lithium is fluid-mobile (Brenan et al., 1998; Marschall et al., 2006) and during fluid–rock equilibration, ^7Li preferentially enters fluids over most minerals, leading to high δ^7Li in fluids and lower Li concentration and δ^7Li in rocks (Wunder et al., 2006, 2007). The extent of Li depletion and isotopic fractionation are determined by the amount of fluids released, the mineralogies of metamorphic rocks (which influences both isotopic fractionation and Li partitioning) and the temperature (Wunder et al., 2006; Marschall et al., 2007; Teng et al., 2007; Wunder et al., 2007). In addition, the amount of isotopic fractionation, quantified by α ($[^7Li/^6Li]_{fluid}/[^7Li/^6Li]_{rock}$), is dependent on temperature, with lower temperatures leading to greater isotopic fractionation.

The depletion of Li during prograde metamorphism, regardless of protolith, is well demonstrated by a comprehensive study of crustal rocks in eastern China (Gao et al., 1998a). Shales are the most water- and Li-rich protoliths and show the largest amount of Li and H_2O depletion in their granulite-facies equivalents (~75% loss of Li and of H_2O), followed by mafic intrusive rocks (~53% loss of Li and of H_2O) and TTG (~39% loss of Li and ~16% loss of H_2O, going from protolith to amphibolite-facies mineralogy).

In contrast, the effects of dehydration on Li isotopic fractionation during prograde metamorphism are less clear. Zack et al. (2003) studied Li isotopic compositions of alpine eclogites and found δ^7Li values vary significantly but are consistently lower than their protoliths — altered oceanic basalts (−11 to +5 vs. +7 to +14). They interpreted this to reflect equilibrium Li isotopic fractionation during the early stages of regional metamorphism of altered oceanic crust (Zack et al., 2003). However, a recent study of worldwide orogenic eclogites found even lighter Li isotopic compositions than those seen by Zack et al. (2003), but with higher Li concentrations (Marschall et al., 2007). Marschall et al. (2007), aided by the new isotopic partitioning data of Wunder et al. (2006), found that metamorphic dehydration of altered basalt is unlikely to produce such dramatic isotopic effects and interpreted the isotopically light Li signatures of eclogites to be the result of kinetic isotopic fractionation produced during diffusive infiltration of Li into the eclogites from surrounding country rocks. Similarly negligible effects of metamorphism on δ^7Li were found for metapelites from a contact metamorphic aureole surrounding the Onawa granite (Teng et al., 2007). Here, metapelites that were metamorphosed from regional chlorite-zone to sillimanite zone nearest the pluton lost ~70% of their H_2O and ~50% of their Li, yet showed little change in δ^7Li. Teng et al. (2007) found that the effect of dehydration reactions on Li isotopic fractionation may not be significant unless Li partition coefficients between fluids and rocks are large enough to cause the loss of >50% of the original Li (Teng et al., 2007).

The metamorphic rocks studied here show distinct Li signatures depending on sample type: the terrane samples not only have higher Li concentrations than granulite xenoliths but they also exhibit significantly less variability in Li isotopic compositions (Figs. 2 and 3). This difference may partly reflect the higher metamorphic grade of the xenoliths compared to terrane samples, but it is unlikely that metamorphic dehydration accounts for the large range in δ^7Li seen in the xenoliths. Instead, the differences between terranes and xenoliths likely result from other factors discussed later in this section (e.g., fluid-enhanced homogenization, kinetic isotopic fractionation associated with basaltic underplating).

5.4. Exhumation and retrograde metamorphism of terranes

Terrane samples range from felsic to mafic compositions, derive from eight different metamorphic terranes and have diverse lithologies and mineralogies that are typical of amphibolite-facies to lower granulite-facies metamorphic conditions. Lithium concentrations and isotopic compositions of their protoliths may thus vary widely. Despite this diversity, these samples display a relatively small spread in δ^7Li ($+4.0\pm1.4, 1\sigma$). The question posed here is whether this relative homogeneity in δ^7Li is an original feature of these rocks or resulted from processes involved in the exhumation and retrograde metamorphism that accompanied their exhumation.

One possibility is that the relatively homogeneous Li isotopic composition may have been produced by the manufacturing of these composites, which would tend to attenuate small-scale isotopic heterogeneity. A study of the individual lithologies from one of these terranes may provide further insight.

Another possibility, given the great lithological diversity noted above, is that a general process, operative in all terranes, homogenized Li isotopic composition of metamorphic terranes. High-grade terranes are exhumed over relatively long time scales. Although the rate of exhumation may vary over a few orders of magnitude (from 0.001–10 mm/year), depending on the tectonic setting (Platt, 1993; Duchene et al., 1997; Ernst et al., 1997), the minimum time required for high-grade metamorphic rocks to reach the Earth's surface from deep crustal levels is a few million years. This prolonged exhumation, together with the extremely fast diffusion of Li in melts, minerals and fluid-infiltrated rocks (Lundstrom, 2003; Richter et al., 2003; Lundstrom et al., 2005; Teng et al., 2006b), may buffer and erase any Li isotopic heterogeneity produced during prograde metamorphism.

Alternatively, the homogeneous δ^7Li of these terrane samples may reflect the mantle-like values of their igneous protoliths, which have not been disturbed during metamorphism, uplift or mixing with Li from sedimentary lithologies (i.e., weathering and alteration processes). This hypothesis is the least favored, given it invokes simple additions of juvenile magmas to the crust with no mixing with preexisting crust having diverse isotopic compositions and the absence of kinetic isotope fractionations associated with intrusion (see Section 5.6).

The apparent homogeneity of the mid- to deep crustal terrane suites stands in strong contrast to the xenolith suites. This difference in Li isotopic composition between terranes and xenoliths might reflect a temporal difference in crust composition, since all of these terrane samples are Archean, whereas the xenoliths are all post-Archean and may also reflect a difference in the processes that control Li in xenoliths compared to terranes. Further studies of Li in high-grade metamorphic terranes of both Archean and post-Archean age are needed in order to investigate these possibilities.

5.5. Interactions between granulite xenoliths and host magma

In contrast to metamorphic terranes, the granulite-facies xenoliths from all three locations are isotopically heterogeneous. We explore here the degree to which this heterogeneity is related to interaction between the xenoliths and their host basalts.

Granulite xenoliths are generally carried rapidly to the Earth's surface, with entrainment times estimated to range from a few hours to a few thousand years (Reid, 2003). This rapid ascent and short travel time lessens the likelihood of retrograde reactions occurring in xenoliths. However, other ascent-related transformations are common, such as breakdown of garnet to kelyphite, which, in these samples consists of a very fine-grained mixture of anorthite, spinel and pyroxene (Rudnick and Jackson, 1995), formation of glasses on grain boundaries and breakdown of omphacite (Padovani and Carter, 1977; Rudnick and Taylor, 1991). In addition, xenoliths and host magma are generally not in thermal and chemical equilibrium, which can result in diffusion between xenoliths and host magmas. These processes, together with possible hydrothermal alteration by fluids exsolved from the ascending magma, can potentially modify the Li concentration and isotopic composition of granulite xenoliths and complicate the interpretation of their Li signatures. Indeed, several recent studies of basalt-borne peridotite xenoliths have documented profound Li isotopic disequilibria between coexisting minerals (Magna et al., 2006; Jeffcoate et al., 2007; Rudnick and Ionov, 2007; Tang et al., 2007; Aulbach et al., 2008).

In order to derive the initial Li signatures of the lower continental crust using granulite xenoliths, the ascent-related effects must be evaluated. Based on Li isotopic data of coexisting pyroxene and plagioclase, we divide the granulite xenoliths into three types (Table 5): type 1 — equilibrated ($n=2$): $\delta^7\mathrm{Li}_{\mathrm{plagioclase}}=\delta^7\mathrm{Li}_{\mathrm{pyroxene}}=\delta^7\mathrm{Li}_{\mathrm{whole\ rock}}$; type 2 — transitional ($n=6$): $\delta^7\mathrm{Li}_{\mathrm{plagioclase}}=\delta^7\mathrm{Li}_{\mathrm{pyroxene}}\neq\delta^7\mathrm{Li}_{\mathrm{whole\ rock}}$; type 3 — unequilibrated ($n=6$): $\delta^7\mathrm{Li}_{\mathrm{plagioclase}}>\delta^7\mathrm{Li}_{\mathrm{pyroxene}}\approx\delta^7\mathrm{Li}_{\mathrm{whole\ rock}}$ or $\delta^7\mathrm{Li}_{\mathrm{pyroxene}}>\delta^7\mathrm{Li}_{\mathrm{plagioclase}}\approx\delta^7\mathrm{Li}_{\mathrm{whole\ rock}}$. We discuss each of these types, in turn.

5.5.1. Type-1 granulite xenoliths: equilibrated

The first type of xenoliths is isotopically homogeneous throughout. Although equilibrium Li isotopic fractionation at high temperatures is not well constrained, given the absence of Li isotopic fractionation during high-temperature magmatic differentiation (Tomascak et al., 1999; Teng et al., 2006c; Halama et al., 2007) and considering that all granulite xenoliths studied here have peak metamorphic temperatures of >600 °C (Rudnick et al., 1986; Rudnick and Taylor, 1987; Liu et al., 2001), minerals in the granulites are expected to be isotopically homogeneous. This group of xenoliths thus appears to be equilibrated with respect to Li isotopes and is the most likely to preserve the pre-eruptive Li isotopic composition of the lower crust. Only two of the 14 xenoliths for which we measured plagioclase and pyroxene separates fall into this group, and both are from Chudleigh (BC and 83-131).

5.5.2. Type-2 granulite xenoliths: transitional

In the second type of xenoliths, pyroxene and plagioclase are in isotopic equilibrium but are different from the whole rocks. Thus Li isotopic composition of the whole rocks must have been modified and phases with Li isotopic composition distinct from fresh pyroxene and plagioclase in the whole rock are required to balance the Li isotopic budget. One case is that the whole rock is isotopically lighter than fresh minerals (e.g., Chudleigh sample 83-110) i.e., $\delta^7\text{Li}_{\text{plagioclase}}=\delta^7\text{Li}_{\text{pyroxene}}>\delta^7\text{Li}_{\text{whole rock}}$. This may result from diffusion of Li from the host magma into the grain boundaries of the xenoliths. The other case is that the whole rock is isotopically heavier than fresh minerals (e.g., McBride sample 85-107) i.e., $\delta^7\text{Li}_{\text{plagioclase}}=\delta^7\text{Li}_{\text{pyroxene}}<\delta^7\text{Li}_{\text{whole rock}}$. This may reflect alteration of whole rocks by interactions with isotopically heavy fluids. In both cases, only a small part of the whole rock has been altered and fresh minerals are still in isotopic equilibrium and thus preserve their initial Li isotopic compositions in the lower crust before they were entrained by the host magma. Six of the 14 samples for which we measured plagioclase and pyroxene separates fall into this group: the single Hannuoba sample (DMP-70), two McBride samples (85-107 and 85-108) and three Chudleigh samples (83-110, 83-114 and 83-125).

5.5.3. Type-3 granulite xenoliths: unequilibrated

Type-3 granulite xenoliths display significant inter-mineral isotopic variations, similar to or greater than those found in peridotite xenoliths (Seitz et al., 2004; Magna et al., 2006; Jeffcoate et al., 2007; Rudnick and Ionov, 2007; Tang et al., 2007; Aulbach et al., 2008) but well beyond the amount of equilibrium isotope fractionation expected at high temperatures. The isotopic disequilibria in these granulites most likely reflects diffusion-driven kinetic isotopic fractionation during the host–xenolith interaction or mineral–mineral exchange, as previous studies have shown the large difference in diffusion rates between Li isotopes can produce significant isotopic fractionation (Richter et al., 2003; Lundstrom et al., 2005; Beck et al., 2006; Teng et al., 2006b). Therefore, the Li isotopic compositions of these type-3 xenoliths do not reflect those of their lower crustal sources but rather interactions between xenoliths and host magma. The preservation of the large inter-mineral Li isotopic variations in granulite xenoliths further suggests that the time for the interaction of xenoliths with host magma is very short, less than tens to thousands of years (Teng et al., 2006a; Aulbach and Rudnick, in press).

In summary, isotopic disequilibrium between coexisting minerals in a number of the granulite-facies xenoliths investigated here is evidence for very late stage kinetic isotopic fractionation associated with the entrainment of the xenolith within the host basalt. In these cases it is possible that the δ^7Li of the whole rocks do not represent their pre-entrainment compositions. However, about half of the xenoliths for which we have mineral pair data are isotopically equilibrated and these should reflect their pre-entrainment isotopic compositions and thus reflect the δ^7Li of the lower continental crust.

Table 6
The average Li concentration of granulite xenoliths worldwide

Locations	Li (ppm)	n[*]
Northern Hessian Depression, Germany[a]	14	32
Massif Central, France[b]	7	95
Hannuoba, China[c]	4	27
North Queensland, Australia[d]	6	26

[*] n = number of samples.

[a] Mengel (1990) and Mengel and Hoefs (1990).

[b] Dostal et al. (1980), Downes et al. (1989) and Leyreloup et al. (1977).

[c] Liu et al. (2001).

[d] This study.

Table 7
Estimates of Li concentration of the lower crust

Study	Li (ppm)
Heier (1960)[a]	10
Taylor and McLennan (1985)[b]	11
Shaw et al. (1994)[c]	14
Rudnick and Fountain (1995)[d]	6
Gao et al. (1998a)[e]	13
This study[f]	8 (n = 180)

[a] Estimates of Li concentration in the deep crust based on granulite-facies terranes in Norway.

[b] Mass-balance calculation by assuming the lower continental crust is the residue of the bulk continental crust by the removal of the upper continental crust.

[c] Based on the average of map unit compositions in the structural zone in Canadian Precambrian Shield.

[d] Based on Li data from Massif Central, France (Rudnick and Presper, 1990).

[e] Estimates of Li concentration in the East China lower crust based on both granulite xenoliths and terranes.

[f] Based on the averages of each xenolith locality shown in Table 6 (representing over 180 individual samples).

5.6. Kinetic fractionation associated with magmatic intrusions

Given that isotopically equilibrated xenoliths (types 1 and 2, above) still show a spectacular range in δ^7Li values (−14 to +14, set by the average δ^7Li of mineral pairs from Chudleigh samples 83-125 and 83-110, respectively), we explore here whether some of this heterogeneity may be related to the basaltic underplating events that are inferred to have formed the mafic granulites. Several studies have documented kinetic Li isotope fractionation produced by Li diffusion from magmatic intrusions into country rocks (Lundstrom et al., 2005; Teng et al., 2006b; Marks et al., 2007). The isotopic effects produced in this way can be very large (up to 30‰ differences) and will be preserved so long as the system cooled relatively quickly.

As many of the lower crustal xenoliths studied here are interpreted to have formed through magmatic underplating, it is likely that such kinetic effects occurred in the lower crust at the time of the intrusion. In a simple case, assuming Li diffuses from preexisting lower crust into the newly underplated intrusion, the intrusion should become isotopically lighter, due to the faster diffusivity of ^{6}Li compared to ^{7}Li, while the country rock immediately adjacent to the intrusion becomes heavier, having been preferentially depleted in ^{6}Li. The magnitude of the change in δ^7Li depends on the concentration ratio between the preexisting lower crust and intrusion as well as the diffusivity difference between Li isotopes (Richter et al., 2003). Assuming a Li concentration ratio of ~6 between preexisting lower crust (Li = 18 ppm; the most Li-rich granulite xenolith, and similar to the average Li in the terrane samples of 14 ppm) and underplating basalt (Li = ~3 ppm) and a diffusivity difference between Li isotopes (β) of ~0.215 (β in silicate melts, Richter et al., 2003), a change in δ^7Li of 10–15‰ can be produced by diffusion along the diffusion path.

Whether or not these kinetic fractionations are preserved will depend upon the cooling history of the rocks and the diffusion mechanisms of Li. The cooling history is dependent upon the time span between underplating of the basaltic magma and the xenolith entrainment in the host lava. This time span varies widely from suite to suite. For Hannuoba and McBride, the time between intrusion and entrainment is significant (>100 Ma for Hannuoba and ~300 Ma for McBride). For Chudleigh, the time between underplating and entrainment is likely to be much shorter (~50 Ma, see Rudnick et al., 1986), although precise estimates are precluded in the absence of any geochronological data for these samples. Nevertheless, the Chudleigh granulites show abundant evidence for slow cooling in the lower crust in the form of reaction coronas developed between original igneous minerals (see Rudnick et al., 1986; Rudnick and Taylor, 1991 and photomicrographs in electronic supplement). Furthermore, the lower crust is generally dry, so diffusion will occur

Table 8
The average Li concentration and isotopic composition of Earth reservoirs[a]

Reservoirs	Mass (10^{22} kg)	Mass (%)	Li (ppm)	Li (%)	δ^7Li
Continental crust					
Upper	0.63	0.16	35	3.4	0
Middle	0.59	0.14	12	1.1	+4
Lower	0.78	0.19	8	1.0	+2.5
Reservoirs in the Silicate Earth					
Hydrosphere	0.20	0.049	0.2	0.006	+30
Continental crust	2.0	0.49	18	5.5	+1.2
Oceanic crust	0.60	0.15	10	0.93	+5
H+CC+OC[b]	2.82	0.7	15	6.4	+1.8
Mantle	404.3	99.3	1.5	93.6	+4
Silicate Earth	407.1	100	1.6	100	+3.9

[a] Mass of reservoirs from Yoder (1995); weight proportion of the upper: middle: lower crust=0.317:0.295:0.388 from Rudnick and Gao (2003); Li data in hydrosphere are based on seawater values (Millot et al., 2004); Li data of upper crust from Teng et al. (2004); Li concentration of the middle crust from Rudnick and Gao (2003) and its δ^7Li value from this study; Li data of the lower crust from this study. Li data in oceanic crust is the weighted average value of altered and fresh basalts and dikes (Chan et al., 1992; Tomascak et al., 1999; Chan et al., 2002; Chan and Frey, 2003; Bouman et al., 2004; Brooker et al., 2004; Ryan and Kyle, 2004; Nishio et al., 2005; Chan et al., 2006; Elliott et al., 2006; Nishio et al., 2007; Tomascak et al., 2008); Li data of the mantle (Jagoutz et al., 1979; Magna et al., 2006); Li in the silicate Earth is calculated from mass-balance.

[b] H+CC+OC=hydrosphere+continental crust+oceanic crust.

dominantly by solid-state diffusion. Using the diffusivity (D) of Li in pyroxene as representative of the bulk D in the whole-rock granulite, a D value of 10^{-14} m^2/s (D of clinopyroxene at 800 °C, Coogan et al., 2005) and t=50 Myr will produce a characteristic distance ($\sqrt{Dt}$) of ~4 m.

The above calculations show that kinetic isotopic fractionation associated with the original underplating events that formed the mafic granulites can survive even if the cooling rate is slow in the lower crust. Therefore, the variable Li isotopic compositions in isotopically equilibrated xenoliths may partially reflect the kinetic isotopic fractionation induced by the basaltic underplating events.

5.7. Lithium in the deep continental crust

Estimates of the Li concentration of the upper continental crust date back to 1889 (Clarke, 1889; Clarke and Washington, 1924), while the first estimate of Li concentration in the deep crust was not made until 1960 by Heier (1960), who estimated 10 ppm Li in the deep crust by studying samples from lower- to upper-granulite-facies terranes. Later studies follow the same approach of investigating high-grade metamorphic terranes worldwide, except for Taylor and McLennan (1985), who estimated the composition of the deep continental crust based on a model for crust generation. All these studies yield estimates of Li concentration of the deep crust between 6 and 14 ppm (Taylor and McLennan, 1985; Shaw et al., 1994; Wedepohl, 1995; Rudnick and Fountain, 1995; Gao et al., 1998a) and indicate that the deep crust is depleted in Li relative to the upper crust, whose Li concentration is estimated to be between 20 and 35 ppm (Rudnick and Gao, 2003; Teng et al., 2004 and references therein).

The continental crust is vertically stratified in terms of its chemical composition and lithology and is heterogeneous on a variety of scales. Therefore, in order to estimate its average composition, the types and average compositions of lithologies in each part of the crust (upper, middle and lower) need to be defined. Following the approach of Rudnick and Fountain (1995) and Gao et al. (1998a), we divide the deep crust into middle and lower crust, using samples from high-grade metamorphic terranes as representative of the middle crust and granulite xenoliths as representative of the lower crust.

5.7.1. Lithium concentration of the deep continental crust

Compared to estimates of Li concentration of the upper and lower crust, only few estimates have been made of the middle crust. Rudnick and Fountain (1995) calculated 7 ppm Li in the middle crust by modeling the middle crust as a mixture of 45% intermediate amphibolite-facies gneisses, 45% mixed amphibolite and felsic amphibolite-facies gneisses and 10% metapelite. Gao et al. (1998a) estimated Li concentration of the middle continental crust from 14 to 18 ppm with an average of ~16 ppm based on samples from amphibolite-facies terranes in Eastern China. The most recent estimate by Rudnick and Gao (2003) gives an average Li concentration of 12 ppm by averaging the middle crustal compositions of Rudnick and Fountain (1995) and Gao et al. (1998a). The metamorphic terrane samples studied here are a portion of those investigated by Gao et al. (1998a), which have already been used to estimate the composition of the middle continental crust of the East China. We therefore focus on granulite xenolith data and use them to estimate the Li concentration of the lower crust.

Although the entrainment of xenoliths in host magma has significantly modified Li isotopic compositions of some granulite xenoliths, as evidenced by isotopic disequilibria between plagioclase and pyroxene, the effects of host magma infiltration on Li concentrations of most xenoliths are considered negligible because 1) in most cases, only Li-poor plagioclase has been significantly affected; pyroxene, which dominates the Li budget, is less affected; 2) Li concentrations of granulite xenoliths are generally similar to or greater than those of host basaltic magma, making it difficult to change the Li concentration of granulites by small-scale infiltration of host lava.

The average Li concentration of granulite xenoliths from Australia, China, France and Germany varies from 4 to 14 ppm, with a mean of 8 ppm (Table 6). Granulite xenoliths from Nova Scotia, Canada, have been excluded in this compilation because their relatively low equilibration pressures (0.45 to 0.6 GPa, Owen et al., 1988) place them at middle crustal levels, their high Li concentrations (the average=44 ppm) may reflect extensive retrograde overprinting (Eberz et al., 1991) and they appear to have been dissolved for ICP-MS analyses using a sodium peroxide flux fusion method for which the Li blank is unknown. The globally average Li concentration of the lower crust is therefore estimated to be 8 ppm (the average of the four locality averages in Table 6), which is similar to previous estimates, ranging from 6 to 14 ppm (Table 7). The comparison is not straightforward, however, since many of these previous estimates were based on data from terranes (which may more closely represent middle crust) and some, like the Taylor and McLennan (1985) estimate, combines middle and lower crust.

The Li concentration of the bulk continental crust is estimated to be 18 ppm by combining the average Li concentrations of the upper, middle and lower crust (Table 8), with their respective weight proportions 0.317:0.295: 0.388 (Rudnick and Gao, 2003). Thus, Li concentration decreases with depth in the continental crust, but is higher, at any depth, than in the mantle. This vertical decrease in Li concentration most likely reflects Li incompatibility during intracrustal differentiation and, to a lesser extent, Li depletion in the deep crust caused by metamorphic dehydration. The latter is likely to be the cause of the overall Li depletion seen in felsic and metasedimentary granulite-facies xenoliths (1–8 ppm, Tables 2 and 3) compared to the Li concentrations in comparable lithologies from terranes (6 to 33 ppm Li) and upper crustal lithologies (8 to 187 ppm, average upper crust=35 ppm, Teng et al., 2004).

5.7.2. Lithium isotopic composition of the deep continental crust

The average δ^7Li of the middle crust is estimated to be +4.0±1.4 based on the high-grade metamorphic terrane data (1σ, simple average, concentration weighted average=+3.7). The Li isotopic composition of the lower crust is estimated by averaging the δ^7Li of granulite xenoliths that show no inter-mineral isotopic fractionation. These samples are the least likely to have been affected by the host lava and may still preserve the lower crustal Li signatures. δ^7Li of eight such granulite xenoliths ranges from −14.0 to +14.3, with a concentration weighted average of +2.5 and a simple average of +1.6±8.9 (1σ). For comparison, the concentration weighted δ^7Li for all whole-rock granulite xenoliths is −1.3 while the simple average is −1.1±7.2 (1σ).

The concentration weighted average of +2.5 is considered to be the best estimate of the average δ^7Li of the lower continental crust.

The lower continental crust is extremely isotopically heterogeneous, with ~30‰ isotopic variation. The extremely light Li isotopic compositions of some granulite xenoliths, with δ^7Li down to −14, may reflect a small amount of Li isotopic fractionation during progressive metamorphism or arrested Li diffusion effects near intrusions (e.g., Teng et al., 2006b; Marks et al., 2007). The origins of the isotopically heavy xenoliths, with δ^7Li up to +14.3, are unclear. These samples may reflect unusually heavy Li isotopic compositions of the protoliths, or equilibration with isotopically heavy Li in fluids (e.g., Marks et al., 2007) at some stage before they were entrained by the host magma. Nevertheless, the Li isotopic heterogeneity in the lower crust indicates either that pervasive fluid migration and equilibration did not occur or it occurred on only a very small scale and prevented the homogenization of Li isotopic composition of the lower crust. This finding is consistent with previous studies showing B elemental and O isotopic heterogeneity in granulite-facies xenoliths and granulite terranes (Valley and O'Neil, 1984; Kempton and Harmon, 1992; Leeman et al., 1992).

Following the method used above for estimating the average Li concentration of the bulk continental crust, the average δ^7Li of the continental crust is estimated to be ~+1‰. The middle crust appears to be isotopically similar to the mantle and somewhat heavier than the upper and lower crust. This vertical stratification of Li isotopic composition of the continental crust may reflect isotopic fractionation during various geological processes such as weathering (for the upper crust) and progressive metamorphism (for the lower crust).

6. Conclusions

Samples from Archean high-grade metamorphic terranes in East China and granulite xenoliths from China and eastern Australia have been measured to constrain the average Li concentration and isotopic composition of the middle and lower continental crust. Thirty samples from eight metamorphic terranes show limited variability in δ^7Li (from +1.7 to +7.5) with an average value of +4±1.4 (1σ). These results suggest that the middle continental crust is relatively homogenous in Li isotopic composition and indistinguishable from the upper mantle.

In contrast to metamorphic terrane samples, all three suites of granulite xenoliths, including both whole rocks and mineral separates, have lower Li concentrations and exhibit a much larger range in δ^7Li values, from ~−18 to ~+17, with pyroxene equal to or lighter than coexisting plagioclase by up to −16‰. This large Li isotopic variation between minerals and in whole-rock granulites likely reflects diffusion-driven kinetic isotopic fractionation during interactions of xenoliths with host magma. Only those xenoliths that lack inter-mineral isotopic fractionation may still preserve their lower crustal Li isotopic signatures. Eight of such samples have been used to estimate the average Li isotopic composition of the lower continental crust, which has δ^7Li from −14 to +14.3, with a concentration weighted average of +2.5. The isotopically heterogeneous lower continental crust likely reflects the combined effects of isotopic fractionation during prograde metamorphism, arrested kinetic Li isotopic fractionation associated with basaltic intrusions and variable protolith compositions.

Based on available data for granulite xenoliths, the average Li concentration of the lower crust is estimated to be ~8 ppm. Together with previous estimates of Li concentration of the upper and middle crust, the average Li concentration of the bulk continental crust is estimated to be 18 ppm, similar to previous estimates. Collectively, the average Li isotopic composition of the continental crust is estimated to be +1, isotopically lighter than fresh basalts.

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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.chemgeo.2008.06.009.

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