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Lithium isotopic systematics of A-type granites and their mafic enclaves: Further constraints on the Li isotopic composition of the continental crust

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ABSTRACT

Lithium concentrations and isotopic compositions of 39 A-type granites and mafic enclaves from 11 plutons in Northeast China and the North China craton are used to constrain their genesis and to characterize further the average composition of the continental crust. Lithium concentrations (2.8 to 80 ppm) in 29 A-type granites are slightly higher than those of average I-type granites and lower than those of average S-type granites, reflecting source differences. Lithium isotopic compositions ($\delta^7\text{Li} = -1.8$ to $+6.9$) of A-type granites fall within the range of worldwide I-type and S-type granites. By contrast, 10 mafic enclaves have significantly higher Li concentrations (32 to 179 ppm) and less variation in Li isotopic compositions ($\delta^7\text{Li} = -3.2$ to $+3.1$) than their corresponding granites, due to the high modal abundance of amphiboles and biotites. Overall, the weighted mean $\delta^7\text{Li}$ for A-type granites, as well as I-type and S-type granites is lighter than that of the mantle.

Lithium concentrations in granites vary as a function of fractional crystallization and are mainly controlled by modal mineralogy. Lithium mostly behaves as an incompatible element during granite differentiation, although Li is compatible in hornblende and biotite during crystallization of mafic enclaves. By contrast, Li isotopic compositions of A-type granites and mafic enclaves are not controlled by fractional crystallization, comparable to that for I- and S-type granites, indicating negligible Li isotope fractionation during granite differentiation. Instead, they reflect source heterogeneity produced by mixing of isotopically heterogeneous lower crust and/or variable amounts of re-equilibration between enclaves and host granites.

The Li isotopic compositions of A-, I- and S-type granites can be used to derive an independent estimate of the average Li isotopic composition of the continental crust (i.e., $\delta^7\text{Li} = +1.7$, weighted mean of all granites), comparable to our previous estimate ($\delta^7\text{Li} = +1.2$) that relies on large-scale sampling of upper, middle and lower continental crust. Compared to the mantle, the continental crust has lower $\delta^7\text{Li}$, indicating the influence of weathering and recycling in controlling the Li isotopic composition of the continents.

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1. Introduction

The composition of the continental crust places constraints on the mechanisms by which the crust has been generated and differentiated through time. However, the continental crust is heterogeneous in chemical and lithological compositions, both vertically and horizontally, with a dehydrated, refractory, generally mafic lower crust and an evolved, incompatible element rich, more felsic middle and upper crust (Holbrook et al., 1992; Rudnick, 1995; Wedepohl, 1995; Rudnick and Fountain, 1995; Christensen and Mooney, 1995; Gao et al., 1998; Rudnick and Gao, 2003). This heterogeneity makes it difficult to derive an average composition of the continental crust. Two approaches have been traditionally used to derive the average crust composition. One is to establish the average compositions of the upper and deep (middle and lower) continental crust first, then derive an average crust composition (Heier, 1960; Shaw et al., 1994; Wedepohl, 1995; Rudnick and Fountain, 1995; Gao et al., 1998;). The other is based on a model of how the crust grows, and mixes bi-modal Archean igneous rocks with "average andesite" for post-Archean crust (Taylor and McLennan, 1985).

A third way to estimate the average composition of the continental crust is through studies of the products of crustal melting, e.g., granites. Granites are major components of the upper crust and their metamorphosed counterparts dominate the middle crust. Most granites are produced by partial melting of preexisting rocks in the continental crust. For example, S-type granites are inferred to derive primarily from melting of clastic sedimentary source rocks in the deep crust and I-type granites are inferred to derive from melting of meta-igneous source rocks (Chappell and White, 1974, 1992, 2001). A-type

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granites have been interpreted to form by melting previously depleted lower crustal rocks (Loiselle and Wones, 1979; Collins et al., 1982) or melting of mafic rocks formed by underplating (Wu et al., 2002). In addition, some A- and I-type granites may evolve from differentiation of basaltic magma from the mantle, modified by crustal contamination when the magma ascends (Brown, 1994; Kemp and Hawkesworth, 2003). During these processes, elements from the deep crust are transferred to the upper crust, resulting in chemical differentiation of the continental crust. Therefore, in addition to sampling the upper crust, granites can potentially image their source rocks and provide compositional information on the deep crust. However, elements are partitioned between melts and crystals during fractional crystallization and partial melting in the crust. As a result, their concentrations in the sources cannot be estimated directly from granites. Isotopes, on the other hand, are not expected to fractionate at high temperatures (Bigeleisen and Mayer, 1947; Urey, 1947), which has been demonstrated in case studies of Li and Mg isotopes (Tomascak et al., 1999; Bryant et al., 2004; Teng et al., 2004, 2006b, 2007b; Halama et al., 2007; Marks et al., 2007; Schuessler et al., 2009). Therefore, crustal melts (i.e., granites) can be used to constrain the isotopic compositions of their source regions.

Here we report Li concentrations and isotopic compositions of A-type granites from 10 plutons from Northeast China and A-type granites and mafic enclaves from the Qianshan pluton in the North China craton. Our results suggest that Li isotopes do not fractionate during A-type granite differentiation, that mafic enclaves and host granites have similar Li isotopic compositions but have different Li concentrations, and that granites can provide an average Li isotopic composition of the continental crust.

2. Geological background and samples

Eastern China is composed of the Xing'an–Mongolia (Xing–Meng) orogenic belt in the north, the North China craton (NCC) in the center and the Dabie–Sulu ultrahigh-pressure orogenic belt and Yangtze craton in the south (Wang and Mo, 1996) (Fig. 1). Our samples are mainly from the Xing'an–Mongolia orogenic belt and the North China craton.

2.1. A-type granites from Northeast China

The Xing'an–Mongolia orogenic belt in Northeast China can be divided into three blocks (Wu et al., 1995): Xing'an in the northwest,
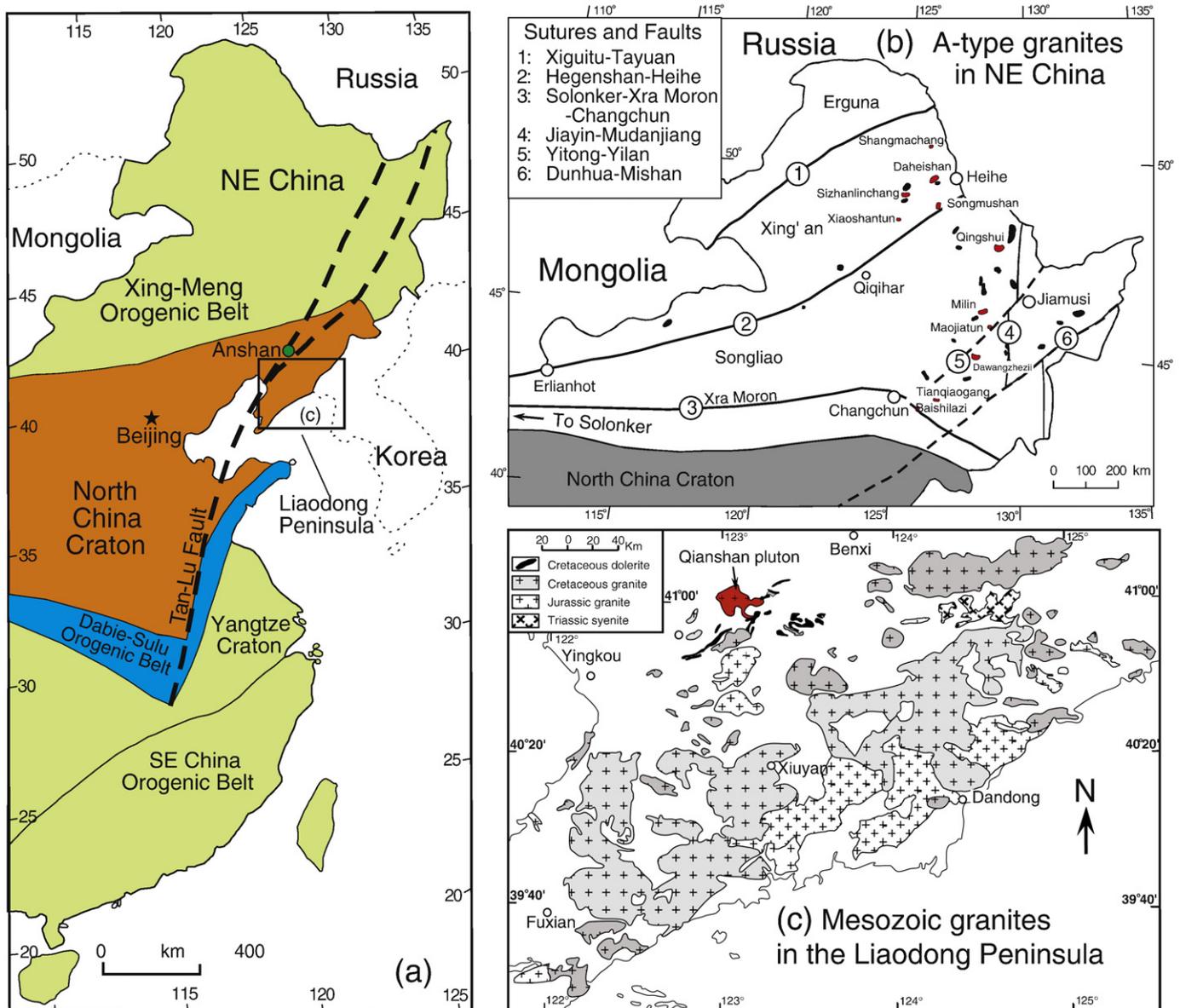
Fig. 1. Simplified geologic map of eastern China showing sample locations. The major tectonic divisions are also plotted. Modified from Wu et al. (2002) and Yang et al. (2006).

Songliao in the center, and Jiamusi in the southeast (Fig. 1). A-type granites are widely distributed, and are closely associated with I-type granites, mainly located in the Great Xing'an Range of the Xing'an block, in the Zhangguangcai Range of the Songliao block (Fang, 1992; Wu et al., 2002) and were emplaced in three episodes: late Paleozoic, Triassic and late Mesozoic (Jahn et al., 2001; Wu et al., 2002).

The samples are fresh, as indicated by petrographic studies (Wu et al., 2002). The 10 A-type granitic plutons selected for this study cover the compositional and age spectra (Fig. 1). A-type granites from these plutons are leucocratic, with a coarse- to medium-grained granitic texture. Miarolitic cavities are common but enclaves are rarely seen. Quartz (25–35%), perthite (50–75%) and Na-rich plagioclase (2–10%) are the major phases. Quartz occurs as either embayed bipyramidal crystals or interstitial grains, and quartz-feldspar intergrowths are common. The A-type granites can be divided into two subgroups: aluminous and peralkaline (Fig. 2). The aluminous A-type granites are usually red in color and contain annite and/or calcic- or sodic–calcic amphibole as the mafic phase (<5%), and calcic plagioclase. The peralkaline type is always white in color and contains alkali mafic minerals (<5%) such as sodium amphibole (riebeckite), sodium pyroxene and sodic plagioclase.

These samples are highly evolved, with SiO_2 ranging from 72.7% to 77% and total alkalis ($K_2O + N_2O$) ranging from 8.2% to 10.2%. The aluminous types have lower Ga/Al ratio than peralkaline ones (2.58–3.57 vs. 4.16–6.23) and have higher contents of Al_2O_3, MgO, CaO, Ba and Sr, but lower contents of Rb and Ga (Wu et al., 2002). Overall, these samples have similar Sr and Nd isotopic features to I-type granites in Northeast China, indicating the A-type and associated I-type granites are derived from the same source, i.e., they are the products of partial melting of middle to lower crustal rocks (Wu et al., 2000, 2002, 2003). Neodymium and Sr isotopic data suggest these lower crustal rocks are dominated (up to 85%) by juvenile mantle materials (Wu et al., 2002).

2.2. A-type granites and mafic enclaves from the Qianshan pluton, North China craton

The North China craton can be divided into three parts: western block, trans-North China orogen and eastern block (Zhao et al., 2001, 2005). The Qianshan granite intrusion is one of several A-type plutons in the Liaodong Peninsula, which is in the eastern block of the North China craton (Fig. 1). These granites crop out in an E–W belt and intruded 126 ± 2 Ma years ago (Wu et al., 2005) into Archean TTG gneiss, Proterozoic granites and metamorphic rocks and Neoproterozoic sandstones.
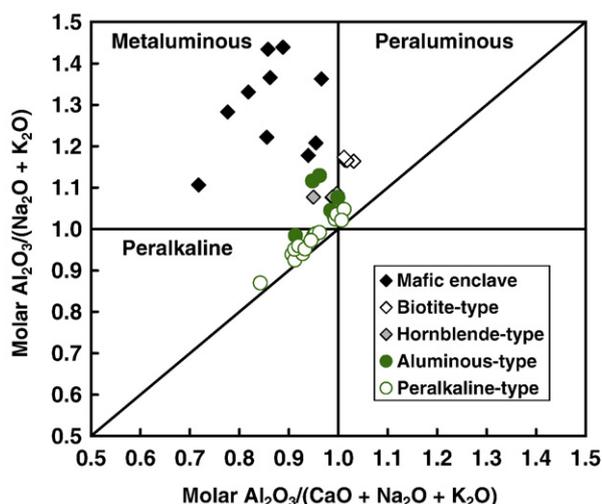
Fig. 2. Plots of molar $Al_2O_3/(Na_2O + K_2O)$ vs. $Al_2O_3/(CaO + Na_2O + K_2O)$ for A-type granites and mafic enclaves. Data are from Wu et al. (2002) and Yang et al. (2006).

All these samples are fresh, as indicated by petrographic studies (Yang et al., 2006). The A-type granites from the Qianshan pluton can be divided into two types: orange to white biotite granites in the core of the complex and orange to red-brown hornblende granites on the periphery of the complex (Yang et al., 2006). The biotite granites consist of 60% subhedral alkali feldspar, 0–5% plagioclase, 32% anhedral quartz, 1–5% biotite and <1% zircon and apatite, while hornblende granites have similar amounts of alkali feldspar, plagioclase and quartz but 1–5% hornblende and <1% zircon and allanite. Both types of granites contain mafic microgranular enclaves, which show both sharp and gradational contacts with the host felsic magma, locally chilled margins or thin biotite-rich reaction rims. These mafic enclaves are ~ 10 cm in diameter, range from diorite to monzogranite in composition and are characterized by having a higher percentage of mafic minerals than the host granites: 20–30% hornblende, 30–40% alkali feldspar, 5% biotite and <1% acicular apatite (Yang et al., 2006).

All granites from the Qianshan pluton are aluminous, with biotite granites mostly peraluminous and hornblende granites metaluminous (Fig. 2). They have SiO_2 ranging from 66.7% to 71.3% and total alkalis ($K_2O + N_2O$) ranging from 9.2% to 11%. Mafic enclaves are metaluminous and have lower SiO_2 contents (57.5 to 67.0%) and higher Fe_2O_3, MnO, CaO, TiO_2, P_2O_5, Ba, Sr but lower K_2O, Zr and Rb/Sr (Yang et al., 2006). These granites and enclave compositions produce relatively coherent trends for most elements when they are plotted against SiO_2 (Yang et al., 2006). The hornblende granites have high Rb/Sr and $^{87}Sr/^{86}Sr$ ratios, low ε_{Nd} and zircon ε_{Hf} values, and the lowest $Mg^{\#}$ (≤ 1), while biotite granite and mafic enclaves have similar isotopic features, with low Rb/Sr and $^{87}Sr/^{86}Sr$ ratios, relatively higher ε_{Nd} and zircon ε_{Hf} values, and higher $Mg^{\#}$ (up to 54). Based on the distinct isotopic signatures, Yang et al. (2006) suggest that A-type granites from the Qianshan pluton were produced by mixing crustal melts with 10–20% mantle-derived melts. The hornblende granites represent crustal melts that are mixed with the least amount of mantle-derived melts while biotite granites and mafic enclaves are cogenetic and represent crustal melts that are mixed with 10–20% of mantle-derived melts. Fractional crystallization further diversifies the chemical and mineralogical compositions of biotite granites and mafic enclaves (Yang et al., 2006).

Nineteen samples, including 10 mafic enclaves, five biotite granites and four hornblende granites from throughout the pluton, were measured to define the relationship between mafic enclaves and their host felsic magma. Of these, two pairs of enclaves and their enclosing host biotite granites (samples JH-15-2, JH-15-1 and JH-17-2 and JH-17-1) allow in situ evaluation of the interaction between mafic enclaves and their host magma (Yang et al., 2006).

3. Analytical methods

All sample powders are the same as those used in previous studies (Wu et al., 2002; Yang et al., 2006). All Li measurements were performed at the Geochemistry Laboratory, University of Maryland, College Park.

Detailed procedures for sample dissolution, column chemistry, and instrumental analyses are reported in Rudnick et al. (2004) and Teng et al. (2006b). 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 standard-bracketing method on a Nu Plasma MC-ICPMS. The external precision of Li isotopic analyses, based on 2σ of repeat runs of rock solutions, is $\leq \pm 1.0‰$. For example, an in-house shale standard AO-12 gives $\delta^7Li = +3.6 \pm 0.6$ (2σ, $n = 50$ runs with 4 replicate sample preparations over a 3-year period) (Teng et al., 2007a). δ^7Li values of international rock standards measured during the course of this study are within the uncertainty of previously published results for JB-2 ($+3.6 \pm 0.9$, 2σ, $n = 4$ vs. $+3.9$ to $+5.2$, see compilation in Seitz et al., 2004) and BCR-1 ($+2.0 \pm 0.7$, 2σ, $n = 9$ vs. $+2.7$, Rudnick et al., 2004). The uncertainty in Li concentration measurements, determined

Table 1
Lithium concentrations and isotopic compositions of aluminous and peralkaline A-type granites from Northeast China.

Sample	Pluton	Age (Ma)	SiO_2 (wt.%)	Al_2O_3 (wt.%)	Rb (ppm)	Ga (ppm)	ε_{Nd}	Li* (ppm)	δ^7Li
Aluminous									
9715-1	Tianqiaogang	190	74.1	13.1	113	19.1	2.34	4.7	+2.8
9717-1	Tianqiaogang	190	73.0	13.4	130	19.8	0	17	+3.2
9718-1	Tianqiaogang	190	72.8	13.3	93	23.5	1.34	24	+0.8
9767-1	Milin	197	77.0	11.7	54	18.2	−0.16	2.8	+0.8
9801-2	Xiaoshantun	285	75.7	12.2	158	23.0	2.62	11	+6.9
9832-2	Shangmachang	106	76.3	12.3	129	18.0		13	+3.1
9849-1	Songmushan	260	74.4	12.1	99	23.0	2.09	5.3	+5.1
Peralkaline									
DW-2	Dawangzhezi	229	72.9	12.5	118	30.9	0	17	−1.8
DW-3	Dawangzhezi	229	74.5	11.7	113	29.0	3.09	25	+2.9
9757-3	Maojiatun	213	75.9	11.0	248	26.6	0.25	23	+0.7
9757-4	Maojiatun	213	76.2	11.1	228	28.1	−0.89	21	+1.2
9780-1	Qingshui	196	76.2	11.8	228	34.0	−1.93	35	+4.6
9781-1	Qingshui	196	76.3	11.4	357	32.4	−1.20	71	+0.7
9781-2	Qingshui	196	76.3	11.1	373	36.6		80	+3.5
9781-4	Qingshui	196	75.8	11.2	273	29.3		73	+0.5
9781-5	Qingshui	196	76.8	11.0	355	32.2	−0.81	64	+1.5
9782-1	Qingshui	196	76.6	11.9	330	31.9	−0.86	74	+1.7
Baishi-1	Baishilazi	123	76.1	12.0	295	29.2	2.01	37	+2.4
Baishi-2	Baishilazi	123	76.1	12.0	284	26.2		48	+2.4
9843-1	Daheishan	292	74.9	11.7	127	27.1	5.06	14	+1.1
9843-6	Daheishan	292	75.7	11.8	128	22.6	4.24	12	+3.2

*Lithium concentration was measured by comparison of signal intensities with 50 or 100 ppb LSVEC with uncertain <10%. $\delta^7Li = [(^7Li/^6Li)_{Sample} / (^7Li/^6Li)_{LSVEC} - 1] \times 1000$ with uncertainty $\leq \pm 1\permil$ (2σ), based on both pure Li solutions and natural rocks (see text for details). L-SVEC is a pure Li isotopic standard (Flesch et al., 1973). The remaining data are from Wu et al. (2002). GPS data: Tianqiaogang: N42°57′, E127°15′; Milin: N46°29′, E129°35′; Xiaoshantun: N48°48′, E125°55′; Shangmachang: N50°37′, E126°12′; Songmushan: N49°19′, E127°15′; Dawangzhezi: N43°5′, E129°10′; Maojiatun: N46°18′, E130°05′; Qingshui: N48°07′, E129°10′; Baishilazi: N42°30′, E126°30′; Daheishan: N50°18′, E126°57′, estimated by using Google Earth.

by voltage comparison between sample solution and that measured for 50 or 100 ppb L-SVEC standard solution and then adjusting for sample weight, is $< \pm 10\%$ (1σ) (Teng et al., 2007a).

4. Results

Lithium concentrations and isotopic compositions of A-type granites and mafic enclaves are reported in Tables 1 and 2, along with previously published SiO_2, Al_2O_3, Fe_2O_3, Rb, Ga and ε_{Nd} from Wu et al. (2002) and

Yang et al. (2006), respectively. Overall, Li concentrations and isotopic compositions of these A-type granites and mafic enclaves fall within the range previously reported for I-type and S-type granites (Bryant et al., 2004; Marks et al., 2007; Teng et al., 2004, 2006b).

4.1. A-type granites from Northeast China

Lithium concentrations of 21 samples from 10 A-type granite plutons from Northeast China vary significantly, from 2.8 ppm to

Table 2
Lithium concentrations and isotopic compositions of mafic enclaves and aluminous A-type granites from Qianshan, North China craton.

Sample	Location	SiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	Rb (ppm)	Ga (ppm)	ε_{Nd}	Li* (ppm)	δ^7Li
Mafic enclaves									
JH-10	Xiashiqiao	57.5	16.3	8.9	184	30.9	−13.6	107	+3.1
JH-11	Xiashiqiao	58.9	15.8	9.0	198	31.9		129	−1.2
JH-13	Xiashiqiao	60.2	16.6	7.5	222	32.0	−12.9	79	+0.4
JH-14	Xiashiqiao	56.0	17.0	8.7	180	25.9	−12.8	179	+0.3
JH-15-2	Xiashiqiao	62.6	14.4	7.5	191	26.7	−13.8	128	−1.0
JH-17-2	Xiashiqiao	61.4	15.8	6.2	82	24.8	−13.5	92	+1.8
JH-21	Xiashiqiao	67.0	15.2	3.6	181	25.4		32	+2.8
JH-22	Xiashiqiao	59.9	15.8	5.0	113	21.6	−14.3	43	+1.7
JH-25	Xiashiqiao	62.9	16.7	5.1	226	25.2	−11.9	52	−3.2
JH-30	Duizhangshan	60.0	15.2	6.4	134	22.1	−14.5	40	−2.2
Biotite A-type granite									
JH-09	Xiashiqiao	70.8	15.3	2.0	203	27.2	−13.3	18	+2.1
JH-12	Xiashiqiao	71.3	14.7	2.6	202	27.0		22	+2.1
JH-15-1	Xiashiqiao	71.2	15.1	2.3	211	26.5	−13.6	25	+0.9
JH-17-1	Xiashiqiao	70.5	15.1	2.2	205	26.3	−12.9	26	+0.2
JH-26	Xiashiqiao	70.3	14.4	2.9	202	26.7		27	+1.7
Hornblende A-type granite									
JH-27	Duizhangshan	69.7	15.3	2.0	141	25.8	−15.9	12	+1.8
JH-28	Duizhangshan	68.9	15.7	2.0	140	27.2	−15.8	12	+0.9
JH-29	Duizhangshan	69.1	15.7	2.0	137	25.9	−15.9	11	+2.9
JH-31	Duizhangshan	66.8	15.7	3.6	138	29.4	−16.5	10	+3.0

*Lithium concentration was measured by comparison of signal intensities with 50 or 100 ppb LSVEC with uncertain <10%. The analytical uncertainty of δ^7Li is $\leq \pm 1\permil$ (2σ), based on both pure Li solutions and natural rocks (see text for details). The remaining data are from Yang et al. (2006). Granites JH-15-1 and JH-17-1 are the *in situ* hosts of mafic enclaves JH-15-2 and JH-17-2 respectively. GPS data: Xiashiqiao: N41°01′13.1″,E123°04′06.7″; Duizhangshan: N40°59′37.0″,E123°03′40.7″.
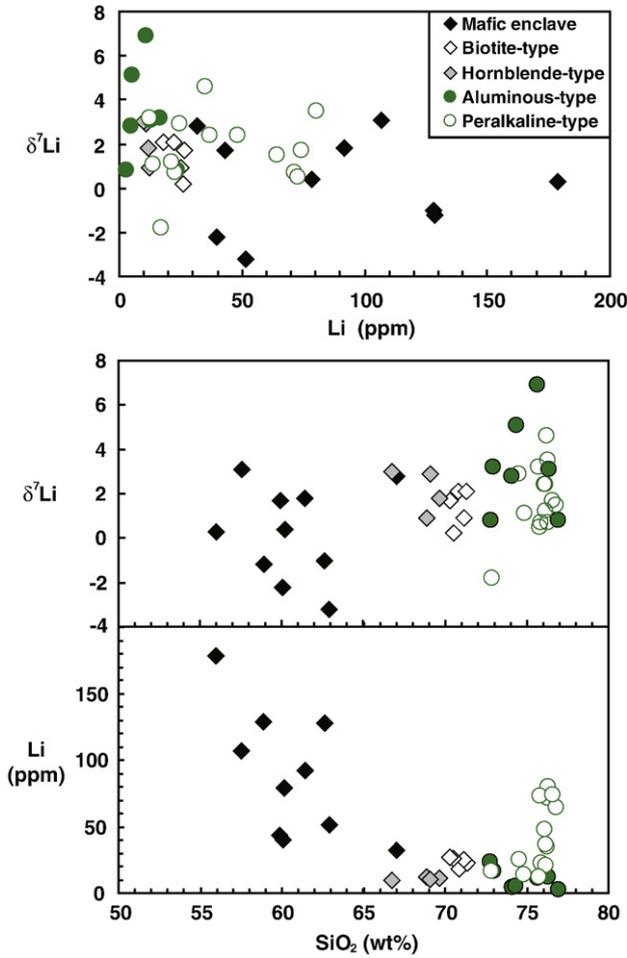
Fig. 3. Plots of Li and δ^7Li vs. SiO$_2$ for A-type granites and mafic enclaves. Data are from Tables 1 and 2 and references cited therein.

80 ppm (Fig. 3). Aluminous granites have lower Li concentrations (2.8 to 24 ppm, mean = 11 ± 7 ppm, 1σ, n = 7) than peralkaline granites (12 to 80 ppm, mean = 42 ± 25 ppm, 1σ, n = 14). Lithium isotopic

compositions show more than 8‰ variation, with δ^7Li varying from +0.8 to +6.9 in aluminous types and −1.8 to +4.6 in peralkaline types (Fig. 3).

4.2. A-type granites and mafic enclaves from the Qianshan pluton, North China craton

The Li concentrations of aluminous A-type granites from the Qianshan pluton fall within the range of those from Northeast China (Fig. 3). Biotite granites have higher Li concentrations than hornblende granites (18 to 27 ppm vs. 10 to 12 ppm). In contrast to host granites, mafic enclaves have much higher and more variable Li concentrations (32 to 179 ppm) (Fig. 3). The δ^7Li values for Qianshan A-type granites show a restricted range, from +0.2 to +2.1 in the 5 biotite granites and +0.9 to +3.0 in the 4 hornblende granites. δ^7Li, however, varies more significantly in mafic enclaves, from −3.2 to +3.1 but still falls within the range of A-type granites from Northeast China (Fig. 3). Two mafic enclaves and their *in situ* host granites have different Li concentrations but similar Li isotopic compositions (within ±1‰ uncertainty).

5. Discussion

5.1. Lithium concentration and isotopic systematics of A-type granites

A-type granites crystallize from relatively high temperature, water-undersaturated magmas (Clemens et al., 1986; Eby, 1990, 1992). Geochemical and isotopic studies suggest that the parental magma of A-type granites is derived either from partial melting of mafic lower crust or from differentiation of crustally contaminated mantle-derived magma (Collins et al., 1982; Whalen et al., 1987; Eby, 1990; 1992). Compositional and mineralogical variations within granite suites can potentially be produced by source heterogeneity, magma mixing and/or fractional crystallization.

5.1.1. Negligible Li isotope fractionation during A-type granite differentiation
Lithium isotope fractionation during magmatic differentiation has been widely investigated and appears to be insignificant during mantle melting and fractional crystallization of basaltic melts (Tomascak et al., 1999; Schuessler et al., 2009) or carbonatites (Halama et al., 2007). Little isotope fractionation is found to occur during crustal melting and
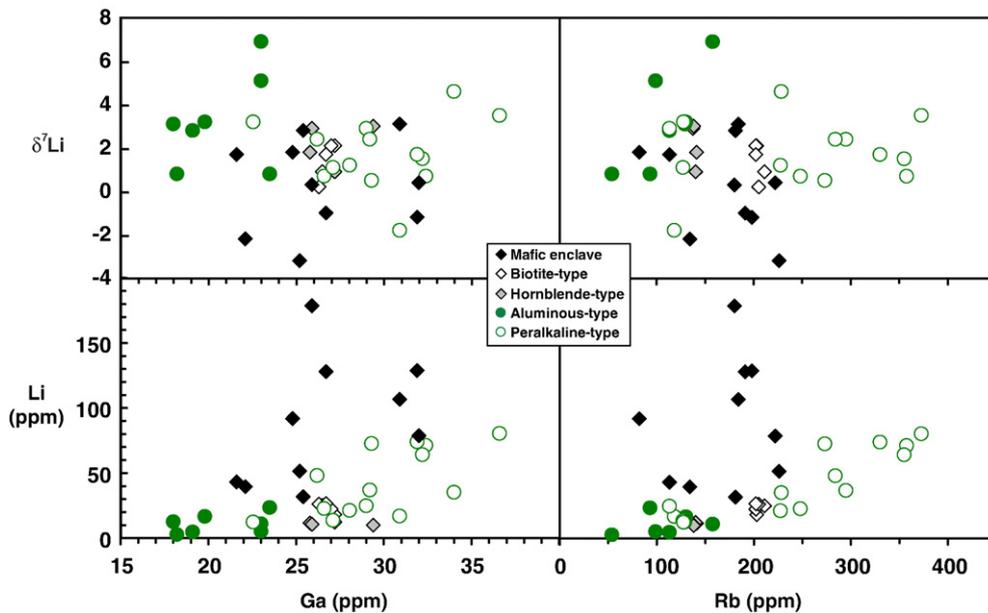
Fig. 4. Plots of Li and δ^7Li vs. Ga and Rb for A-type granites and mafic enclaves. Data are from Tables 1 and 2 and references cited therein.
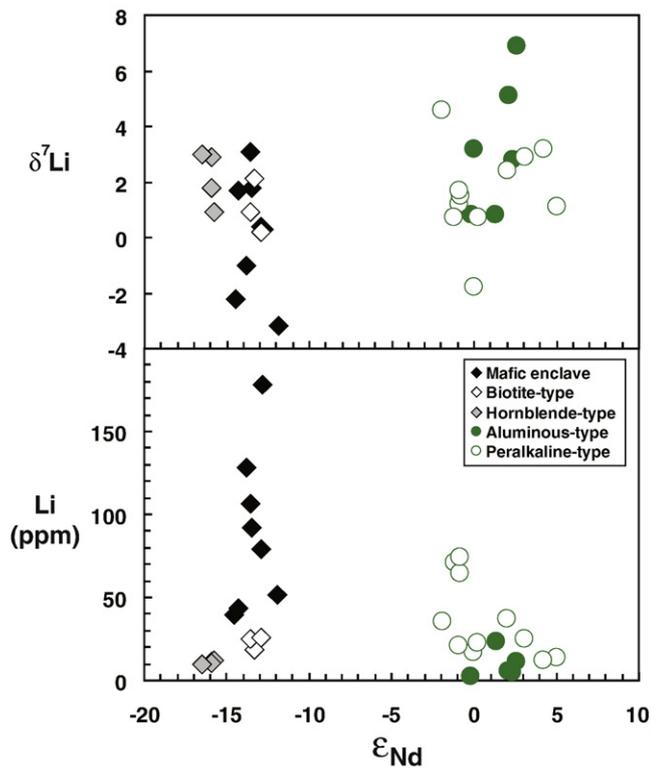
Fig. 5. Plots of Li and δ^7Li vs. ε_{Nd} for A-type granites and mafic enclaves. Data are from Tables 1 and 2 and references cited therein.

magmatic differentiation either, be it for S-type (Bryant et al., 2004; Teng et al., 2004, 2006b), or I-type (Bryant et al., 2004; Teng et al., 2004; Marks et al., 2007) granitoids. Lithium isotopic compositions of A-type granites from Northeast China as well as those from the Qianshan pluton, do not show any significant correlations with the degree of magmatic differentiation, as inferred from various compositional parameters (e.g., SiO$_2$, Li, Rb and Ga, Figs. 3 and 4). This suggests insignificant Li isotope fractionation during A-type granite differentiation, which is consistent with previous studies of I- and S-type granites.

5.1.2. Lithium in A-type granites

Sr and Nd isotopic studies indicate the parental magma of A-type granites from the Qianshan pluton, North China craton, was produced by mixing crustal melts with different amounts (up to 20%) of mantle-derived melts (Yang et al., 2006), while granites from Northeast China from all three granite-producing episodes were formed by melting of juvenile, mafic, middle to lower crustal materials (Jahn et al., 2001; Wu et al., 2002). Lithium isotopic compositions of these samples vary by ~8‰ and do not correlate with ages of the plutons, radiogenic isotopic compositions (Fig. 5) or chemical and mineralogical parameters. The Li isotopic heterogeneity therefore likely reflects heterogeneous source rocks, i.e., a heterogeneous deep crust, consistent with previous studies of granulite xenoliths (Teng et al., 2008).

By contrast, Li concentrations of the granites vary significantly as a function of magmatic differentiation in both areas and are controlled by their modal mineralogy. In the Qianshan pluton, biotite-rich granites tend to have higher Li concentrations than hornblende-bearing granites, consistent with the larger partition coefficient for Li in biotite in equilibrium with a rhyolitic melt than that for hornblende in equilibrium with rhyolitic melt (Icenhower and London, 1995; Trompetter et al., 1999). In Northeast China, Li concentrations of A-type granites vary ~30 fold and increase with differentiation, as indicated by the positive correlations of Li vs. Rb and Ga (Fig. 4), suggesting that crystal fractionation of Li-poor minerals such as feldspar and quartz is the main process that controls Li concentration in these A-type granites.

Peralkaline granites have higher Li concentrations than aluminous ones, due to a larger partition coefficient for Li in sodium-rich amphibole/pyroxene in peralkaline granites than that for calcic amphibole/pyroxene in aluminous granites (Marks et al., 2007).

5.2. Lithium concentration and isotopic systematics of mafic enclaves

Mafic enclaves are widely distributed in granites and provide constraints on the role of mantle-derived magmas in the genesis and evolution of granitoids (Didier, 1973; Barbarin and Didier, 1991). Three models have been proposed for their genesis: a) mixing of mantle-derived melts into crustal melt (Didier, 1973; Barbarin and Didier, 1991), b) they represent unmelted portion of the granite source — the restite model (Chappell, 1996; White et al., 1999) and c) they represent crystal-cumulates (Dahlquist, 2002; Donaire et al., 2005). Mafic enclaves from the Qianshan pluton are interpreted to be cogenetic with the biotite granites and their parental magmas are crustal melts that were mixed with 10–20% mantle-derived melts, while hornblende granites are derived from partial melting of upper crustal rocks (Yang et al., 2006). The chemical and mineralogical diversity in the mafic enclaves and host granites are produced by fractionation of hornblende, biotite and plagioclase (Yang et al., 2006).

5.2.1. Lithium isotopic compositions of mafic enclaves

δ^7Li values (-3 to $+3$) of mafic enclaves do not correlate with any index of magmatic differentiation, e.g., Rb, Ga, SiO$_2$ and Fe$_2$O$_3$ contents (Figs. 3, 4 and 6), suggesting that fractional crystallization of hornblende, biotite and plagioclase does not control the Li isotopic compositions of enclaves, as suggested by Bryant et al. (2004). The ~6‰ Li isotopic variations in these mafic enclaves therefore must reflect source heterogeneity in the lower crust or variable degrees of re-equilibration between enclaves and host granites.

The lower continental crust is heterogeneous in terms of δ^7Li. Based on measurements of equilibrated granulite xenoliths, δ^7Li of the lower crust varies from -14 to $+14$, and this is coupled to large Li concentration variations (Teng et al., 2008). The parental magma of mafic enclaves from the Qianshan pluton are interpreted to be crustal
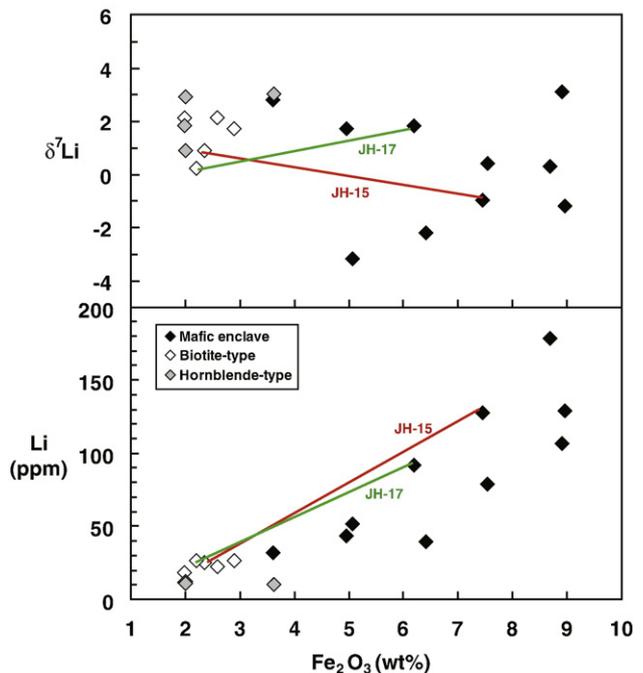
Fig. 6. Plots of Li and δ^7Li vs. Fe$_2$O$_3$ for mafic enclaves and A-type granites from the Qianshan pluton, North China carton. Tie-lines show the mafic enclaves JH-15-2 and JH-17-2 and their adjacent host granites JH-15-1 and JH-17-1 respectively. Data are from Table 2 and references cited therein.
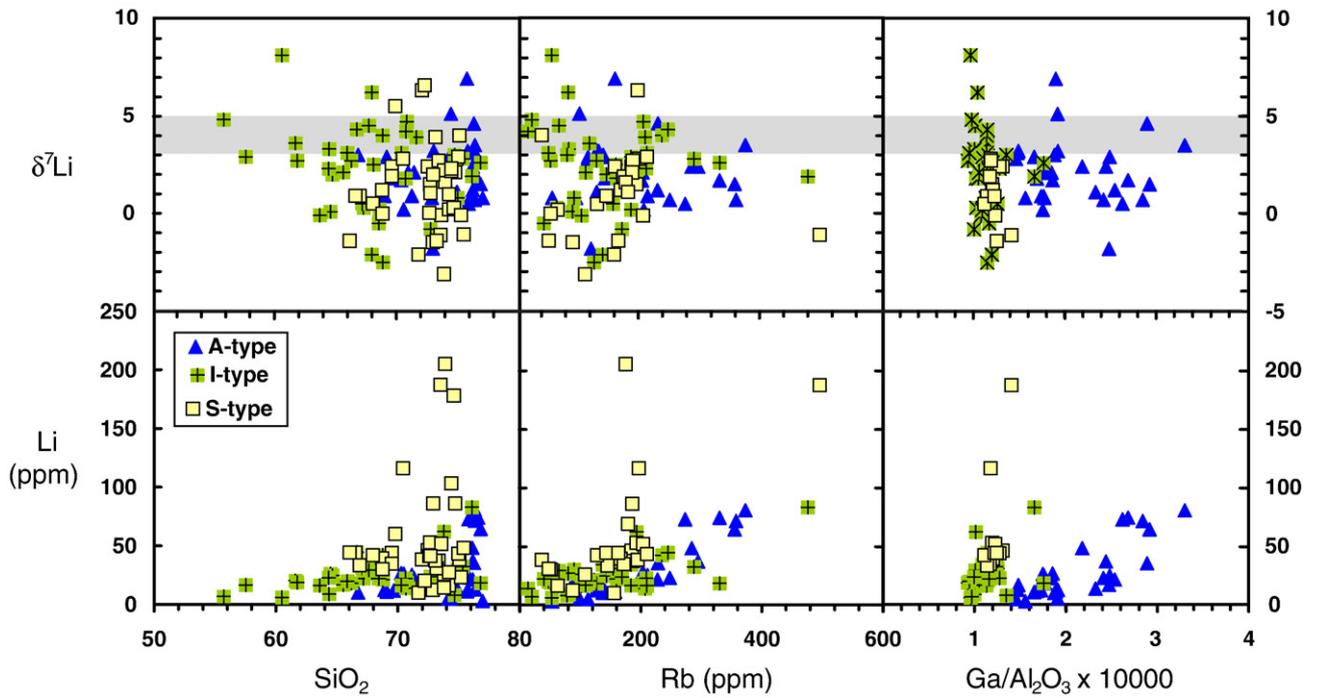
Fig. 7. Plot of Li concentrations and isotopic compositions vs. SiO_2, Rb and $Ga/Al_2O_3 \times 10,000$ for worldwide post-Archean A-, I- and S-type granites (see data compilation provided in the on-line supplement). A-type granite data are from Tables 1 and 2; I-type granite data are from Bryant et al. (2004), Teng et al. (2004) and Marks et al. (2007); S-type granite data are from Teng et al. (2004, 2006b) and Bryant et al. (2004). The gray bar represents the Li isotopic compositions of fresh oceanic basalts (Ryan and Langmuir, 1987; Chan et al., 1992; Chan and Frey, 2003; Ryan and Kyle, 2004; Elliott et al., 2006; Tomascak et al., 2008; Schuessler et al., 2009).

melts that mixed with 10–20% mantle-derived melts (Yang et al., 2006). The Li isotopic diversity of the mafic enclaves may therefore reflect an isotopically heterogeneous lower crustal source.

Alternatively, Li, relative to other lithophile elements, diffuses rapidly and its isotopes can be greatly fractionated during diffusion because ^6Li can diffuse up to 3% faster than ^7Li (Richter et al., 2003; Lundstrom et al., 2005; Teng et al., 2006a; Jeffcoate et al., 2007; Parkinson et al., 2007; Rudnick and Ionov, 2007; Tang et al., 2007; Aulbach et al., 2008; Teng et al., 2008). The distinct chemical and mineralogical differences between enclaves and host granite could drive Li diffusion and produce diffusion-driven kinetic isotope fractionation, which results in Li isotopic variations in the mafic enclaves. When the limits of the analytical uncertainty are considered, the two mafic enclave-host granite pairs have identical Li isotopic compositions, which suggests that Li isotopes reached equilibrium between mafic enclaves and their hosts. However, about half of the mafic enclaves have lower δ^7Li values compared to their host granites (Figs. 3, 4 and 6). This suggests that not all host granites and enclaves reached isotopic equilibrium and their Li isotopic variations may represent variable degrees of kinetic Li isotope fractionation during re-equilibration of enclaves and host granites.

The general similarity of Li isotopic compositions between mafic enclaves and host granites (within a few per mil vs. >10‰) stands in sharp contrast to that observed for xenolith samples from the lower crust and subjacent lithospheric mantle, both of which show diverse and distinct Li isotopic compositions relative to their host basalts (Jeffcoate et al., 2007; Rudnick and Ionov, 2007; Tang et al., 2007; Aulbach et al., 2008; Teng et al., 2008). This contrasting behavior of Li between mafic enclaves in granites and granulite and peridotite xenoliths in basalts likely reflects the long duration of granite magmatism (Brown, 1994; Petford et al., 2000) compared to xenolith entrainment and transport in basalt magmas (Spera, 1980) as well as the possibly faster diffusion rate of Li in feldspar (e.g., Giletti and Shanahan, 1997) than in pyroxene and olivine (e.g., Coogan et al., 2005; Jeffcoate et al., 2007; Parkinson et al., 2007).
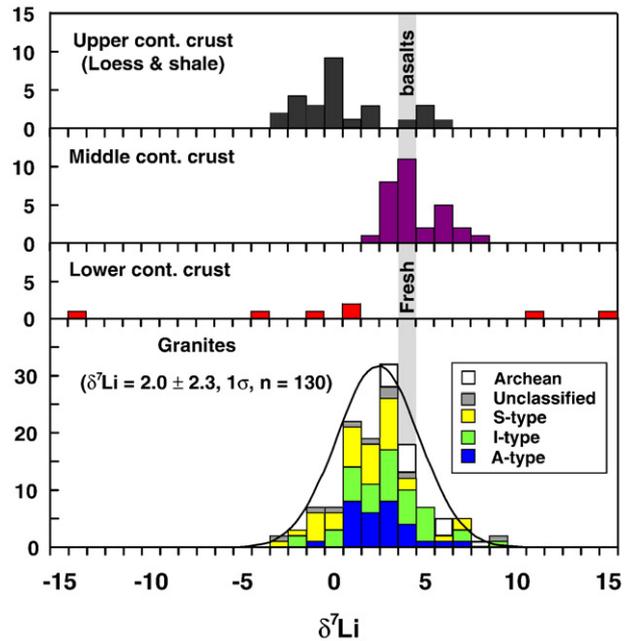
Fig. 8. Lithium isotopic compositions of 130 worldwide post-Archean A-type, I-type and S-type granites, as well as unclassified granites and Archean TTG gneisses (See data compilation provided in the on-line supplement). The data form a normal distribution, with a weighted average δ^7Li of +1.7 and an arithmetic mean of +2.0 ± 2.3 (1σ). The normal distribution curve calculated from the arithmetic mean and standard deviation is also shown. The Li isotopic compositions of the upper (Teng et al., 2004), middle (Teng et al., 2008) and lower (Teng et al., 2008) continental crust, as well as fresh oceanic basalts, are plotted for comparison. Data sources for post-Archean A-, I- and S-type granites, as well as fresh oceanic basalts, are the same as for Fig. 7. Unclassified granite data are from James and Palmer (2000), Pistiner and Henderson (2003), Rudnick et al. (2004), Teng et al. (2004) and Tomascak et al. (2003). Archean TTG gneiss data are from Teng et al. (2008).

5.2.2. Lithium concentrations of mafic enclaves

Lithium concentrations are more variable in the mafic enclaves than in the granites, correlate negatively with SiO_2 (Fig. 3) and correlate positively with Fe_2O_3 (Fig. 6). The negative correlation between Li and SiO_2 in the enclaves is opposite to the trend seen in the granites (Figs. 3 and 7). The more mafic enclaves are more enriched in Li, contain more hornblende and biotite, have less SiO_2 and more Fe_2O_3 than the more evolved intermediate enclaves. These distinctive trends are consistent with a mineralogical control of Li concentrations of granites and mafic enclaves.

During granite differentiation, the partition coefficients for Li between felsic minerals (e.g., feldspar and quartz) and melts are generally <1 and hence Li is incompatible when these minerals dominate. By contrast, Li is compatible during hornblende-biotite-dominant crystallization, with partition coefficients for Li >1 between minerals and melts (Icenhower and London, 1995; Trompetter et al., 1999; Marks et al., 2007). Therefore, the distinct behavior of Li seen in granites and mafic enclaves reflect a mineralogical control of Li partitioning during magmatic differentiation.

5.3. Comparison of Li and δ^7Li values in A-, I- and S-type granites

Granites are, for the most part, derived by melting of crustal rocks, with some role played by the mantle, which may act as a source of heat and/or materials. Except for S-type granites, which are suggested to be mainly derived from partial melting of sedimentary rocks and thus represent recycling of older crust, the petrogenesis of I- and A-type granites remains controversial and the role of the mantle in the genesis of these granites is uncertain. For example, I-type granites are traditionally considered to be melts of deep crustal meta-igneous rocks (Chappell and White, 1974, 1992). A recent study, however, suggests that I-type granites form from reworking of sedimentary materials by mantle-like magmas, instead of by melting of ancient metamorphosed igneous rocks (Kemp et al., 2007).

In terms of their Li concentrations and isotopic compositions, A-, I- and S-type granites cannot be clearly distinguished. All three types of granite are heterogeneous and, on average, lighter than fresh, mantle-derived basalts. The spread in δ^7Li values are similar in all three types of granites and δ^7Li in none of the granite types correlates with SiO_2, Rb or Ga/Al_2O_3 (Fig. 7), which is consistent with no fractionation of δ^7Li during granite differentiation. This suggests that the amount of mantle Li involved in the different types of granites is insignificant relative to Li from crustal melts and that crustal melts are isotopically light compared to mantle melts.

Lithium concentrations vary significantly in all three types of granite and generally increase with SiO_2 contents (Fig. 7). S-type granites have higher and more variable Li concentrations than A- and I-type granites, which may either reflect their Li-rich sedimentary sources (Teng et al., 2004) or extensive fractional crystallization (Teng et al., 2006b).

5.4. Granites as a probe of the deep continental crust

The negligible fractionation recorded by Li isotopes during granite genesis and differentiation allows us to use granites as a probe of the deep crust. Compared with granulite xenoliths, which only sample a small part of the lower crust, granites are derived from large-scale melting of deep crustal rocks, and thus sample large volumes of the deep crust, obscuring any small-scale compositional variation and provide a natural average of the deep crust, analogous to studying the composition of the upper mantle through mantle-melting products: oceanic basalts.

On a worldwide basis, Li isotopic compositions of granites display a normal distribution and have a weighted average δ^7Li value of $+1.7$ (arithmetic mean $= +2.0 \pm 2.3$, 1σ) (Fig. 8), identical to the average δ^7Li value ($+1.2$) of the bulk continental crust estimated by large-scale sampling of the upper, middle and lower crust (Teng et al., 2004, 2008). This suggests that granite can be used as a probe of the bulk
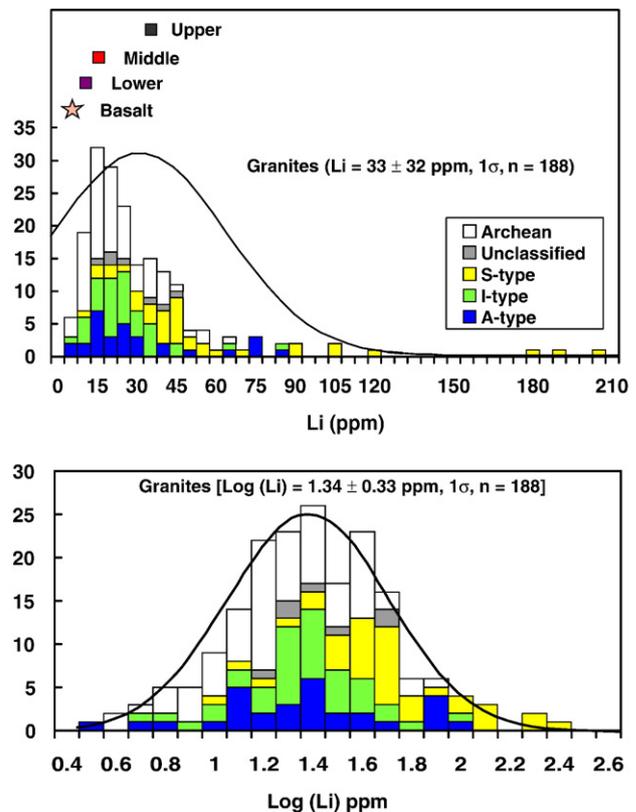
Fig. 9. Upper panel: Li concentrations of 188 worldwide post-Archean A-type, I-type and S-type granites, as well as unclassified granites and Archean TTG gneisses (see data compilation provided in the on-line supplement). The distribution of Li concentration in these granites is skewed to higher values, yielding an arithmetic average Li of 33 ± 32 ppm (1σ). The average Li concentration of the upper, middle and lower continental crust, as well as fresh oceanic basalts are plotted for comparison. Lower panel: distributions of Log (Li) concentrations of the same population as in the upper panel. The data form a normal distribution with an arithmetic average Log (Li) of 1.34 ± 0.33 ppm (1σ), corresponding to a geometric average Li concentration of 22 ppm, a lower limit of 10 ppm and the upper limit of 47 ppm. The normal distribution curves calculated from the means and standard deviations are shown. Data sources are the same as for Fig. 8 except Archean TTG gneiss, which are from Mohan et al. (2008) and Teng et al. (2008).

isotopic composition of the continental crust for those isotope systems that do not fractionate during granite magmatism. The variability of δ^7Li in all three types of granites provides an indication of the degree of isotopic heterogeneity in the deep continental crust.

The Li concentration of granites is skewed to higher concentrations, displaying a log-normal distribution (Fig. 9). These observations agree with "the fundamental law and its subsidiary concerning the distribution of element concentration": "the concentration of an element is lognormally distributed in a specific igneous rock" and "the abundance of an element in an igneous rock is always greater than its most prevalent concentration; the difference may be immeasurably small or very large and is determined solely by the magnitude of the dispersion of its concentration" (Ahrens, 1954). Using the log-normal distribution, the average Li concentration of granites is 22 ppm, with a lower limit of 10 ppm and an upper limit of 47 ppm (1σ). This value is more similar to the upper crust (~35 ppm) than the middle (~12 ppm) and lower (~8 ppm) crust and mantle-derived basalts (~5 ppm) (Fig. 9), which reflects the fact that granites are major components of the upper continental crust (Teng et al., 2004). The lower Li concentrations in the deep crust reflect a higher proportion of mafic rock types and possibly Li depletion during metamorphic dehydration (Teng et al., 2008).

6. Conclusions

The data presented here, coupled with the previously published Li data for I- and S-type granites, provide insights into the nature of

granite genesis and the average composition of the continental crust. The main conclusions are:

1. A-type granites from eastern China have δ^7Li values between -1.8 to $+6.9$ and Li concentrations from 2.8 to 80 ppm, falling within the ranges of I- and S-type granites.
2. Compared to A-type granites, mafic enclaves have similar Li isotopic compositions (δ^7Li $= -3.2$ to $+3.1$) but significantly higher Li concentrations (32 to 179 ppm).
3. Li concentrations in A-, I- and S-type granites and mafic enclaves are controlled by mineralogy. Lithium is incompatible during crystal fractionation of granites involving feldspar and quartz and compatible during crystallization of hornblende and biotite in mafic enclaves. The higher Li concentration of mafic enclaves relative to their host granites is inconsistent with these enclaves being mantle-derived melts or restites although Li concentrations may have been elevated in the enclaves by diffusion from the surrounding granite.
4. δ^7Li values do not correlate with any index of granite differentiation in A-type granites and mafic enclaves, as well as I- and S-type granites, suggesting insignificant Li isotope fractionation during granite differentiation.
5. Granites and mafic enclaves are, on average, isotopically lighter than the mantle, indicating they are mainly derived from weathered crustal materials.
6. The weighted average δ^7Li of all granites is $+1.7$, identical to the previously estimated Li isotopic composition of the continental crust (δ^7Li $= +1.2$) based on large-scale sampling of different portions of the continental crust.
7. Granites can be used to constrain the isotopic composition of the continental crust for stable isotopic systems that do not fractionate during granite genesis.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2009.02.009.

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