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Lithium isotopic composition and concentration of the upper continental crust

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Abstract—The Li isotopic composition of the upper continental crust is estimated from the analyses of well-characterized shales, loess, granites and upper crustal composites (51 samples in total) from North America, China, Europe, Australia and New Zealand. Correlations between Li, δ^7Li, and chemical weathering (as measured by the Chemical Index of Alteration (CIA)), and δ^7Li and the clay content of shales (as measured by Al_2O_3/SiO_2), reflect uptake of heavy Li from the hydrosphere by clays. S-type granites from the Lachlan fold belt (–1.1 to –1.4‰) have δ^7Li indistinguishable from their associated sedimentary rocks (–0.7 to 1.2‰), and show no variation in δ^7Li throughout the differentiation sequence, suggesting that isotopic fractionation during crustal anatexis and subsequent differentiation is less than analytical uncertainty (±1‰, 2σ). The isotopically light compositions for both I- and S-type granites from the Lachlan fold belt (–2.5 to + 2.7 ‰) and loess from around the world (–3.1 to + 4.5‰) reflect the influence of weathering in their source regions. Collectively, these lithologies possess a limited range of Li isotopic compositions (δ^7Li of −5‰ to + 5‰), with an average (δ^7Li of 0 ± 2‰ at 1σ) that is representative of the average upper continental crust. Thus, the Li isotopic composition of the upper continental crust is lighter than the average upper mantle (δ^7Li of + 4 ± 2‰), reflecting the influence of weathering on the upper crustal composition. The concentration of Li in the upper continental crust is estimated to be 35 ± 11 ppm (2σ), based on the average loess composition and correlations between insoluble elements (Ti, Nb, Ta, Ga and Al_2O_3, Th and HREE) and Li in shales. This value is somewhat higher than previous estimates (~20 ppm), but is probably indistinguishable when uncertainties in the latter are accounted for. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Assessing the Li isotopic compositions of crustal rocks and minerals is important for tracing weathering processes in the crust and documenting interaction between the crust and mantle. Our knowledge of Li isotope geochemistry, however, is mostly limited to the hydrosphere and mantle. Little is known about its general characteristics in the continental crust, which is of fundamental importance for using Li as a geochemical tracer of crustal recycling. The published data that existed before this study suggest the continental crust is isotopically lighter than seawater (~30‰, see caption of Table 1 for definition of δ^7Li), but heavier than mantle-derived magma (~+4 ± 1‰ for MORB) and the mantle itself (Chan et al., 1994; You et al., 1995; Huh et al., 1998; James et al., 1999; James and Palmer, 2000; Huh et al., 2001). If so, it raises the dilemma that all major reservoirs in the silicate Earth appear to have heavier Li isotopic compositions than the upper mantle, which is generally considered to reflect the isotopic composition of the bulk Earth.

To better constrain the Li isotopic composition of the upper continental crust, we have undertaken a systematic study of granite, upper crustal composites and sedimentary rocks. These data place constraints on the average Li concentration and Li isotopic composition of the continental crust, particularly the upper continental crust, and thus yield further insights into the Li budget of the silicate Earth.

2. SAMPLES

Two approaches have generally been used to determine the composition of the upper continental crust (for details, see Rudnick and Gao, 2003). One is to establish weighted averages of the compositions of rocks exposed at the surface. This is the method used to derive estimates of the concentrations of major elements and a number of soluble trace elements in the upper continental crust. The other approach is to determine the average concentrations of insoluble elements in fine-grained clastic sedimentary rocks or glacial deposits and use these to infer the average composition of their source regions.

Here we use both methods to evaluate the Li concentration and isotopic composition of the upper continental crust. Samples investigated here include all major upper crustal silicate rock types i.e., both I (igneous)- and S (sedimentary)-type granites from the southeastern Australia type localities (Chappell and White, 1974), upper crustal composites from China that include graywackes, shales and granites (Gao et al., 1991; 1992; 1998), loess from around the world (Taylor et al., 1983) and the suite of Post Archaean Australian Shales (PAAS), ranging in age from Proterozoic to Triassic, which S.R. Taylor and co-workers used to constrain the rare earth element (REE)

content of the upper crust (Nance and Taylor, 1976). All of the samples we measured have been extensively characterized in previous investigations and previously published chemical data are supplied as an electronic annex (Elsevier, Science Direct).

2.1. Granites

Granite is a significant component of the upper continental crust, so the Li isotopic composition of granite can be used to place constraints on the δ^7Li value of the upper crust. Moreover, given their origin as infracrustal melts, and assuming that Li does not fractionate significantly at magmatic temperatures (Tomascak et al., 1999b), granites may provide insight into the isotopic composition of their source regions in the middle and lower crust. To date, only a few δ^7Li data have been published for felsic igneous rocks (2 granite and 1 diorite standards), and these vary from –1.2 to + 2.3‰ (James and Palmer, 2000).

We have analyzed eight I-type granites from the Bega Batholith and two S-type granites from the Wagga Batholith, Southeastern Australia, which is the type locality for defining I- and S-type granites (Chappell and White, 1974). The Bega Batholith is subdivided into eight supersuites, within which the rocks share similar compositional features (Chappell, 1984; Chappell and White, 1992; Chappell et al., 2000). I-type granites from seven of these supersuites were chosen for this study. The two S-type granites represent the two end members of the S-type granite spectrum from the Koetong suite: (1) the most mafic rock (VB30), a mafic biotite-cordierite granodiorite, and (2) the most felsic rock (VB98), a strongly fractionated two-mica granite. The temperature of formation of this suite is estimated to range from ~800 to 720°C, using the zircon saturation thermometrer of Watson and Harrison (1983). We have also analyzed two sedimentary rocks that are interpreted to be similar to the source for the S-type granites, although less feldspathic (Chappell et al., 2000). They cover most of the observed compositional range for Ordovician sedimentary rocks from the Lachlan Fold Belt, ranging from clay-rich (OS35) to quartz-rich (OS37) bulk compositions (for mineralogical description of these samples, see Wyborn and Chappell, 1983). All samples are fresh, having been sampled far from weathering surfaces, and, in the case of the sedimentary rocks, deep underground during construction of water tunnels through the Snowy Mountains.

2.2. Loess and Shales

Loess is wind-blown sediment derived from glacial outwash and desert regions. It has been used to study the average composition of the upper continental crust (e.g., Taylor et al., 1983; Gallet et al., 1998; Barth et al., 2000; Peucker-Ehrenbrink and Jahn, 2001) because it samples large geographical areas and is produced by the mechanical abrasion of glaciers, thus limiting the chemical effects of weathering (Flint, 1947; Smalley and Cabrera, 1970). Quartz, feldspar and muscovite (or illite) are the most important minerals in the loess investigated here, along with small amount of clay minerals (generally <10%) (Taylor et al., 1983). In addition, some samples (e.g., those from Kaiserstuhl) contain calcite and dolomite. The major element compositions of loess deposits demonstrate that their source lithologies have experienced at least one cycle of aqueous sedimentary processing (Gallet et al., 1998). To date, there are no published Li isotopic compositions for loess, although a δ^7Li value of ~+15‰ is plotted for one loess sample from Mississippi in a diagram in Huh et al. (1998).

Loess from a number of different geological provinces have been investigated here (e.g., New Zealand, China, North America, Europe). Most of these samples were previously studied by Taylor et al. (1983) and Barth et al. (2000) to define the composition of the upper continental crust. The provenance of these samples is diverse. Loess from Banks Peninsula, New Zealand, derive from Mesozoic graywackes in the Southern Alps. Loess from the Kaiserstuhl, Germany, derive from glacial erosion of the Alps. Chinese loess derives from non-glacial alluvium in the Gobi desert, and the loess from the midwestern USA are probably derived from river outwash from the Rocky Mountains (Taylor et al., 1983). The loess studied here typically show a restricted range of weathering, as reflected by their relatively low chemical index of alteration (CIA) values between 50 and 75, with an average of 60 (CIA = molar $Al_2O_3/(Al_2O_3+CaO*+Na_2O+K_2O)$), where CaO* refers only to Ca that is not in carbonate and phosphate, Nesbitt and Young, 1982; McLennan, 1993). Unweathered igneous rocks typically have CIA around 50 ± 5 (Nesbitt and Young, 1982). The relatively restricted range and low values of CIA in loess suggests a similar degree of moderate weathering for loess source regions (Gallet et al., 1998).

Shales are fine-grained sedimentary rocks, composed primarily of clays and silt-sized quartz that provide another means of accessing the insoluble element composition of the upper continental crust. In contrast with loess, shales form by more complex processes (e.g., chemical and physical erosion, transportation, deposition and lithification, including diagenesis and metamorphism) and generally reflect higher degrees of weathering. Nevertheless, insoluble element ratios vary little in shales (e.g., La/Yb, La/Th, Taylor and McLennan, 1985; McLennan, 2001), thus allowing one to use the composition of shales to derive an estimate of the average composition of their upper crustal source regions. Previously, only three Li isotopic values have been reported for shales: two from an accretionary prism in Japan at −1.5‰ and –2.7‰ (Moriguti and Nakamura, 1998a) and one international shale standard SCO-1, with a δ^7Li value of +5.2‰ (James and Palmer, 2000).

The shales measured here were originally studied by Nance and Taylor (1976) to determine the average REE composition of the upper continental crust (the PAAS samples, which are further described in Taylor and McLennan, 1985). They were deposited in four separate basins in Australia (Perth Basin, Canning Basin (both in western Australia), Amadeus Basin, Central Australia and State Circle, Australian Capitol Territory). The age of deposition of these samples ranges from upper Proterozoic (850 Ma) to Triassic. All samples were obtained as well cores to avoid problems of surface weathering and leaching. CIA values of the samples measured here range from 58 to 80, with an average value of 70 (cf. 60 in loess).

2.3. Crustal Composites

The composite samples were previously used to study the chemical composition of the upper continental crust in eastern China (Gao et al., 1991; 1992; 1998) and comprise all major upper continental crust rock types including graywackes,

pelites, granites, granodiorites and one diorite. Each composite was produced from between 10 to 100 individual rock samples of the same age and lithology. The samples range in age from Precambrian to Phanerozoic and derive from three tectonic units in China: the North Qinling Belt, the South Qinling Belt and the Yangtze craton, each of which is further divided into different subunits. Samples from the North Qinling Belt and the South Qinling Belt are slightly metamorphosed (up to green-schist-facies with one graywacke (D059) that is amphibolite-facies), while those from the Yangtze craton are unmetamorphosed. Care was taken during sampling to avoid any weathered material by sampling road cuts and fresh stream cuts.

3. ANALYTICAL METHODS

Samples used in this study were dissolved in a 3:1 mixture of concentrated HF-HNO$_3$ in Savillex screw-top beakers on the hotplate (T < 120°C), followed by replenishment of the dried residua with HCl until solutions were clear. After drying, the samples were re-dissolved in 5 mL 1M HNO$_3$ and mixed with 3 mL of 100% methanol (CH$_3$OH); these solutions were added to the cation exchange column (12 mL columns of BioRad AG50W-x8). Lithium is eluted completely with 100 mL 1.0 M HNO$_3$ in 80% methanol elution solution (Tomascak et al., 1999a; 1999b). The total Li procedural blank during this study was ~200 pg, having a δ^7Li value of ~ −20‰. Compared with samples used in this study (≥100 ng Li with δ^7Li values within 0 ± 5‰), the Li procedural blank is negligible at present levels of precision (e.g., ±1‰, 2 σ).

Before analyses, the Na/Li voltage ratio of each solution is evaluated semiquantitatively on the mass spectrometer. Solutions with a high Na/Li voltage ratio (≥5) are reprocessed through a 2nd clean-up column (similar to the 3rd column procedure of Moriguti and Nakamura 1998b), with 11 mL of 0.5 M HCl in 30% ethanol (CH$_3$CH$_2$OH) solution eluted through 1 mL of cation exchange resin (BioRad AG50W-x12). The procedural blank for this step is <10 pg. Samples with Na/Li voltage ratios <5 consistently give accurate and precise δ^7Li values.

Purified Li solutions (~100 ppb Li in 2% (v/v) HNO$_3$ solutions) are introduced to the Ar plasma using an auto-sampler (ASX-100 Cetac Technologies) through a desolvating nebulizer (Aridus Cetac Technologies) fitted with a PFA spray chamber and micro-nebulizer (Elemental Scientific Inc.). Samples are analyzed using a Multi-Collector-Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS) from Nu-Plasma (Belshaw et al., 1998), with ^{7}Li and ^{6}Li measured simultaneously in two opposing Faraday cups (^{7}Li in the high mass Faraday cup (H6) and ^{6}Li in the low mass faraday cup (L5)). Each sample analysis is bracketed before and after by measurement of the L-SVEC standard (Flesch et al., 1973) having similar solution concentration (within ~50%). At least two other Li standards (e.g., the in-house Li-UMD-1 [a purified Li solution from Alfa Aesar] and IRMM-016 (Qi et al., 1997)) were routinely analyzed during the course of an analytical session. For a solution with ~100 ppb Li and solution uptake rate of 30 μL/min, we typically measure a ^{7}Li$^+$ ion current of 50 pA (10^{11} ohm resistor) or 5 V, thus the ion yield for Li is ~0.007%. In comparison, the procedural blank is ~10 mV on mass 7. The in-run precision on ^{7}Li/^{6}Li measurements is ≤±0.2‰ for two blocks of 20 ratios each, with no systematic change in isotope ratio. The external precision, based on 2 σ of repeat runs of pure Li standard solutions, is ≤±1.0‰. For example, IRMM-016 gives δ^7Li = −0.1 ± 0.2‰ (2 σ, n > 100 runs); and in-house standard Li-UMD-1 gives δ^7Li = +54.7 ± 1‰ (2 σ, n > 100 runs).

The Li concentrations of shales and loess samples were determined by isotope dilution using a ^{6}Li-enriched spike (^{ID}Li), following the same preparation procedure for isotopic analysis. We have also measured the Li concentration in unspiked samples by voltage comparisons (^{V}Li) with that obtained for L-SVEC standard of known concentration and then adjusting for sample weight. Both methods yield results to

within 5% of one another (Table 2). The precision obtained by isotope dilution is better than ±2%.

4. RESULTS

Lithium concentrations and isotopic compositions are reported in Table 1 for granite samples, Table 2 for loess and shale samples, and Table 3 for Chinese composite samples. All sample sets show a limited spread in δ^7Li values (Fig. 1), with a distinct mode in δ^7Li values at ~0‰ and a comparable dispersion ± 3‰ (1σ). This figure also shows the data for suspended load from the Orinoco River, which is mainly supplied by the three largest tributaries of the Andes and less so from the Guayana shield (Huh et al., 2001). The similar and relatively restricted range of Li isotopic compositions observed for all of the crustal samples provide a coherent picture of the δ^7Li value of the upper continental crust.

4.1. Granites

The southeastern Australian I- and S-type granites and the associated Ordovician sedimentary rocks show a relatively restricted range in Li isotopic compositions (−2.5 to +2.7‰) regardless of their diverse lithologic origins, bulk compositions and markedly different Li concentrations. The mafic S-type granite end member has a Li concentration within the range observed for the Ordovician sedimentary source rocks, and is on the high side of concentrations observed for the I-type granites. In contrast, the most evolved S-type granite has the highest Li concentration observed in the suite (187 ppm). Both S-type granites have Li isotopic compositions within uncertainty of those of the Ordovician sedimentary rocks. Lithium concentration in the I-type granites ranges from 16 to 62 ppm and δ^7Li ranges between −2.5 to +2.7‰.

4.2. Loess and Shales

Shales have δ^7Li values that range from −3.2 to +3.9‰ and show a factor of 3 spread in Li concentrations (28 to 109 ppm). Loess have a comparable spread of δ^7Li values (−3.1 to +4.8‰). However, in contrast to shales, loess have a relatively constant Li content at 29 ± 16 ppm (2 σ), matching their restricted range of CIA values (57–64). A comparison of these features for shales and loess are shown in Figure 2.

The relatively low CIA values in loess are consistent with these sediments having experienced limited weathering. In contrast, shales, which show a greater spread in Li concentrations and CIA values, are more strongly weathered (i.e., higher clay component). Shales show a positive, albeit weak, correlation of CIA values with Li concentrations and δ^7Li values, whereas loess show no trend (Fig. 2). Lithium and Al$_2$O$_3$ contents correlate positively for most sediments (Holland, 1984) and the Australian shales follow the global correlation, although PAAS cover a narrower range of Al$_2$O$_3$ contents (Fig. 3f). In addition, these shales also define weak positive correlations between Li and insoluble elements (e.g., Ti, Ga, Nb, Ta, HREE and Th concentrations; Fig. 3).

Table 1. Lithium concentration and isotopic composition of granites (I- and S-types) and sedimentary rocks from Southeastern Australia and previously published felsic international rock standards.

Sample	Unit	Rock type	$\delta^7 Li^a$	$^V Li$ (ppm)[b]	CIA[c]
Ordovician sedimentary rocks					
OS35		Shale	1.2	49	72
OS38		Graywacke	−0.7	31	65
Lachlan fold belt granites					
VB30	Ganmain	S-type, mafic end member	−1.4	44	57
VB98	Mt. Flakney	S-type, felsic end member	−1.1	187	58
MG14	Moruya	I-type	+0.3	22	50
MG20	Bodalla	I-type	+0.8	30	52
AB40	Kameruka	I-type	−2.5	21	52
AB105	Bemboka	I-type	−2.1	34	51
AB128	Cobargo	I-type	+0.1	26	48
AB249	Yalgatta	I-type	+2.7	18	49
AB289	Cann Mtn	I-type	+1.8	62	51
AB293	Braidwood	I-type	−0.1	16	48
Felsic rock standards					
G-2	Inter. Rock Std.[d]	Granite	−1.2	34	
JG-2	Inter. Rock Std.[d]	Granite	−0.3	43	
DR-N	Inter. Rock Std.[d]	Diorite	2.3	40	

[a] The Li isotopic compositions are average values from at least 2 repeat measurements that agree within 1‰ for the same solution. $\delta^7 Li = [(^7 Li/^6 Li)_{Sample}/(^7 Li/^6 Li)_{LSVEC} − 1] \times 1000$. Analytical uncertainty is ±1‰ (2σ), based on analyses of pure Li solutions (see text).

[b] $^V Li$ = Li measured by voltage comparison with standard of known concentration. See text for details.

[c] CIA refers to the chemical index of alteration and is the molar ratio of $Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)$ as defined by Nesbitt and Young (1982), where CaO^* represents Ca in the silicate fraction only. Higher CIA values are characteristic of more altered samples. McLennan's (1993) correction to the measured CaO content for the presence of Ca in carbonates and phosphates is used here. Major element data for CIA calculations are from Chappell (1984), Chappell and White (1992) and Chappell et al. (2000).

[d] Data from James and Palmer (2000).

4.3. Crustal Composites

The Chinese composites have similar Li isotopic compositions to one another, and are comparable to those seen in the other upper crustal samples. Four composite graywackes have very uniform $\delta^7 Li$ values from –1.1 to + 0.6‰, whereas the seven composite pelites show a larger spread in $\delta^7 Li$ values from –5.2 to +1.2‰ (average = −1.1‰). The –3.4 to +3.0‰ range of $\delta^7 Li$ values in Chinese granite composites is only slightly greater than that observed for the southeastern Australian granites. The Li concentrations of the composite samples vary considerably (from 8 to 77 ppm Li); the pelites have the highest concentrations and the granites the lowest.

5. DISCUSSION

The similar average $\delta^7 Li$ composition for each group of upper crustal samples we investigated here is surprising considering the diversity of processes that gave rise to these samples (e.g., weathering, sedimentation, mechanical erosion, partial melting, crystal fractionation, vapor-melt equilibrium), and the fact that Li is a fluid-mobile (soluble) element that experiences large fractionation between minerals and fluids at low temperatures. In this section we evaluate how these processes may have affected the Li content and isotopic composition of the samples and then use our data to derive estimates of the Li abundance and isotopic composition of the upper

continental crust. We finally use our upper crustal estimate to model Li mass balance in the silicate Earth.

5.1. Behavior of Li during Weathering and Mineral-Fluid Exchange

Shales arise through chemical and physical weathering of preexiting rocks (igneous, metamorphic and sedimentary), which produces clays and detrital minerals that are transported through water, deposited and lithified. There are thus multiple opportunities for fluid-mineral interaction and element exchange during the formation of shales, and this might be expected to be reflected in their Li isotopic compositions. On the other hand, loess, with its lower clay content, is primarily a mechanically-generated sediment that experienced limited fluid-rock interaction during its formation. The Li isotopic composition of loess should therefore reliably reflect its source lithologies, which may also include preexisting sedimentary rocks (e.g., Peucker-Ehrenbrink and Jahn, 2001).

During shale formation, there are two main opportunities for Li isotope fractionation: during weathering of the protolith and fluid-rock exchange during transport and deposition. During weathering, $^7 Li$ is preferentially leached into ground waters, as witnessed by the very light isotopic composition of saprolites and laterites compared to their protoliths (Rudnick et al., 2004; Kisakurek et al., 2004) and the slightly lighter Li compositions in a weathering profile on an Icelandic basalt compared to that

Table 2. Lithium concentration and isotopic composition of loess and shales.

Location	Sample ID	δ^7Li^a	^{ID}Li (ppm)[a]	$^VLi^b$ (ppm)	CIA[c]
		Loess			
Banks Penn.,	BP-1	−2.6	37	40	59
New Zealand	BP-2	−1.7	37	38	59
	BP-3	−3.1	30	28	61
	BP-4	+1.4	40	39	57
	BP-5	−0.7	41	41	57
Kaiserstuhl,	1	−0.9	26	26	65
Germany	2	−0.7	23	25	65
Hungary	H	−0.6	29		
	H replicate[a]	−1.1			
Kansas	CY-4a-A	+4.5	17	18	59
Kansas	CY-4a-B	+4.8	18	18	59
Kansas	CY-4a-C	+4.2	17	16	58
Iowa	I	−0.3	26	37	64
Long Island	LI	−1.0	34	32	
China	CH	+0.7	34		
		Shales			
Perth Basin	PW-5	+2.0	109	104	80
Canning Basin	PL-1	−0.3	96	92	80
	PL-1 replicate[a]	−1.4			
State Circle	SC-7	−0.7	30	30	77
State Circle	SC-8	−0.2	28	29	75
Amadeus Basin	AO-6	−2.9	67	65	66
	AO-6 replicate[a]	−3.2			
Amadeus Basin	AO-7	−2.3	51	46	67
Amadeus Basin	AO-9	−2.6	71	77	70
Amadeus Basin	AO-10	−0.7	61	59	72
Amadeus Basin	AO-12	+2.9	80	71	66
	AO-12 replicate[a]	+3.9			
	AO-12 replicate[a]	+3.4			
Japan[d]	S-605	−2.7	57		72
Japan[d]	S-606	−1.5	40		65
North America[d]	SCO-1	+5.2	45		

Analytical uncertainty is ±1‰ (2σ), based on analyses of pure Li solutions (see text).

[a] ID = Isotope dilution; replicate = repeat dissolution and chemical separation of individual samples.

[b] ^VLi = Li measured by voltage comparison with standard of known concentration. See text for details.

[c] The major element data for CIA calculations are from Nance and Taylor (1976) for PAAS and Taylor et al. (1983) for loess (see electronic data annex). The three loess samples (LI, H, CH) are from Diane McDaniel for which major elements are not available. The major element compositions of the Japanese shales are from E. Nakamura (personal communication, 2002) (see data annex for full chemical analyses).

[d] Japanese shales are from Shimanto accretionary prism. Li isotopic data and concentrations reported in Moriguti and Nakamura (1998a). The international Rock Standard data (SCO-1) is from James and Palmer (2000).

of unweathered basalt (Pistiner and Henderson, 2003). Water-mineral exchange experiments also document preferential sorption of ^6Li onto some weathering products (e.g., gibbsite and ferrihydrite), although sorption onto smectite did not result in isotopic fractionation (Pistiner and Henderson, 2003).

From the above discussion, one can conclude that both weathering and mineral-fluid exchange should result in isotopically light weathered products and heavy waters. However, our results reveal that shales, which represent the most weathered of the upper crustal samples we investigated, have, on average, δ^7Li values that are within uncertainty of those of the less weathered samples (loess, greywacke composites, granites). The reasons for this unexpected result may lie in the uptake of heavy Li from the hydrosphere by the clays of shales and the presence of weathered materials in the source regions of the granites and loess.

Lithium is concentrated in the clay fraction of shales and this Li is isotopically heavy. Support for this idea comes from the correlations observed in shales between Li concentration and δ^7Li, CIA (Fig. 2), and Al_2O_3 (Fig. 3), and δ^7Li and Al_2O_3/SiO_2 (Fig. 4). The trend on the latter diagram reflects mixing between clays (illite and smectite with Al_2O_3/SiO_2 between 0.3 to 0.9) and quartz ($Al_2O_3/SiO_2 = 0$), and shows that the clay-rich shales have heavier Li isotopic compositions. This mixing is similar to that observed in low-T alteration of mid-ocean ridge basalts, which results from the uptake of heavy seawater Li by clays (Chan et al., 1992). Such reactions have also been documented experimentally (Seyfried et al., 1998; James et al., 2003).

If this explanation is correct, sorption of Li onto clays results in increased Li concentrations, with the isotopic composition of the added Li being a function of the composition of the waters

Table 3. Lithium concentration and isotopic composition of upper crustal composites from China.

Sample	Unit[a]	n[b]	Age	Rock type	δ^7Li	$^VLi^c$ (ppm)	CIA[d]
D059	II	82	Paleoproterozoic	Graywacke	−1.1	49	55
D060	II	36	Mesoproterozoic	Graywacke	+0.4	31	64
D062	II	5	Paleoproterozoic	Graywacke	+0.6	65	55
D075	IV	16	Neoproterozoic	Graywacke	−0.1	21	56
D100	III	16	Devonian	Pelite	+0.9	51	60
D104	III	2	Carboniferous	Pelite	−5.2	77	80
D111	III	24	Silurian	Pelite	−0.1	46	72
D119	IV	15	Neoproterozoic	Pelite	+1.2	41	66
D122	IV	25	Silurian	Pelite	−2.1	48	72
D124	IV	7	Jurassic	Pelite	+0.1	49	79
D355	III	172	Devonian	Pelite	−2.6	42	77
D276	II	23	Cretaceous	Granodiorite	+1.3	18	51
D284	III	21	Neoproterozoic	Diorite	−3.4	22	51
D308	IV	12	Neoproterozoic	Granodiorite	+0.2	18	48
D312	IV	12	Neoproterozoic	Granite	−0.5	22	52
D314	IV	15	Neoproterozoic	Granite	+3.0	8	51

Analytical uncertainty is ±1‰ (2σ), based on analyses of pure Li solutions (see text).

[a] Unit. II = The North Qinling Belt; III = The South Qinling Belt; IV = The Yangtze craton. For details, see Gao et al. (1998)

[b] n = Number of individual samples comprising the composite.

[c] ^VLi = Li measured by voltage comparison with standard of known concentration. See text for details.

[d] The major element data for CIA calculations are from Gao et al. (1998) and are provided in the electronic data annex.

from which it is derived and the amount of isotopic fractionation that occurs during sorption. Assuming Pistiner and Henderson's (2003) results for smectite are generally applicable to clays (i.e., no isotopic fractionation during sorption), the added Li reflects the isotopic composition of the water. We expect Li in continental waters to be relatively heavy, as heavy Li is preferentially leached during weathering (Rudnick et al., 2004; Kisakurek et al., 2004; Pistiner and Henderson, 2003). Indeed, heavy Li is observed in groundwaters (+7 to +31‰, with 3-14 ppb Li, see Hogan and Blum, 2003; Tomascak et al., 2003) and the dissolved loads of rivers (+7 to +36‰, with 0.2 to 5 ppm Li; Huh et al., 2001). Moreover, seawater, in which shales are deposited, has very heavy Li (~+30‰, 0.2 ppm Li; see Fig. 6 for references). Thus, the final Li isotopic composition of shales reflects the balance between light Li generated during weathering and heavy Li added by sorption during transport and deposition of the clays.

5.2. Behavior of Li during Granite Genesis

Granites are derived from melting of the middle and lower crust followed by crystal fractionation and/or restite unmixing during magma ascent, assimilation of upper crustal rocks and finally, fluid exsolution at relatively shallow levels. It has previously been demonstrated that Li isotopes do not fractionate during differentiation of basaltic magmas at temperatures >1050°C (Tomascak et al., 1999), however, the temperature dependence of the fractionation factor (α) for Li isotopes is not well constrained. In principle, Li isotopes could fractionate during any of the above granite-forming steps. The data reported here allow us to evaluate the influence of some of these processes.

The two S-type granites have δ^7Li values similar to the Ordovician sedimentary rocks, suggesting that Li is not significantly fractionated at the temperatures of their formation (~800°C). Moreover, although the Li concentration increased four-fold during differentiation within the S-type suite, δ^7Li

remains unchanged, again suggesting no discernable fractionation at temperatures as low as 720°C. Finally, it is possible that exsolution of a vapor phase may cause Li isotope fractionation. Although we cannot evaluate this possibility with the data we have here, the remarkable similarity of δ^7Li in the granites we measured suggests either that these granites did not exsolve a magmatic vapor phase, or if they did, this exsolution did not significantly fractionate Li isotopes within the granites. We thus conclude the δ^7Li values of the granites faithfully record the isotopic composition of their middle- to lower-crustal sources and these sources are isotopically lighter than the mantle, as sampled by MORB.

Previous work (O'Neil and Chappell, 1977) showed that I- and S-type granite plutons of the Berridale Batholith (Southeastern Australia) are distinct in $\delta^{18}O$, with I-types having $\delta^{18}O$ values between +7.9‰ to +10‰ (well above mantle values) and S-types having $\delta^{18}O$ values >+10‰. More significantly, unpublished data (J. O'Neil, pers. comm.) for the I-type Bega Batholith (samples from this study) also show that the most isotopically primitive suites on the eastern side of the batholith (average $^{87}Sr/^{86}Sr \sim 0.704$ and $\varepsilon_{Nd} \sim +2.2$) have an average $\delta^{18}O$ value of +8.2‰. In at least these cases, I-type granites with Sr and Nd isotopic compositions closest to mantle values have oxygen isotopic compositions significantly higher than values typical of the mantle ~ +5.4‰ (Eiler, 2001). Elevated values of $\delta^{18}O$ require that at least some of the source materials for these I-type granites experienced a low temperature weathering cycle. The significance for this study is that such weathering is expected to fractionate Li isotopes to lower δ^7Li values, which may account for the observed displacement of Li isotopic compositions of the granites relative to mantle values. In this context it is noteworthy that I-type granites from the New England Batholith (NEB), Australia, which are believed to represent an accreted intraoceanic arc that formed far from the continent, range to heavier Li isotopic
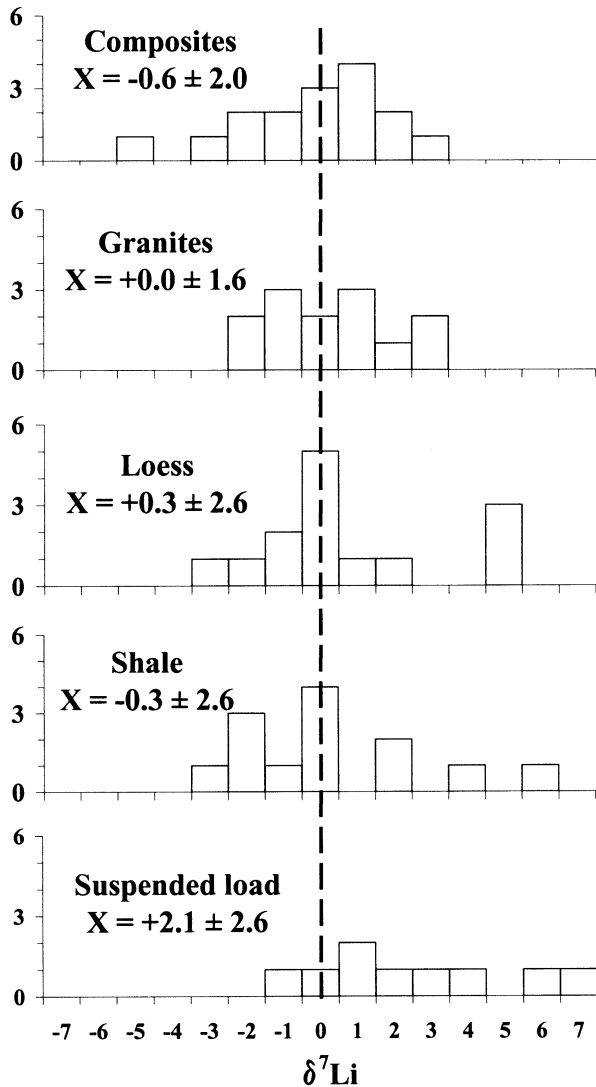
Fig. 1. Histograms of Li isotopic compositions of different continental crustal rocks. Data are from Tables 1, 2 and 3. Suspended load data are from Huh et al. (2001). X = average δ^7Li value (‰) with σ. The vertical dashed line is drawn at δ^7Li of 0 for reference. See text for explanation.

Fig. 2. (a) δ^7Li (‰) vs. CIA (b) Li vs. CIA (c) δ^7Li vs. Li. CIA ranges for granite are from Nesbitt and Young (1982). Data from Tables 1 and 2. See text or Table 2 for definition of CIA.

compositions (δ^7Li = −2 to +8‰), whereas NEB S-type granites are light (−0.1 to +2.1‰), with compositions that overlap those observed here (Bryant et al., 2003a).

Since the Li concentration in shales is significantly greater than that of unaltered mafic igneous rocks (e.g., ~60 vs. 4 ppm, average of data in Table 2 and value from the literature, respectively), relatively small amounts of shales in the I-type source region will have a dominating influence on Li, but little influence on oxygen. For example, a mixture of 20% shale (having δ^7Li = 0‰ and 60 ppm Li and δ^{18}O = +20‰) and 80% mantle-derived gabbro (having δ^7Li = +4‰ and 4 ppm Li and δ^{18}O = +5‰), would have δ^7Li = +0.8‰ and δ^{18}O = 8.0‰ (assuming oxygen contents of shale and gabbro are equal). This explains why the oxygen signature of I- and S-type granites are distinct, whereas the Li signatures are similar.
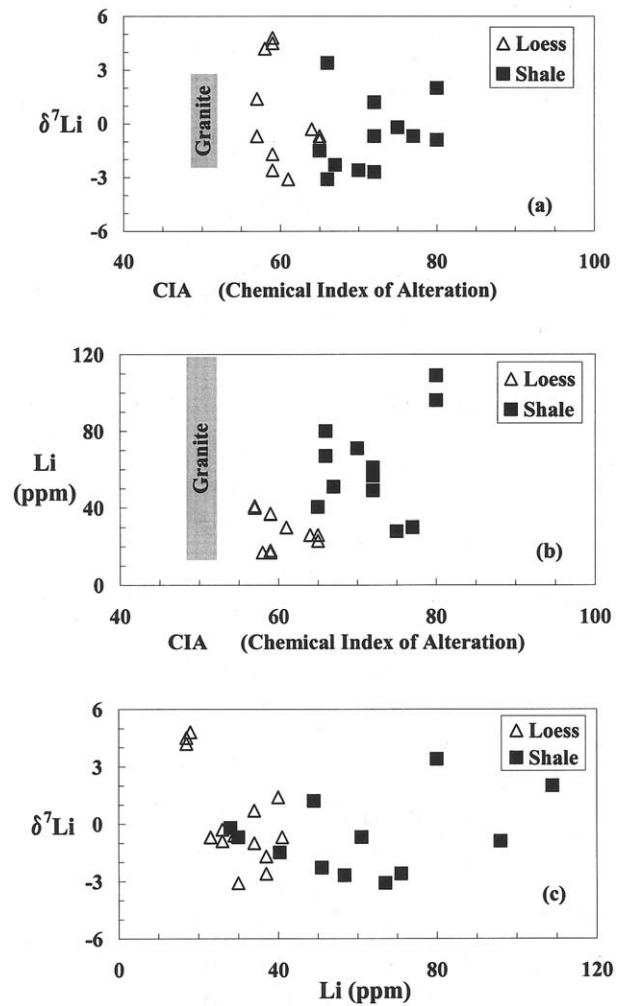
5.3. Lithium in the Upper Continental Crust

Collectively, our data suggest that the isotopically light Li observed in all of the upper crustal samples investigated here results from weathering of the continents and release of heavy Li to the oceans. In this section we use our data to derive the Li concentration and isotopic composition of the upper continental crust.

5.3.1. Lithium concentration in the upper continental crust

Estimates of the Li content of the upper continental crust date back to the pioneering work of F. W. Clarke (Clarke, 1889; Clarke and Washington, 1924), who suggested that there is ~50 ppm Li in the crust, based on an average of hundreds of analyses of exposed rocks. More recent studies have converged on a lower Li content, ca. 20 ppm, for the upper continental crust (Table 4).

The loess samples investigated here show a relatively restricted range of Li concentrations, from 17 ppm to 41 ppm,
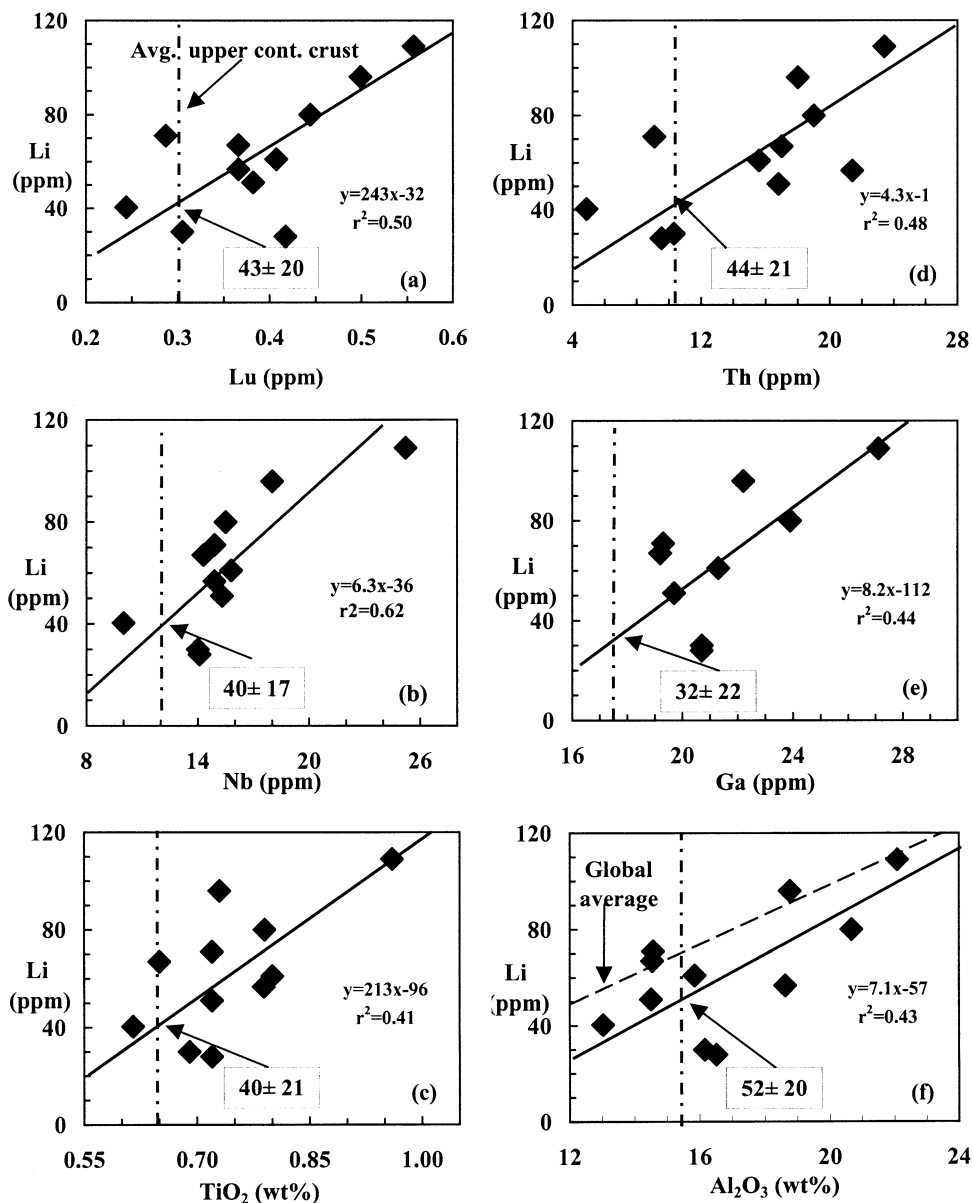
Fig. 3. Li ppm verses concentrations of insoluble elements in shales. Data are from Table 2 and Barth et al. (2000) (all data are available in the electronic data annex). Nb and Al_2O_3 data for the two Japanese shales are from E. Nakamura (pers. comm., 2002). Ta (not shown) produces a similar correlation to Nb, and yields a Li concentration of 27 ± 17. The dot-dashed line represents the element concentration in the upper continental crust from Rudnick and Gao (2003). The global average correlation for Li vs. Al_2O_3 (f) is from Holland (1984). The Li concentration of the upper continental crust and associated uncertainty (1 σ) is shown in each panel, as well as the linear regression (calculated in Isoplot (Ludwig, 1998), using analytical uncertainties as errors for individual data points). The least squares method of Isoplot minimizes distance from the regression line (as opposed to minimizing y-axis deviations from the line, as in other software such as Excel). The weighted mean Li content from these regressions is 39 ± 14 ppm (2 σ), derived from the following expression (Bevington and Robinson, 2003):

$$\text{weighted mean} = \frac{\Sigma \dfrac{\bar{x}}{\sigma^2}}{\Sigma \dfrac{1}{\sigma^2}} \quad \text{variation on mean} = \sqrt{\frac{1}{\Sigma \dfrac{1}{\sigma^2}}}$$

where $\bar{x}$ = mean from linear regression, σ is one standard deviation from regression.

which is the result of physical mixing of glacially eroded sediments derived from a large variety of upper crustal rock types (igneous, metamorphic and sedimentary). The population shows a distribution with an average value of 29 ± 16 ppm (2 σ); this number provides a first-order estimate of the Li concentration of the upper continental crust.
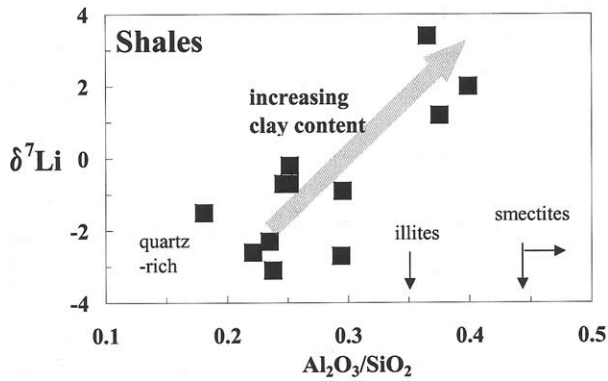
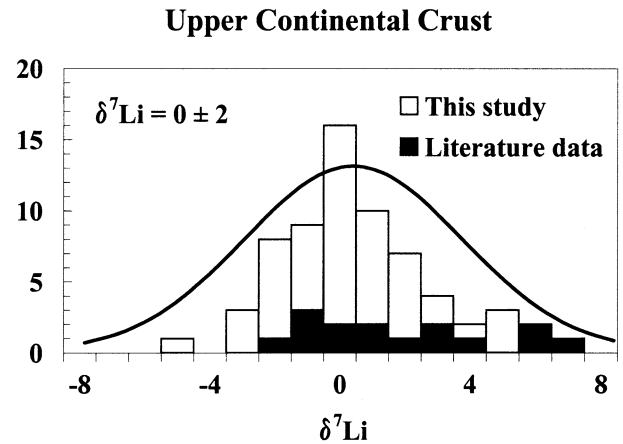Fig. 4. δ^7Li vs. Al_2O_3/SiO_2 for shales (data from Tables 1, 2 and electronic data annex).

Fig. 5. Lithium isotopic composition of the upper continental crust. Literature data are from Tables 1, 2 and Figure 1. All these data form a gaussian distribution with an average δ^7Li (‰) value at 0 and standard deviation at 2. Solid line is the fitted gaussian curve.

Due to the weathering and sorption processes discussed above, the Li contents of shales vary considerably from 28 to 109 ppm, depending on their proportion of clays to quartz. To compensate for these effects, we examined the positive correlation between Li and elements considered to be immobile during weathering (see Fig. 4 of Rudnick and Gao, 2003). Lithium correlates positively ($R^2 \geq 0.4$) with the following elements: Ti, Nb, Ta, Ga, Al_2O_3, Th and HREE (Fig. 3). Using these correlations and average upper crustal concentrations of these insoluble elements (Rudnick and Gao, 2003), we determined a Li concentration of the upper crust from each correlation (Fig. 3). The weighted mean of these results is 39 ± 14 ppm (2 σ) (see figure caption for details of calculations). Combining these estimates from loess and shales, we obtain a weighted mean upper crustal Li concentration of 35 ± 11 ppm (2 σ). This value is somewhat higher than the more recent estimates of the lithium concentration of the upper continental crust (Table 4), however, no uncertainties are provided for these previous estimates and it is likely that they would agree, within uncertainty, of the value obtained here.

Table 4. Estimates of the Li concentration in the upper continental crust.

Li (ppm)	References
50[a]	Clarke (1889)*, Clarke and Washington (1924)
20[b]	Taylor (1964)*, Wedepohl (1969), Taylor and McLennan (1985, 1995), McLennan (2001)
22[c]	Shaw et al. (1967*, 1976, 1986); Wedepohl (1995)
21[d]	Gao et al. (1998)
35 ± 11[e]	This study

* Original estimate; later papers shown used this same estimate.
[a] Based on an average of hundreds of analyses of exposed rocks.
[b] Assuming the upper crust consists of a 1:1 mixture of granites (30 ppm) and basalts (10 ppm), and using Li data compiled by Heier and Adams (1964).
[c] Based on averages of surface samples from Canadian Precambrian shield.
[d] Based on composite samples from China.
[e] Based on Li-immobile element trends in shales and average concentration of loess (see text and Fig. 3 for derivation). Uncertainty is 2 σ.

5.3.2. Lithium isotopic composition in the upper continental crust

The average δ^7Li of the samples studied here is -0.2 ± 2.1‰ (1 σ). This result is in agreement with the scant published data for other rocks from the upper continental crust (i.e., granites, diorite, shales and suspended load sediments from the Orinoco River; Fig. 2 and Tables 1-3 and references therein). Based on all of these data, the Li isotopic composition of the upper continental crust is estimated at $\delta^7Li = 0 \pm 2$‰ (Fig. 5). This light isotopic value relative to the mantle (i.e., MORB-source region) reflects the influence of weathering on the composition of the upper crust, a conclusion supported by the higher CIA of the average upper continental crust (53) compared to that of the middle and lower crust (49 for both, data from Rudnick and Gao, 2003).

5.4. Lithium Budget of the Silicate Earth

The continental crust comprises ~0.6% of the mass of the silicate Earth, and contains <10% of its Li budget (Taylor and McLennan, 1985). Various studies of Li show that it is incompatible during mantle melting, with a bulk partition coefficient comparable to Dy, a HREE (Ryan and Langmuir, 1987). The upper crust has 1 to 3 times as much Li as the deeper crust (Rudnick and Gao, 2003) and both the upper and deeper crust are important for understanding Li isotopic composition of the whole crust, and consequently the Li isotopic balance of the silicate Earth.

The range of Li isotopic compositions in various terrestrial rocks and seawater is illustrated in Figure 6. The mantle, as represented by fresh basalts (i.e., MORB, and Hawaiian basalts, the later being representative of the ocean island basalts), appears to have an average δ^7Li value of about +4‰. Likewise, modern seawater has a homogeneous δ^7Li value of ~+30‰. Altered basalts and most marine sediments have δ^7Li values that are generally intermediate between that of the mantle and seawater, due to the uptake of heavier seawater Li. The upper continental crust, in contrast, is isotopically lighter (~0‰) than all of these other reservoirs. Only orogenic eclogites have δ^7Li values substantially lighter than the upper crust, and reflect loss of heavy Li
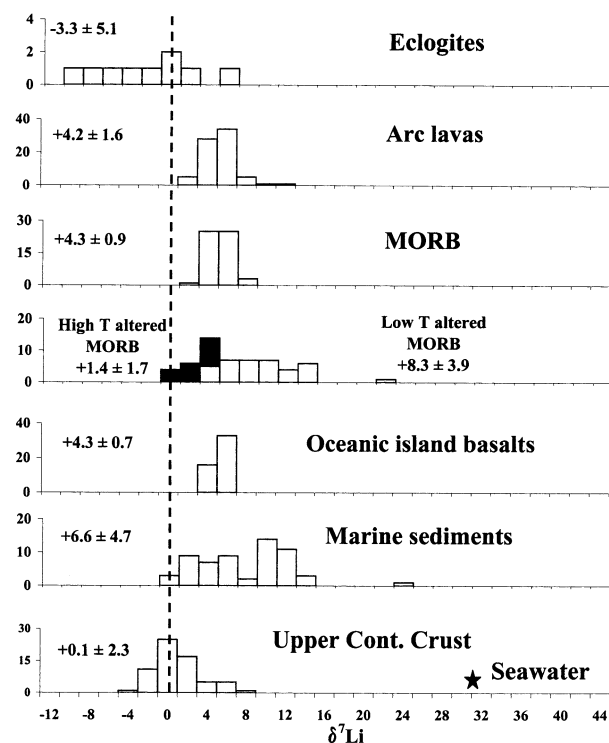
Fig. 6. Histograms of δ^7Li values for a variety of terrestrial rock types. The vertical dashed line is drawn at 0 for reference. Eclogite data (Zack et al., 2003); Arc lava data (Moriguti and Nakamura, 1998a; Tomascak et al., 2000; Chan et al., 2002b; Tomascak et al., 2002). Fresh basalt data (Chan et al., 1992; Moriguti and Nakamura, 1998a; Tomascak and Langmuir, 1999; Chan et al., 2002b). Altered basalt data (Chan et al., 1992; 2002a). Oceanic island basalt (OIB) data (Tomascak et al., 1999b; Chan and Frey, 2003). Marine sediment data (Chan et al., 1994; Zhang et al., 1998; James et al., 1999; Chan and Kastner, 2000). Seawater (Chan and Edmond, 1988; You and Chan, 1996; Moriguti and Nakamura, 1998b; Tomascak et al., 1999b; James and Palmer, 2000; Bryant et al., 2003b).

during metamorphic dehydration in the upper portions of a subducting slab (Zack et al., 2003). Thus, it is yet unclear how recycling of altered oceanic basalts into the mantle at subduction zones influences the δ^7Li of various mantle reservoirs.

A first-order model for the distribution of Li in the silicate Earth is presented in Table 5. Most of the Earth's Li is in the mantle (>90%), with the remainder concentrated mostly in the continental crust and lesser amounts in the oceanic crust and hydrosphere. The composition of the lower continental crust is the independent variable and was calculated in this model from mass balance.

While offering a perspective on various reservoirs in the silicate Earth, this Table highlights where there are still significant uncertainties in our understanding of Li (i.e., mantle reservoirs and the lower continental crust). A minor change in the δ^7Li value for the mantle (e.g., measurement uncertainty, $\pm1‰$) will shift the calculated Li isotopic composition of the lower continental crust reservoir greatly (>$\pm50‰$). Therefore, to make more precise models for the Li isotopic budget of the Earth we need to gain insights into the size and composition of the mantle reservoir that supplies ocean island basalts, as well as insights into the Li composition of the lower continental crust.

The only region in the Earth where Li isotopes are significantly fractionated is in the outermost layer (hydrosphere, continental and oceanic crust). Considering that continental growth occurs mainly either at convergent margins or intraplate settings, both of which produced lavas with δ^7Li values greater than that of the upper continental crust, there must be processes that shift the Li isotopic compositions of these new continental additions towards lighter values. Two major processes involving fluid-rock interactions might accomplish this Li isotopic fractionation: weathering (on or near the Earth surface, see Rudnick et al., 2004; Kisakura et al., 2004; Pistiner and Henderson 2003) and metamorphic dehydration (in the deep crust, see Williams and Hervig, 2003; Zack et al., 2003). During both processes, light Li is preferentially partitioned into minerals relative to fluids, which ultimately drives Li in the continental crust to lighter compositions and Li in the hydrosphere to heavier compositions relative to the mantle.

6. CONCLUSIONS

The main conclusions to be drawn from our data are

1. Loess from North America, China, Europe and New Zealand have a narrow range of Li isotopic compositions (δ^7Li = 0 ± 3‰ σ) and Li concentrations (29 ± 16 ppm, 2 σ) offering important insights into the average composition of Li in the upper continental crust.
2. Shales, which are more weathered than loess, provide less robust estimates for the upper crust, but offer insight into the

Table 5. Mass balance model for Li in the silicate Earth and its reservoirs.[a]

Reservoirs	Mass (10^{22} kg)	Mass (%)	Li (ppm)	Li (%)	δ^7Li (‰)
Hydrosphere	0.2	0.049	0.2	0.006	30
Upper continental crust	1.0	0.25	35	5.3	0
Lower continental crust	1.0	0.25	13	2.0	0 ± 50
Oceanic crust	0.6	0.15	10	0.9	5
Mantle	404.3	99.3	1.5	91.8	4
Silicate Earth	407.1	100	1.6	100	4

[a] Mass of reservoirs from Yoder (1995); Li data in hydrosphere is based on seawater values; Li data of upper continental crust (this study); Li concentration of the lower continental crust (Rudnick and Gao, 2003) and its δ^7Li value is calculated assuming all the other reservoirs known; Li data in oceanic crust is average value of altered and fresh basalts (Chan et al., 1992, 2002a); Li concentration in the mantle (Jagoutz et al., 1979) and its δ^7Li value from Figure 6. Li concentration in the silicate Earth is from McDonough and Sun (1995); its δ^7Li value is taken as that for fresh basalts.

processes that lead to Li isotope fractionation at the Earth's surface. Correlations between Li and δ^7Li with CIA or Al_2O_3/SiO_2 in shales reflect uptake by clays of isotopically heavy Li from the hydrosphere.

3. The similar Li isotopic composition of shales and loess (δ^7Li = 0 ± 3‰), reflect the competing influences of loss of heavy lithium during weathering and its re-introduction during transport and deposition in shales, and the presence of weathered materials in the source regions of loess.

4. The similarity between S-type granite δ^7Li values and that of associated sedimentary rocks interpreted to be similar to their source, coupled with the similar and restricted range of δ^7Li in I-type granites, suggests little lithium isotopic fractionation has occurred during granite genesis (temperatures of 720 to 800°C). The isotopically light δ^7Li of both types of granites reflects the presence of weathered material in their source regions.

5. Southeastern Australian granites, crustal composites from China, and previously published data for suspended river load sediments all have relatively similar δ^7Li values (0 ± 3‰), comparable to those found in loess and shales. Collectively these observations show that the upper continental crust has a relatively homogeneous δ^7Li value (0), which is significantly lighter than that of the mantle and probably reflects the influence of weathering on upper crustal composition.

6. Based on the average Li concentration of loess and Li-immobile element correlations in shales, we propose that the average upper crustal Li content is 35 ± 11 ppm (2 σ).

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APPENDIX

SUPPLEMENTARY DATA