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Geochimica et Cosmochimica Acta 144 (2014) 43–58

Geochimica et Cosmochimica Acta

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Sedimentary input to the source of Lesser Antilles lavas: A Li perspective

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Received 7 May 2014; accepted in revised form 1 September 2014; Available online 16 September 2014

Abstract

Li isotopes in compositionally diverse Martinique lavas, as well as sea floor sediments cored at the southern (DSDP Site 144) and northern part (DSDP Site 543) of the subducting slab were analyzed in order to investigate the origin of the continental crust compositional signature seen in Lesser Antilles lavas and to investigate Li cycling in arcs. Although the subducting sediments display marked mineralogical and chemical shifts from south to north, the concentration-weighted mean δ^7Li for sediments from the two cores are indiscernible from each other (bulk $\delta^7\text{Li} = -0.5 \pm 1.8$, 1σ, $n = 15$, $\delta^7\text{Li} = -4.4$ to $+2.9$). This is the lowest bulk δ^7Li seen in subducting sediments from any trenches, and is significantly lower than that of MORB ($\delta^7\text{Li} \sim +4 \pm 1$). These low δ^7Li values reflect the dominance of terrigenous input and the influence of chemical weathering in the sediment's continental provenance. With a few exceptions, the Li isotopic compositions of the Martinique lavas are also systematically lighter than MORB, yielding an average δ^7Li of $+1.8 \pm 1.3$ (1σ, $n = 24$, excluding three outliers that are isotopically heavy, erupted below seawater and may have incorporated sea water Li). The δ^7Li values in the lavas show no correlation with most radiogenic isotope ratios (^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf), Li/Y, La/Sm or SiO_2. There is also no correlation between δ^7Li and radiogenic isotopes in the subducting sea floor sediments. Thus, the low δ^7Li in the Martinique lavas likely reflects a mantle source that incorporated isotopically light subducted sediments. A two-end-member mixing model requires sedimentary input of <1% to 5% by mass to a depleted mantle source to reproduce the Li isotopic compositions of the mafic samples, consistent with the range of sediment input (0.1–5%) inferred from radiogenic isotope data. The Lesser Antilles is the first arc shown to have δ^7Li systematically lower than MORB, reflecting the influence of subducted terrigenous sediments. Our data suggest that the enrichment of Li in most arc lavas is due to the addition of subducted sediment-derived Li, and that the isotopic signature of this Li can traverse the mantle wedge with little modification. It is only in arcs such as the Lesser Antilles where the Li isotopic composition of subducted sediments is very different from MORB that the slab signature is apparent in the lavas.

1. INTRODUCTION

Crustal materials are recycled to the mantle and juvenile arc crust is generated via arc magmatism above subduction zones. Arc lavas are chemically distinct from mid-ocean ridge basalts (MORB), in part due to incorporation of subducted continental and oceanic crustal components in their source regions (Ryan and Chauvel, 2014, and references therein). Understanding the origin of crustal signatures in arc lavas provides insights into the mass exchange and recycling processes in subduction zones.

Lithium isotopes are potentially useful tracers of recycling in subduction zones as they are readily fractionated at the Earth's surface because of the relatively large mass

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http://dx.doi.org/10.1016/j.gca.2014.09.003
0016-7037/Published by Elsevier Ltd.

difference between ^{6}Li and ^{7}Li (17%). Significant Li isotopic fractionation is generated during both sea floor and subaerial weathering of silicate rocks (Chan et al., 1992; Huh et al., 1998; Pistiner and Henderson, 2003; Bouman et al., 2004; Kisakürek et al., 2004, 2005; Rudnick et al., 2004; Pogge von Strandmann et al., 2006; Wimpenny et al., 2010; Liu et al., 2013). The net effect is that the fluid phase is enriched in ^{7}Li relative to the rock. Therefore, the Li isotopic compositions of rivers (δ^7Li = +6 to +32, Huh et al., 1998) and seawater (+31, Millot et al., 2004) are significantly heavier than those of the continental crust (~+1, Teng et al., 2008) and mantle (~+4, Seitz et al., 2004; Pogge von Strandmann et al., 2011) (see caption to Table 1 for definition of δ^7Li). Moreover, the upper continental crust (δ^7Li $= 0 \pm 2$ at 1σ, Teng et al., 2004) is lighter than the upper mantle, as inferred from fresh MORB compositions ($+3.7 \pm 1.0$ at 1σ, all MORB, Tomascak et al., 2008), which has been attributed to a weathering signature in the continental crust. It has been shown that equilibrium Li isotopic fractionation is limited during metamorphic dehydration, partial melting and fractional crystallization (Tomascak et al., 1999; Marschall et al., 2007; Teng et al., 2007, 2009; Qiu et al., 2009, 2011a,b). Therefore, Li isotopes may provide direct evidence for mass exchange between isotopically distinct reservoirs.

Previous studies of Li isotopes in intraoceanic arc lavas have, with a few exceptions (e.g., Moriguiti et al., 1999; Tomascak et al., 2000), found no systematic difference between arc lavas and MORB (Chan et al., 2002a,b; Tomascak et al., 2002; Moriguti et al., 2004). The lack of slab Li signature in most intraoceanic arc magmas has led to the suggestion of a "mantle chromatograph", which attenuates the Li signal during slab fluid ascent through the mantle wedge (e.g., Tomascak et al., 2002; Halama et al., 2009; Caciagli et al., 2011). However, this process fails to explain the evident Li enrichment (relative to Y) in arc magmas (Plank, 2014).

The Lesser Antilles island arc is a compositional endmember of global intraoceanic arcs due to the high proportion of continental crustal materials and a consequently large range of chemical and isotopic compositions in its lavas (White and Dupré, 1986; Davidson, 1987; Labanieh et al., 2010). However, the source of the crustal signature is debated. Does it come from crustal contamination during magma ascent (Thirlwall and Graham, 1984; Thirlwall et al., 1994, 1996; Davidson, 1985, 1986; Davidson and Harmon, 1989; Van Soest et al., 2002; Bezard et al., 2014)? Or does it originate from melting of subducted slab components in the source region (White and Dupré, 1986; Carpentier et al., 2008; Labanieh et al., 2010, 2012)? Or could both processes have influenced lava compositions?

Previous work employed chemical compositions and Sr–Nd–Pb–Hf–O isotopes in the lavas to address this question. Early work (e.g., Davidson, 1983) suggested the incorporation of subducted sediments in the source of Lesser Antilles lavas. However, later studies (e.g., Davidson, 1986; Davidson and Harmon, 1989; Van Soest et al., 2002) found that the Pb isotopes in the subducting sediments cored at DSDP Site 543 (Fig. 1) are not radiogenic enough to cover the most radiogenic lavas found in the southernmost islands of the arc (from Martinique to Grenada). These authors thus argued that crustal contamination is required

Table 1
Li isotope compositions of the sediments from DSDP Sites 543 and 144.

Sample ID	Depth, m	CaO, wt.%	Al_2O_3, wt.%	Lithology	δ^7Li	[Li], ppm	Y/Li
Site 144 (9.454 N, 54.342 W)							
144-9	41	36.3	4.6	Chalk ooze	−3.9	19	0.73
144-12	62	38.2	2.4	Chalk ooze	−4.1	11	0.84
144-12 replicate					−4.6		
144-18	144	42.8	2.8	Gray marl	−3.3	7.1	1.49
144-18 replicate					−1.7		
144-20	163	33.2	4.5	Gray marl	−4.2	12	1.23
144-20 redissolution					−4.0		
144-28	190	23.0	3.2	Black shale	+2.0	9.2	1.75
144-33	295	14.3	6.5	Terrigenous seds	+3.5	25	0.65
144-33 replicate1					+2.9		
144-33 replicate2					+2.4		
144-34	299	3.4	14.4	Terrigenous seds	−1.1	58.	0.31
144-35	299	8.0	11.5	Terrigenous seds	+0.6	49.	0.44
144-35 replicate					−0.1		
Site 543 (15.712 n, 58.654 w)							
543-4	220	0.5	18.5	Pelagic clays	−2.1	77	0.31
543-7	248	1.2	18.6	Pelagic clays	−2.4	74	0.32
543-8	280	0.6	13.9	Pelagic clays	−0.9	62	0.58
543-10	295	0.4	14.5	Pelagic clays	−0.9	58	0.34
543-12	315	0.4	12.0	Pelagic clays	−1.6	41	0.39
543-19	364	0.7	17.6	Pelagic clays	+0.8	61	0.53
543-24	408	26.3	7.2	Carb/pelagic clays	+1.8	22	1.59

Note: Major and trace element data are from Carpentier et al. (2009).
$\delta^7\text{Li} = ({}^7\text{Li}/{}^6\text{Li}_{\text{sample}}/{}^7\text{Li}/{}^6\text{Li}_{\text{L-SVEC}} - 1)^{*}\,1000$, where L-SVEC is the internationally recommended reference material introduced by Flesch et al. (1973), is used to describe Li isotopic composition.

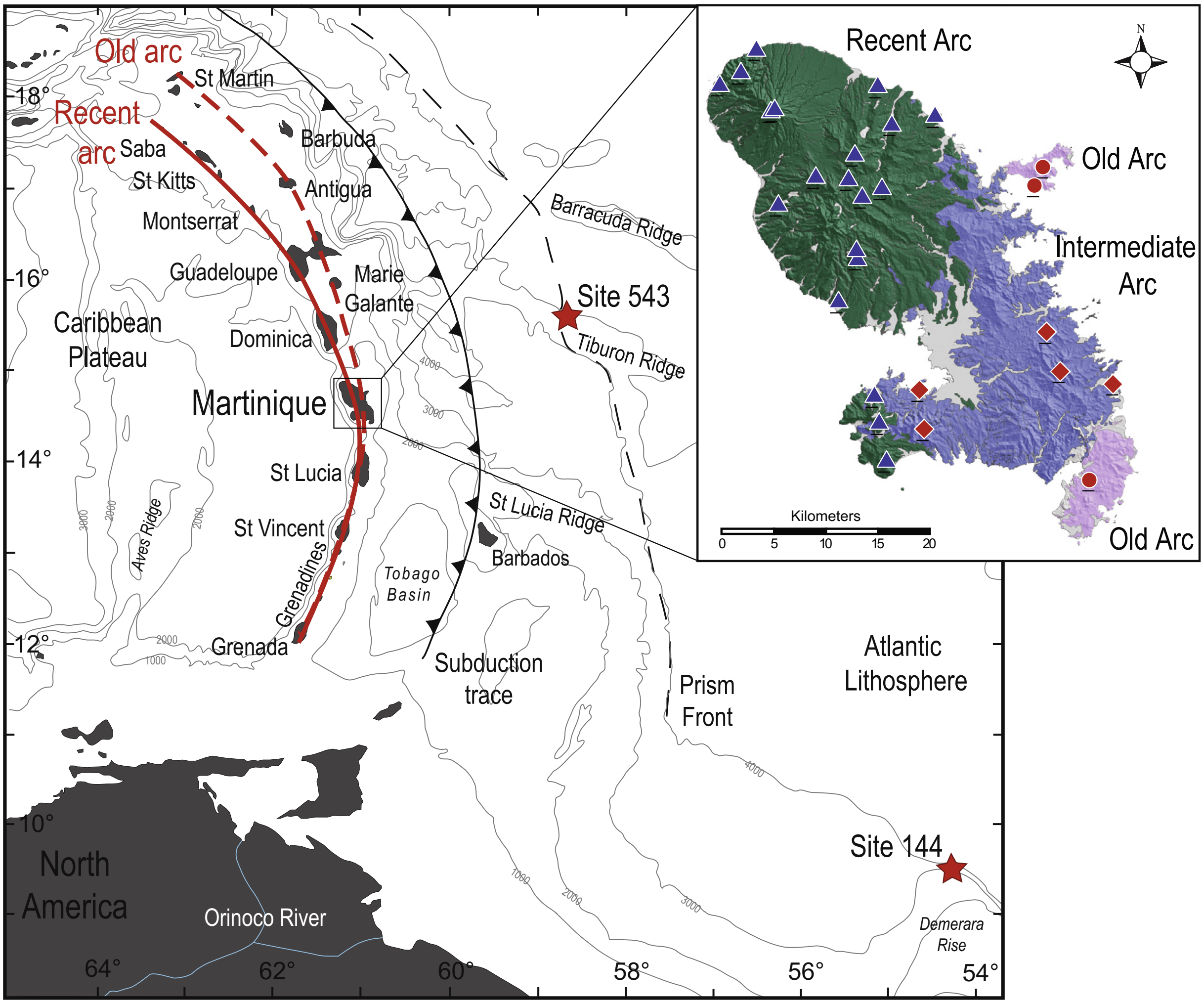

Fig. 1. Geological map showing Martinique Island in the Lesser Antilles arc and the two DSDP sites (from Labanieh et al., 2010). The inset shows the locations of lavas measured for Li isotopes (red dots – old arc lavas, red diamonds – intermediate arc lavas, blue triangles – recent arc lavas). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to account for the extreme Pb isotopic compositions in these lavas. This argument was also supported by the high $\delta^{18}O$ of whole-rock samples from Martinique Island (Davidson, 1985, 1986; Davidson and Harmon, 1989). Recently, Carpentier et al. (2008, 2009) published a Sr–Nd–Pb–Hf isotope study of sediments cored at DSDP Site 144 (Fig. 1) and showed that these sediments may provide a potential crustal component in the genesis of the southern Lesser Antilles lavas, including highly radiogenic Pb isotopes found in a black shale unit. More recent studies by Labanieh et al. (2010, 2012) confirmed this hypothesis and showed that the composition of Martinique lavas can be reproduced by mixing between depleted mantle and sediments from DSDP Sites 543 and 144.

We have analyzed Li isotopes in Martinique lavas and subducting sea floor sediments from DSDP Sites 144 and 543 near the Lesser Antilles trench in order to determine the degree to which the Li isotopic signature of subducted sediments is preserved in overlying arc lavas. We find that the terrigenous sediments subducted beneath the arc are isotopically some of the lightest subducting sediments world-wide (as previously documented by Bouman et al., 2004), and that this isotopically light signature is also seen in the Martinique lavas, suggesting that slab Li is not totally consumed in the mantle wedge and makes it through the subduction filter to reappear in arc lavas.

2. GEOLOGICAL BACKGROUND AND SAMPLES

Atlantic lithosphere subducts beneath the Caribbean plateau (Fig. 1) in an east–west direction at a rate of ~2 cm/yr (Jordan, 1975; Minster and Jordan, 1978), producing the Lesser Antilles island arc, which extends 750 km from Saba in the north, to Grenada in the south. Magmatic activity initiated in the Late Oligocene (~25 Ma, Germa et al., 2011a) and has continued until the present. Martinique, located in the middle of the island chain, records the most complete magmatic history of the arc (Coulon et al., 1991; Germa et al., 2011a). Martinique lavas are subdivided into three volcanic groups: the old arc (20.8–24.8 Ma), the intermediate arc (7.1–16.1 Ma) and the recent arc (0–5.1 Ma). Each group is composed of a variety of volcanic phases, which are described in Westercamp et al. (1989), Germa et al. (2010, 2011b) and Labanieh et al. (2012).

The accretionary complex that dominates the forearc of the Lesser Antilles is a mixture of pelagic sediments and terrigenous turbidites. The Orinoco River drains the South American continent, in particular, the Guyana Precambrian shield, and introduces a large amount of detrital materials to the forearc region of the Lesser Antilles (White et al., 1985). The sedimentary pile shows south–north gradients in lithology and thickness, with a thicker accretionary complex (>10 km) and more detrital materials deposited in the southern part, which is consistent with its proximity to the continent.

DSDP 78A Site 543, drilled at 5630 m water depth to the northeast of Martinique Island, samples a 410 m thick sedimentary sequence overlying 82 Ma basaltic oceanic crust. This sedimentary sequence mainly comprises pelagic and radiolarian clays. Seismic reflection profiles reveal a décollement surface at a depth of 170 m (Biju-Duval et al., 1982; Moore et al., 1982; Westbrook and Smith, 1983; Westbrook et al., 1982), beneath which, the underthrusting sediments are subducted into the mantle.

DSDP 14 Site 144 is located to the southeast of Martinique, and recovered a 340 m thick sedimentary sequence at 2960 m water depth. Since this is well above the carbonate compensation depth (CCD), calcium carbonate is a major constituent of all sediments. In addition to calcium carbonate, this sedimentary pile contains terrigenous claystones, sandstones, black shale, chalks and marls. Detailed descriptions of the sediments recovered at Site 543 and Site 144 can be found in Carpentier et al. (2009).

To determine the Li isotopic composition of the subducting sediments, we analyzed eight samples from Site 144 and seven from Site 543 (beneath the décollement surface), chosen to span the range of lithologies present, including chalky ooze, terrigenous sediments, and pelagic clays (Table 1). In addition, Bouman et al. (2004) report Li isotope data for Site 543 pelagic clays. However, their sediments are from above the décollement, and thus do not reflect Li recycling in Lesser Antilles. The chemical and radiogenic isotopic compositions of our samples were reported by Carpentier et al. (2008, 2009). These sediments have highly variable CaO (0.38–53.8%), Al_2O_3 (0.31–18.6%) and SiO_2 (1.4–61.7%) contents, which correlate with the contents of biogenic carbonates, clays, and detrital quartz or biogenic silica in the sediments. Trace element concentrations and radiogenic isotopic compositions of these sediments also vary widely.

We analyzed Li isotopes in 28 lavas, spanning the three age groups found on Martinique Island (Fig. 1). These samples were selected on the basis of freshness, as documented by petrographic examination of thin sections (e.g., no secondary minerals such as chlorite have been observed) (Labanieh et al., 2012). Loss on ignition (LOI, Table 2) is below 2% for 90% of the samples analyzed here and does not exceed 3.8%. The ages of these samples, determined by the K–Ar dating technique, range from 1.9 ka to 24.8 Ma (Germa, 2008; Germa et al., 2010, 2011a,b). Four out of the 28 samples (06MT23, 06MT32, 06MT34 and 06MT73) are lavas that erupted below sea level. In addition, most lavas in the St. Anne series erupted below sea level, but it is unclear whether this holds for the St. Anne samples in our suite (e.g., 06MT53, 06MT54 and 06MT68). The chemical and radiogenic isotopic compositions of all of the lavas studied here were reported in Labanieh et al. (2010, 2012). The lavas have SiO_2 contents between 47.3% and 67.4%, are subalkaline, with $Na_2O + K_2O$ ranging from 2.3% to 5.7%, and show large ion lithophile element enrichment, Nb and Ta depletion, and low Ce/Pb ratios, features typical of arc magmas.

3. ANALYTICAL TECHNIQUES

Lithium isotopic compositions and concentrations of the samples were analyzed at the Geochemistry Laboratory of the University of Maryland, College Park. Samples were dissolved in screw-top Teflon beakers with a combination of $HF–HNO_3–HCl$. To achieve complete digestion, some samples were dissolved in $HF–HNO_3–HClO_4$. Lithium was purified on a cation exchange resin (Bio-Rad AG50w-X12, 200–400 mesh) first in an HCl medium, followed by an HCl–ethanol medium. Before instrumental analysis, sample solutions were diluted to ~50 ppb Li in 2% HNO_3. Lithium isotopes and concentrations were determined on a Nu Plasma MC-ICP-MS using the standard-sample-bracketing method. Four rock reference materials (BHVO-1, AGV-1, AGV-2 and G-2) were analyzed as accuracy benchmarks. The measured δ^7Li are listed in Table 3, together with the previously published Li concentrations. The precision of Li isotopic analyses was determined from our long-term analyses of two reference solutions UMD-1 (~50 ppb) and IRMM-16 (~50 ppb), which gave mean δ^7Li values of 55.2 ± 0.97 (2σ, $n = 34$) and 0.22 ± 0.67 (2σ, $n = 36$), respectively (see plots in on-line Supplement). We adopt ±1‰ as our 2 sigma analytical uncertainty in this work. The total analytical blank for Li is 1.2 ng, which is insignificant for all of the samples analyzed here. A more detailed description of sample dissolution, column separation and instrumental analysis is available in Qiu et al. (2009) and Teng et al. (2006).

The measured δ^7Li for the four rock standards agree with reported values within uncertainty (Table 3), and the measured δ^7Li values for samples with replicated column chemistry or dissolution are reproducible within error (Tables 1 and 2).

4. RESULTS

4.1. Martinique lavas

Lithium isotopic compositions are given in Table 2. The δ^7Li values of most Martinique lavas are lower than those of average MORB ($\delta^7\text{Li} = 3.7 \pm 1$, 1σ, Tomascak et al., 2008) (Fig. 2a). In addition, the Li isotopes of Martinique lavas are generally lighter than those of other arc lavas, which mostly fall within the MORB range (Fig. 2b).

Table 2
Li isotope compositions of the Martinique lavas.

Sample ID	Location	Age, ka	LOI, wt.%	SiO_2, wt.%	δ^7Li	[Li], ppm	Y/Li
Recent arc							
06MT50	14.811	2	0.2	62.0	+1.1	24.7	0.80
06MT50 redissolution[a]	−61.167				+0.3		
06MT51	14.812	2	0	62.7	+1.1	25.8	0.77
06MT51 replicate[b]	−61.165				+2.4		
06MT40	14.849	189	0.8	60.0	+0.8	15.7	1.48
	−61.198						
06MT37	14.675	322	1.1	55.9	+2.1	20.2	0.92
	−61.085						
04MT07	14.725	341	0.46	58.8	+0.6	29.1	1.48
04MT07 redissolution	−61.115				+1.5		
06MT18	14.837	346	1.0	58.4	+2.8	8.6	2.22
	−61.218						
06MT28	14.872	543	1.2	58.5	+1.0	13.5	1.38
06MT28 replicate	−61.182				+2.2		
IAR	14.533	640	0.0	47.7	+4.3	4.9	4.10
IAR replicate	−61.067				+3.1		
06MT21	14.747	893	0.9	63.5	−1	37	0.45
06MT21 redissolution	−61.124				+0.1		
06MT36	14.668	998	1.6	63.0	−0.6	38.9	0.43
06MT36 replicate	−61.083				−0.7		
06MT61	14.507	1,175	0.1	54.4	+1.2	7.0	3.27
	−61.062						
06MT55	14.47	1,332	1.2	59.9	+1.3	10.5	2.94
	−61.055						
06MT14	14.769	1,530	1.0	58.5	+2.7	30.2	0.63
	−61.086						
06MT19	14.72	1750	1.4	57.8	+1.6	24.6	1.07
06MT19 redissolution	−61.161				+2.5		
06MT04	14.626	1,870	1.3	60.0	+4.1	28.7	0.85
	−61.102						
06MT10	14.736	2,111	1.9	59.8	+3.6	26.4	0.96
	−61.059						
06MT13	14.728	2,550	1.2	58.8	+1.0	20.2	1.13
	−61.079						
06MT34*	14.806	4,100	0.6	53.8	+7.1	4.9	6.31
	−61.007						
06MT23*	14.799	4,863	1.2	53.9	+1.4	8.9	2.70
	−61.05						
06MT32*	14.835	5,130	0.7	50.7	+1.0	6.21	4.77
06MT32 redissolution	−61.063				+2.0		
06MT32 replicate					+1.0		
Intermediate arc							
06MT72	14.539	7,100	3.8	67.4	+1.9	53.1	0.34
	−61.022						
06MT60	14.501	8,760	1.3	60.6	+4.9	26.1	1.04
06MT60 redissolution	−61.017				+4.3		
06MT71	14.546	10,300	0.9	49.3	+0.9	17	2.83
	−60.832						
06MT69	14.557	10,640	2.0	47.3	+0.7	18.5	2.25
06MT69 redissolution	−60.885				+1.1		
06MT73*	14.596	16,120	2.9	66.5	+13.9	5.1	8.82
06MT73 replicate	−60.898				+14.6		
Old arc							
06MT54**	14.739	20,800	1.2	53.3	+3.5	10.5	2.47
	−60.91						
06MT53**	14.757	23,400	1.4	58.5	+16.3	6.4	4.07
	−60.901						
06MT68**	14.452	24,800	1.5	49.1	+1.9	5.5	2.51
06MT68 replicate 1	−60.856				+1.7		
06MT68 replicate 2					+2.9		

Notes: Major and trace element data are from Labanieh et al. (2012).

* Erupted below seawater.

** These samples, from the St. Anne's suite, may or may not have erupted below seawater.

[a] Redissolution means independent sample dissolution and column chemistry.

[b] Replicate means independent column chemistry.

Table 3
Measured δ^7Li and [Li] in rock standards compared with reported values.

Rock standards	This work δ^7Li	Literature δ^7Li
BHVO-1		
Dissolution 1	+4.2	+4.0 ~ +6.1
Dissolution 2	+4.5	
Dissolution 3	+4.3	
Dissolution 4	+4.9	
Dissolution 5	+4.4	
Mean	+4.5 ± 0.6	
AGV-1		
Dissolution 1	+5.1	+4.6 ~ +6.7
AGV-2		
Dissolution 1	+6.2	+5.7 ~ +8.1
Dissolution 2	+5.2	
Dissolution 3	+5.3	
Mean	+5.6 ± 1.2	
G-2		
Dissolution 1	−0.6	−1.2 ~ +0.3
Dissolution 2	−0.3	
Dissolution 3	+0.1	
Dissolution 4	−1.3	
Mean	−0.5 ± 1.2	

Notes: ± values are two sigma of the mean. BHVO-1 literature data are from James and Palmer (2000), Pistiner and Henderson (2003), Chan and Frey (2003), Bryant et al. (2004), Rudnick et al. (2004), Bouman et al. (2004), Magna et al. (2004), Rosner et al. (2007), Aulbach et al. (2008), Halama et al. (2008, 2009, 2011), Maloney et al. (2008), Schuessler et al. (2009), Liu et al. (2010, 2013, 2014), Penniston-Dorland et al. (2010, 2012). AGV-1 literature data are from Magna et al. (2004), Liu et al. (2010, 2013, 2014); AGV-2 literature data are from Magna et al. (2004 and 2006) and Tian et al. (2012); G-2 literature data are from James and Palmer (2000), Pistiner and Henderson (2003), Liu et al. (2010) and Barnes et al. (2012).

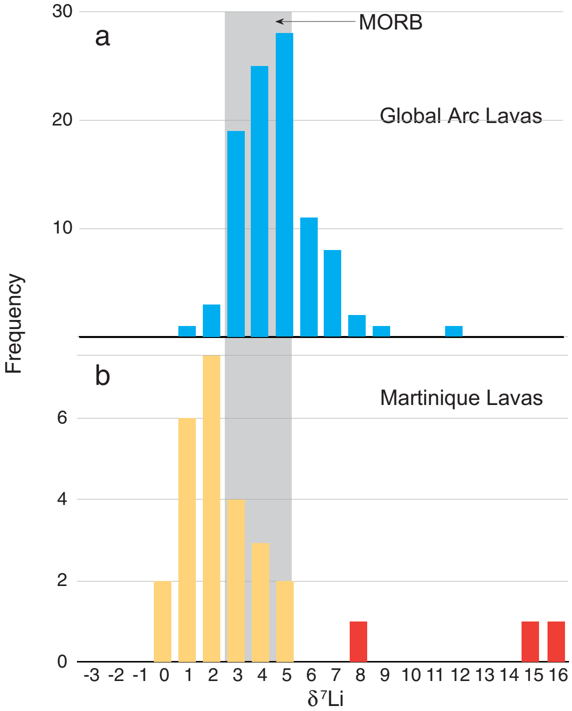

Fig. 2. Histogram showing Li isotopic compositions of Martinique lavas compared with MORB and other arc lavas. Published arc lava data include Central American Volcanic Arc (Tomascak et al., 2000; Chan et al., 2002b), Izu Arc and Northeastern Japan Arc (Moriguti and Nakamura, 1998; 2004), Kurile Arc, Sunda Arc and Aleutian Arc (Tomascak et al., 2002) and Mt. Shasta (Magna et al., 2006). Three isotopically heavy samples from Martinique are shown in red. These samples are likely affected by sea water Li (see text for discussion). MORB average (δ^7Li = 3.7 ± 1, 1σ) from Tomascak et al. (2008).

Three lavas have higher δ^7Li than MORB (Fig. 2, in red). These three samples have the following similarities: (1) they have low $(La/Sm)_N$ (Fig. 3), (2) they are depleted in alkali metals (Fig. 4); (3) they have depleted mantle-like radiogenic isotopes (Fig. 5), and, most importantly, (4) two of the three are lavas that erupted below sea level (e.g., 06MT73, 06MT34), while the origin of the third lava (06MT073) is less clear but it may have also erupted as a sub-marine lava. These features distinguish them from the rest of the lavas and they are shown as red symbols in all plots.

4.2. Sediments from DSDP Sites 543 and 144

Despite the differences in lithology and chemical composition, the sediments recovered from Sites 543 (mean δ^7Li = −0.8 ± 1.5, 1σ) and 144 (mean δ^7Li = −1.3 ± 2.9, 1σ) are indistinguishable from each other in terms of their Li isotopes, and both sections are significantly isotopically lighter than MORB. Bouman et al. (2004) previously analyzed four samples from Site 543 that included radiolarian pelagic clay, Mn stained radiolarian clay, zeolitic pelagic clay and calcareous ferruginous claystone. These samples have δ^7Li ranging from −0.8 to +1.1, with a mean δ^7Li of +0.4 ±0.9 (1σ), falling within the spread of our data. The δ^7Li values of Site 144 sediments are slightly more variable, consistent with the greater variation in lithology and radiogenic isotopic compositions.

5. DISCUSSION

5.1. Low δ^7Li subducting sediments

The sediments (i.e., those below the décollement) sampled at Sites 543 and 144 have the lightest average Li isotopes among global subducting sediments (Fig. 6). Even carbonate-rich sediments from Site 144 have light Li (Table 1), reflecting the clay component, which dominates the Li mass balance, as clays have [Li] up to two orders of magnitude higher than carbonates (e.g., Marriott et al., 2004; Teng et al., 2004). The low δ^7Li values obtained for the Site 543 samples are similar to those seen in sediments from above the décollement at Site 543 (Bouman et al., 2004). The low δ^7Li values of sediments from both drill-cores likely reflect the dominance of terrigenous materials from the South America continent (White et al., 1985),

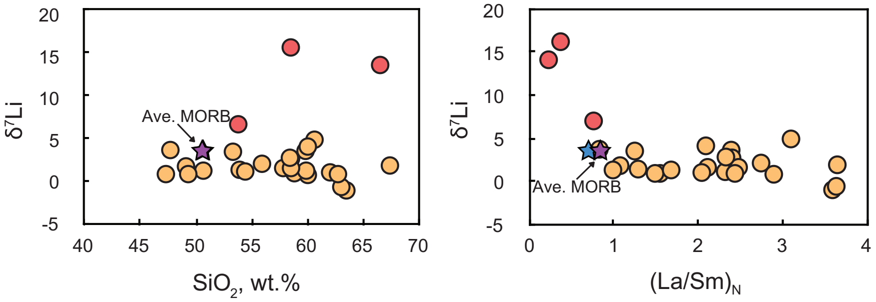

Fig. 3. δ^7Li vs. SiO_2 and $(La/Sm)_N$ for Martinique lavas. The red symbols denote the lavas with Li isotopes heavier than MORB. Notice that the three isotopically heavy samples have relatively high SiO_2 content but low $(La/Sm)_N$ values. A MORB field could not be plotted due to lack of published major and trace element data for many of the samples for which δ^7Li has been determined, but for reference $(La/Sm)_N$ of average global MORB from Arevalo and McDonough (2010) is 0.73 (marked by blue star), average N-MORB is 0.61, while Gale et al. (2013) have average $(La/Sm)_N$ of MORB = 0.86 (purple star). One sigma standard deviation of δ^7Li is about the size of the MORB stars. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

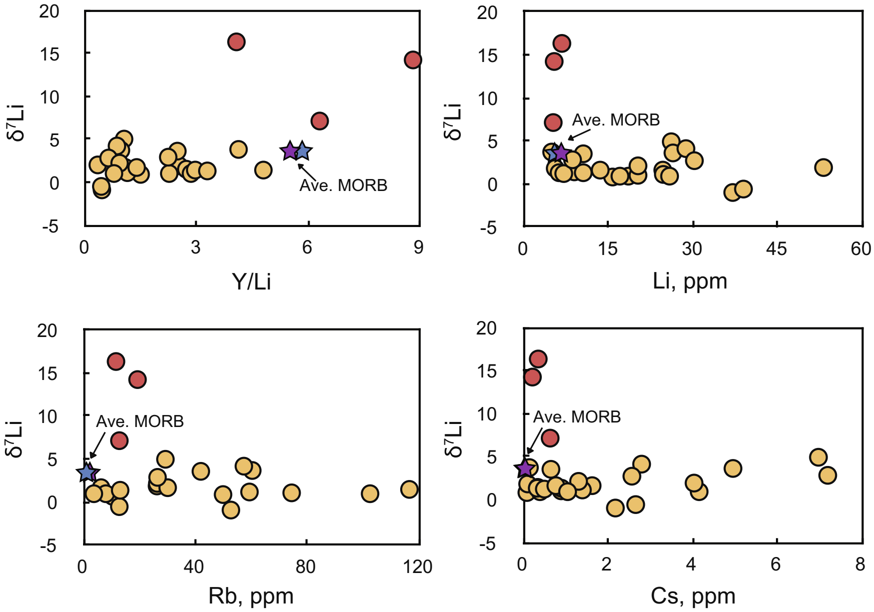

Fig. 4. δ^7Li vs. Y/Li, [Li], [Rb] and [Cs] for Martinique lavas. Note that the three lavas with heavy Li isotopes all have low alkali metal concentrations, even when SiO_2 is as high as 66.5%. MORB averages (stars) as in Fig. 3.

which derive, in part, from the highly weathered Guayana Shield (Huh et al., 2001; Carpentier et al., 2013). Previous studies have demonstrated a correlation between δ^7Li and weathering intensity recorded in terrigenous sedimentary rocks, with shales derived from more highly weathered provenances, as measured by chemical index of alteration (CIA) values (Nesbitt and Young, 1982), having lower δ^7Li and higher [Li] (Qiu et al., 2009). A similar relationship is seen in subducting sediments, of which the Lesser Antilles sediments form an end member (Fig. 7).

At both Sites 543 and 144, δ^7Li in the sedimentary pile increases with depth (Fig. 8). Similar trends have been observed in sediments from the Tonga and Central America Trenches (Chan et al., 2006) where [Li] decreases with depth, and δ^7Li increases up to +12 at the base of the sedimentary sections. While Chan et al. (2006) suggested that these trends might be controlled by lithology and hydrothermal activity, lithology cannot be the sole control for our data, as lithology in the Site 543 sediments is largely invariable with depth (Table 1). At Site 543, [Li] also decreases with depth but at Site 144, the [Li] – depth relationship is variable – it first decreases and then markedly increases with depth (Fig. 8). Understanding the cause of the depth-dependent changes in δ^7Li in these sediments is beyond the scope of this paper, but we provide two suggestions here: (1) the increasing δ^7Li and decreasing [Li] with depth may reflect increasing leaching and sediment-pore water exchange with depth. Pore waters typically have higher δ^7Li than sediments (+7.5 to +45.7, Scholz et al., 2010), and their compositions also tend to change systematically with depth, reflecting Li release during diagenesis as well as uptake of Li during authigenesis (Scholz et al.,

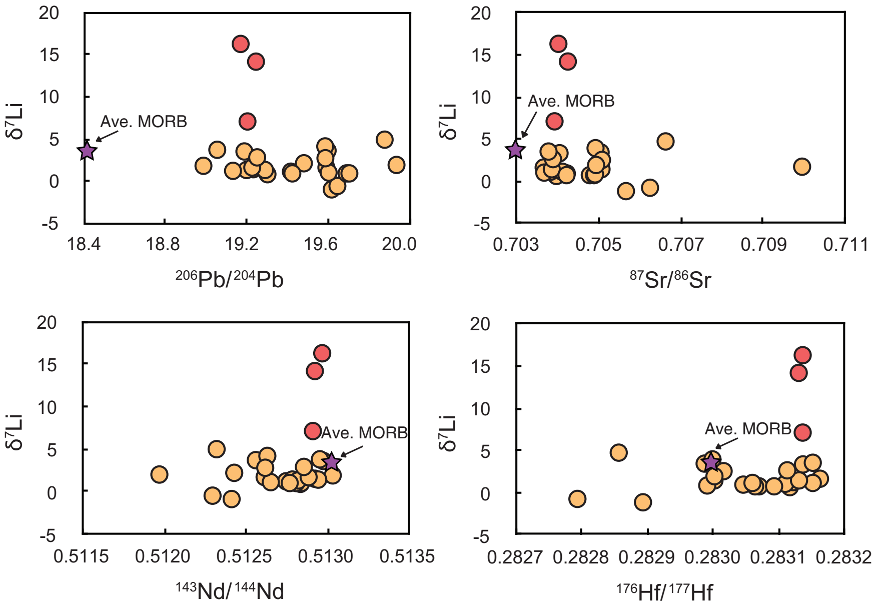

Fig. 5. δ^7Li vs. Sr–Nd–Pb–Hf isotopes for Martinique lavas. The three high δ^7Li samples are characterized by depleted mantle-like radiogenic isotopic compositions. MORB averages (stars) as in Fig. 3.

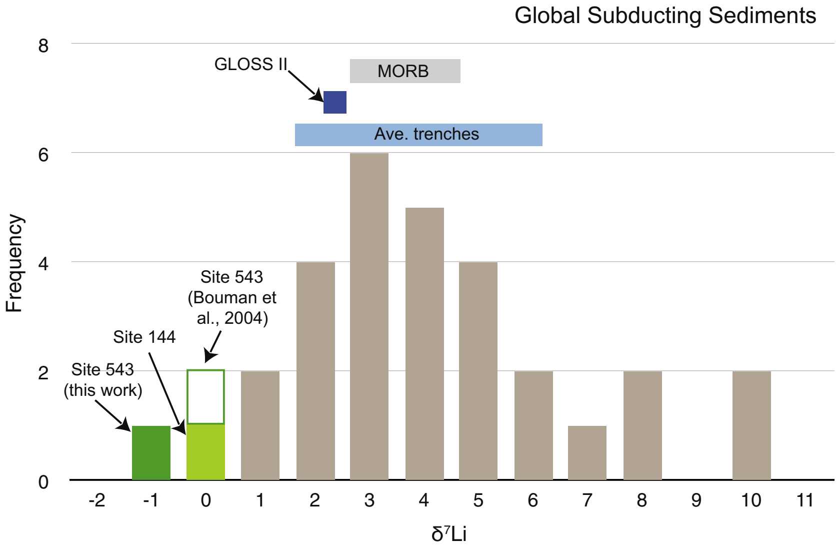

Fig. 6. Distribution of average δ^7Li in subducting sediments from global trenches. Lithium isotopes of subducting sediments from different trenches (lithology weighted averages of 26 trenches, shown in light brown) are from Plank (2014) and this study (Sites 543 and 144). Carbonate-rich samples were excluded from the average for Site 144 (see text for explanation). Also shown is δ^7Li for GLOSS II (Plank, 2014) and the average and standard deviation for the data from the individual trenches ("Ave. trenches"). Readers are referred to Plank (2014) for details of the 26 trenches. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2010); (2) If we exclude the four samples significantly diluted by carbonates ($CaO > 30$ wt.%), δ^7Li shows a rough, negative correlation with Al_2O_3 (Fig. 9), which may indicate temporal variation in the composition of the sediments, hence provenance, because clay-rich components tend to have high Al_2O_3 contents and low δ^7Li, as described above. These two explanations are not mutually exclusive and future studies of marine sedimentary δ^7Li with depth should help to elucidate which of the two processes is most important or if other processes are at work that we have not recognized.

Though variable, δ^7Li values of these sediments show no correlation with other geochemical characteristics such as Li- or LREE-enrichment (Fig. 10), and very poor correlations with radiogenic isotopes, particularly Nd and Pb (Fig. 11), which have been used to trace sedimentary

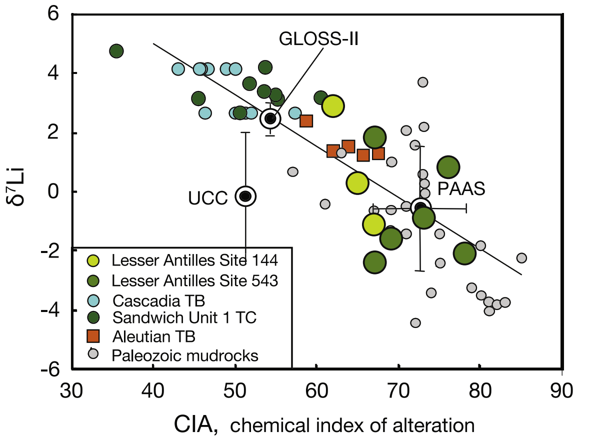

Fig. 7. δ^7Li vs. CIA for subducting sediments from Lesser Antilles (larger symbols) and other arcs after Plank (2014). We excluded the data from Bouman et al. (2004) that appeared on Plank's original figure for Lesser Antilles, as there is no major element data for these samples. The four high-CaO samples from Site 144 (Table 1) are not shown as their CIA values cannot be calculated accurately.

components in subduction zone magmas. Because Nd and Pb are far more concentrated in the sediments than in the mantle relative to Li, their isotopic compositions in the arc lavas are more sensitive to sedimentary input (either in the mantle source or during shallow assimilation). Collectively, the lack of, or poor correlations between Li isotopes and other geochemical tracers in the sediments may also explain the decoupling between Li isotopes and other geochemical tracers seen in the Martinique lavas, if the variable δ^7Li reflects a sedimentary component incorporated into the magma (see Supplementary File for Monte Carlo simulation of sediment mixing to a depleted mantle source).

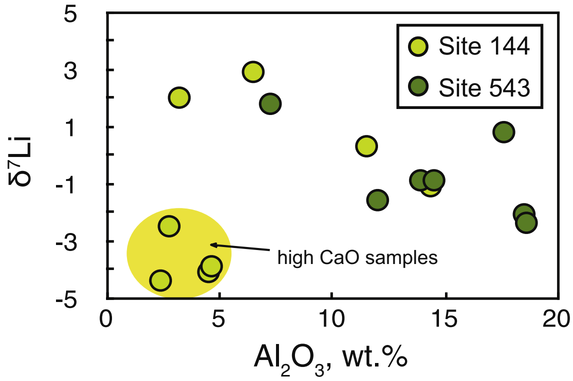

Fig. 9. δ^7Li negatively correlates with Al_2O_3 contents in the subducting sediments if the four high CaO samples are excluded. This may reflect a lithological control on the Li isotopic compositions in the subducting sediments at DSDP Sites 543 and 144.

5.2. High δ^7Li lavas

The three samples with heavy Li isotopes are distinguished from other samples by depletion in alkali metals, low $(La/Sm)_N$, depleted mantle-like radiogenic isotopes, and, most importantly, their submarine eruption. Labanieh et al. (2012) found that submarine lavas are generally marked by negative [Li] anomalies, while subaerial lavas have positive Li anomalies. These observations suggest that the three samples likely interacted with seawater (δ^7Li ~+31), which may have produced their abnormally high δ^7Li. The depletion in alkali metals, including Li, indicates that these elements might have been leached from the lavas during the interaction with seawater, making them more susceptible to change, while the isotopically heavy

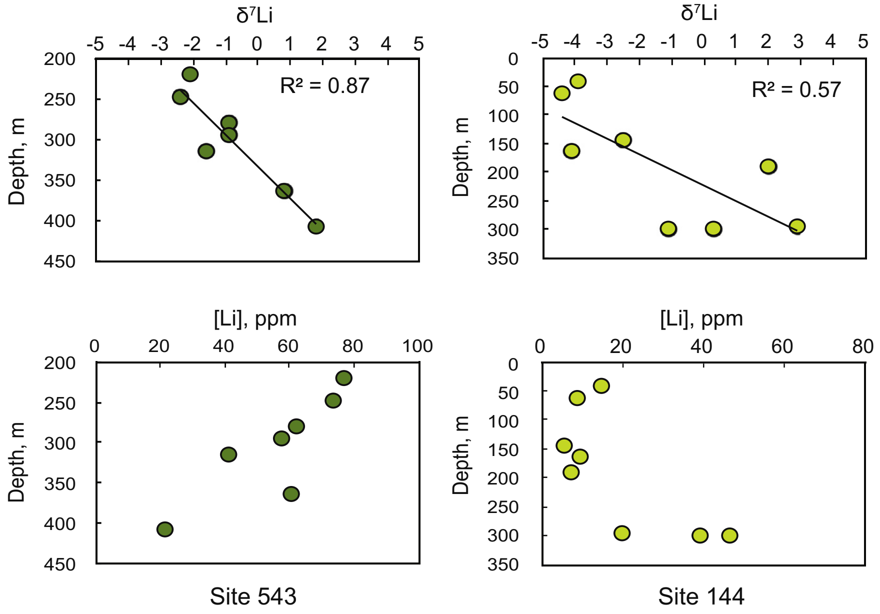

Fig. 8. δ^7Li and [Li] as a function of depth for the sediments from DSDP Sites 543 and 144. Note the general positive correlation between δ^7Li and depth while the relationship between [Li] and depth is less clear, in part due to carbonate enrichment in the upper section of Site 144.

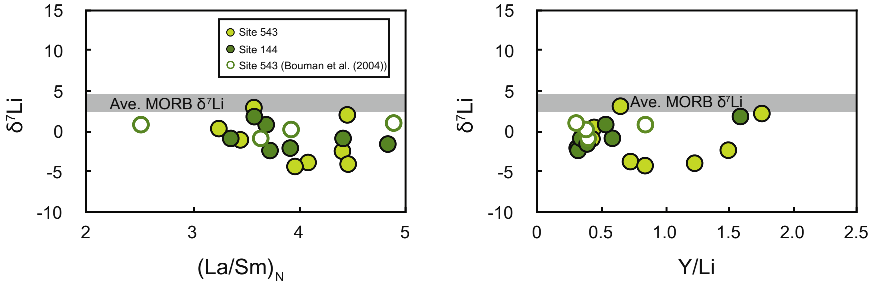

Fig. 10. δ^7Li vs. $(La/Sm)_N$ and Y/Li for the subducting sediments from DSDP Sites 543 and 144. Site 543 sediments are all pelagic clays, whereas the lithology of Site 144 sediments is more highly variable, yet the δ^7Li of the two sites are indistinguishable. Trace element data are from Carpentier et al. (2009). For comparison, we also plot the data from Bouman et al. (2004), though because the latter sediments lie above the décollement, they will not be subducted into the source region of the arc lavas. Average global MORB δ^7Li shown by gray band (Tomascak et al., 2008); $(La/Sm)_N$ for average MORB is below 1 and Y/Li is between 5 and 6 (Arevalo and McDonough, 2010; Gale et al., 2013).

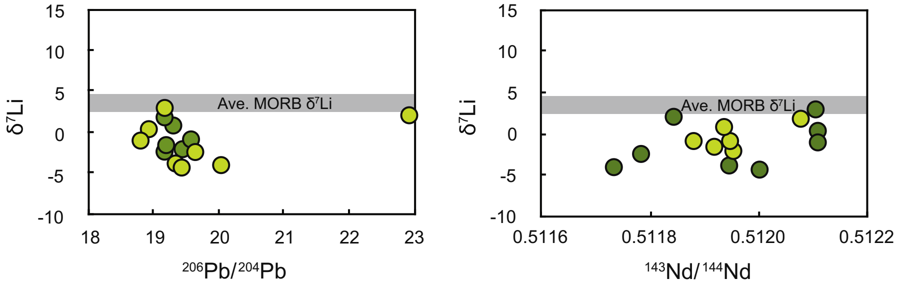

Fig. 11. δ^7Li vs. Pb and Nd isotopes for the subducting sediments from Sites 543 and 144. Li isotopes show only poor correlations with radiogenic isotopes in these sediments. Radiogenic isotope data are from Carpentier et al. (2008). Average global MORB δ^7Li shown by gray band (Tomascak et al., 2008).

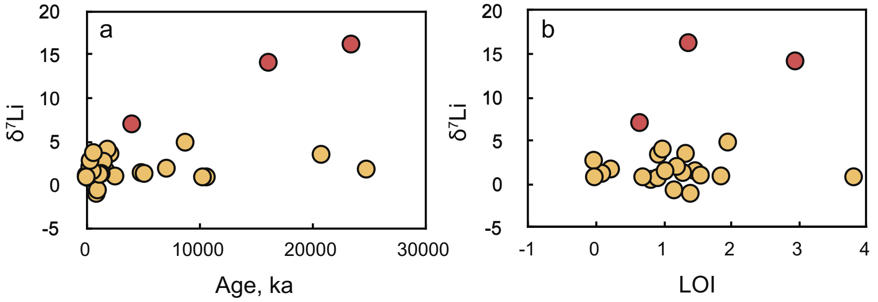

Fig. 12. Plots of δ^7Li vs. age (a) and LOI (b) for Martinique lavas. The red symbols denote the samples with Li isotopes heavier than MORB. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

compositions suggests some amount of uptake of seawater Li. No matter what process is responsible for producing these high δ^7Li values, it seems that they are not primary features of the lavas, and therefore these three samples will not be considered further.

5.3. Low δ ^{7}Li components in Martinique lavas

The δ^7Li values of the remaining lavas show no clear relationship with age (Fig. 12a). Furthermore, the samples with the lowest LOI (~0%) are also isotopically light (Fig. 12b), suggesting that the low δ^7Li values in Martinique lavas are unlikely to be a result of alteration or chemical weathering. The lack of correlation between δ^7Li and SiO_2 and $(La/Sm)_N$ (Fig. 3) indicates that the Li isotopic compositions of the lavas are insensitive to magmatic differentiation and the amount of assimilated crustal materials. The δ^7Li values also show no real correlation with radiogenic isotopes (Fig. 5), and even the least differentiated sample ($SiO_2 = 47.3\%$) has a δ^7Li significantly lower than that of MORB. Collectively, δ^7Li does not correlate with either composition or age of the lavas.

The Martinique lavas have δ^7Li values that overlap with, but are mostly lower than those of MORB (Fig. 2), suggesting incorporation of low δ^7Li components in their source region and/or assimilation of such components during differentiation within the crust. Light Li isotopes were also observed in olivine-hosted melt inclusions from St. Vincent Island (Bouvier et al., 2008), which also belongs to the Lesser Antilles arc. According to Bouvier et al. (2008), the low δ^7Li (down to -10) in the melt inclusions, although seemingly not preserved in bulk lava records, may reflect initial melt heterogeneities and kinetic fractionation in the source region. An alternative explanation is that they reflect diffusive addition of Li into the inclusion from the mineral (e.g., Richter et al., 2014).

5.3.1. Arc source region

Four components may have contributed to the source of arc magmas: depleted mantle, slab fluids, melts derived from fresh/altered oceanic crust (AOC) and melts from marine sediments. As depleted mantle will have the δ^7Li of MORB, it cannot be responsible for the low δ^7Li we observe. We therefore consider each of the remaining components, in turn.

Slab fluids are expected to be isotopically heavy, as ^{7}Li is preferentially partitioned into hydrous fluids (Moriguti and Nakamura, 1998; Tomascak et al., 2000; Chan et al., 2002b; Zack et al., 2003; Wunder et al., 2006; Marschall et al., 2007; Caciagli et al., 2011). High Li, low salinity fluids from forearc seamounts that are interpreted to derive from the slab have high δ^7Li ($\sim$+20), supporting this hypothesis (Chan and Kastner, 2000; Benton et al., 2004). Moreover, Ba is a fluid-mobile element that is often used as a tracer of slab fluids (e.g., Labanieh et al., 2012). The Ba/Th of the seven basaltic samples ($SiO_2 < 55\%$) vary from 51 to 188 with an average value of 112, which is within the 2 sigma range of global MORB ($\sim 80 \pm 52$, 2σ, Arevalo and McDonough, 2010). Therefore, slab fluids are unlikely to account for the isotopically light Li in the Martinique lavas.

Altered oceanic crust has variable Li isotopic composition depending on the temperature of alteration. Low-temperature seafloor weathering of the basaltic crust produces high δ^7Li due to uptake of heavy seawater Li into clays (Chan et al., 1997, 2002a), while hydrothermal alteration generates low δ^7Li as a result of preferential leaching of ^{7}Li (e.g., Chan et al., 2002a,b). Metamorphic dehydration of the altered crust may lower δ^7Li (Zack et al., 2003; Marschall et al., 2007; Halama et al., 2011), but the extremely low δ^7Li observed in some eclogites (down to -21) likely results from kinetic isotopic fractionation during retrograde metamorphism (Marschall et al., 2007). Using the experimentally determined isotopic fractionation factors of Wunder et al. (2006), Marschall et al. (2007) calculated that δ^7Li could be lowered by only $\leqslant 3‰$ during metamorphism of basaltic oceanic crust. These modeling results are supported by later observations on metapelites, which show negligible isotopic fractionation associated with metamorphic dehydration during sub-greenschist to granulite facies metamorphism, even in the presence of significant Li loss (Teng et al., 2007; Qiu et al., 2009, 2011a,b). Thus, any contribution to arc magmas from the altered oceanic crust would come from melts, which should have the same isotopic composition as their source, given that the amount of isotopic fractionation at magmatic temperatures is negligible (Tomascak et al., 1999). However, there is no evidence for melts of the basaltic slab contributing to the source of Martinique lavas. First, the chemical and physical conditions of the slab below Martinique Island ($\sim$780 °C and 4.5 GPa, Syracuse and Abers, 2006; Syracuse et al., 2010) do not meet those required for basaltic slab melting (Schmidt and Poli, 2014). Secondly, the Martinique lavas have uniformly low Sr (28/29 samples < 400 ppm) and Sr/Y ratio (3.5–24.7; mean = 11.3), which is inconsistent with addition of slab melts having Sr concentrations > 400 ppm and Sr/Y > 20 (Defant and Drummond, 1990; Castillo, 2006).

Introduction of subducting sediments, or melts therefrom, to the mantle source of the Martinique lavas may produce their low δ^7Li. As noted earlier, the sediments subducting beneath the Lesser Antilles are end members in having the lowest δ^7Li amongst global subducting sediments (Table 1, Fig. 6). Carpentier et al. (2008, 2009) and Labanieh et al. (2010, 2012) showed that addition of Site 144 sediments to the mantle wedge reproduces the mixing trends seen in plots of radiogenic isotopes in the Martinique lavas. Furthermore, earlier studies have shown that Li may or may not be removed during prograde metamorphism of pelitic rocks, but Li isotopes are unaffected by either metamorphism or partial melting. For example, Penniston-Dorland et al. (2012) suggested that deeply subducted metasedimentary rocks may largely retain their Li inventory to depths of at least 40 km. Bebout (2014) studied ultra high-pressure metasedimentary rocks from the Western Alps and inferred Li retention in such rocks to depths of >90 km. By contrast, significant Li depletion is seen in amphibolite to granulite-facies rocks in both contact metamorphic aureoles (Teng et al., 2007) and metapelitic residues in the Ivrea Zone, Italy (Qiu et al., 2011b), though this apparently did not change their δ^7Li. Alternatively, some have suggested that sediments are physically mixed into the mantle wedge of arcs via the rise of buoyant diapirs (Hacker et al., 2011; Behn et al., 2011). Either process (melting or solid diapirs) is capable of introducing isotopically light Li to the source region of arc basalts.

5.3.2. Crustal contamination?

Our Li data cannot rule out the possibility that crustal contamination influenced the composition of the Martinique lavas since the Li isotopic composition of the arc crust beneath Martinique is yet to be constrained. However, crustal contamination, if present, is unlikely to be the major cause of low δ^7Li for two reasons. First, δ^7Li shows no correlation with SiO_2, and is as low as +0.9 even in the most primitive basalt ($SiO_2 = 47.3\%$). Second, if the low δ^7Li was acquired during magma ascent, 10–20% (by mass) sediment assimilation would be required, assuming the assimilated arc crust has the same [Li] and Li isotopic composition as the bulk Site 543 and Site 144 sediments. This is due to the fact that the basaltic magma has much higher [Li] than peridotite in the mantle wedge, and its isotopic composition is therefore less sensitive to sediment addition. The questions then arise (1) whether the thermal budget of the magma allows for such a large extent of sediment assimilation in the crust; (2) whether these magmas would remain basaltic in their compositions after such extent of assimilation, assuming an assimilation/crystallization ratio of 0.25 (Smith et al., 1996). Labanieh et al. (2010) calculated AFC trends but were unable to reproduce the Sr–O isotope data.

5.4. Sediment mixed into the source

In order to determine the amount of sediment that was added to the mantle source of the lavas, we must first constrain the composition of the source. While δ^7Li in the lavas should reflect that of the source, the same is not true for [Li]. In order to characterize the Li content of the source, we normalize to another element that has a similar partition coefficient: Y. We use the Y/Li ratio, so that mixing will be linear in a plot of Y/Li vs. δ^7Li.

Lithium and Y have nearly identical solid/melt bulk distribution coefficients in basaltic systems (Ryan and Langmuir, 1987), and their ratio, Y/Li, has frequently been used to infer source composition (e.g., Moriguti and Nakamura, 1998; Tomascak et al., 2002; Chan et al., 2002b; Plank, 2014). Here, we use basaltic samples ($SiO_2 < 55\%$) in our mixing model, since Y/Li decreases with differentiation, in order to estimate sedimentary input to the mantle source.

Fig. 13 shows two-component mixing between depleted mantle ([Li] = 0.7 ppm, [Y] = 4.07 ppm (Salters and Stracke, 2004), $\delta^7\text{Li} = +4$), and the subducting sediments from Site 543 and Site 144. We estimated the average composition of the subducted sediment by using Site 543 samples that are located only below the décollement (i.e., all of the Site 543 sediments analyzed here, but not the Boumann et al. sediments which are above the décollement) and for Site 144, only the low carbonate sediments, assuming that the sediments deposited closer to the trench, below the carbonate compensation depth, will have much lower carbonate concentrations. We first calculated the concentration weighted mean δ^7Li for Site 144 and Site 543, respectively. Then we used the two concentration weighted mean δ^7Li and the bulk [Li] and [Y] values for the two sites recommended by Carpentier et al. (2009), and calculated concentration weighted mean δ^7Li for the bulk subducting sediments. This yields a bulk $\delta^7\text{Li} = -0.5$, and a mean [Li] = 49.1 ppm, mean [Y] = 24.2 ppm. The average Li isotopic composition and Y/Li ratio represented by the eight basaltic samples from Martinique Island (concentration weighted mean $\delta^7\text{Li} = +1.6$, mean Y/Li = 2.9) require a bulk sedimentary contribution of ~2% by mass to the source. All basaltic samples can be reproduced by less than 5% sediment addition. If the sediment component was added as a partial melt, instead of bulk mixing, then the sediment proportion is even less. However, this calculation assumes no Li loss during sediment dehydration and no contribution from isotopically heavy components such as slab fluids, which may result in an underestimate of the sedimentary input. These two factors tend to cancel each other out with regard to their effects on the calculated sediment proportion. Our estimate of sedimentary input to the mantle source based on Li isotopes agrees well with that determined from the radiogenic isotopic constraints (0.1–5%, Labanieh et al., 2010).

5.5. Implications for Li in arc systems

Martinique is currently the only example observed, to date, where intraoceanic arc lavas have low average δ^7Li relative to MORB. The Li isotopic compositions of most

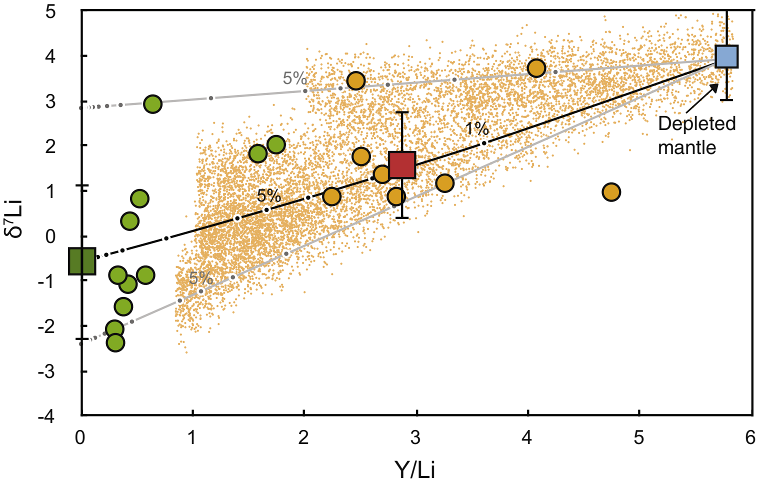

Fig. 13. A two-component mixing model between depleted mantle (blue square) and sediments from Sites 543 and 144 (green dots). The large green square represents the average composition of the sediments (excluding the carbonate-rich sediments from Site 144, which are unlikely to subduct beneath the arc), whereas the large red square represents the average composition of the basalts. We assumed zero Y in the sedimentary component that contributed to the lava source since Y may be largely retained in garnet in the slab. Error bars represent 1 sigma standard deviation. The light Li isotopes in the basaltic Martinique lavas (orange dots) can be formed by less than 5% addition of Site 543 and Site 144 sediments to a mantle source (gray mixing lines). The small orange dots in the background represent random mixing results simulated using the Monte Carlo scheme (see Supplementary File). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

other arcs generally overlap the MORB range (e.g., Chan et al., 2002a,b; Tomascak et al., 2002; Moriguti et al., 2004, Fig. 2). The lack of a clear slab signal in the δ^7Li of arc lavas has led to broad discussion on Li recycling and Li isotopic fractionation in arc systems (e.g., Tomascak et al., 2002; Plank, 2014), as well as investigation of Li isotopic compositions of slab components (e.g., Chan and Kastner, 2000; Chan et al., 1992, 2002a; Zack et al., 2003; Benton et al., 2004; Marschall et al., 2007; Penniston-Dorland et al., 2011; Halama et al., 2011).

Earlier investigations of Li in arc lavas and subarc mantle peridotites explained the similarity in δ^7Li between arcs and MORB as being due to chromatographic exchange between slab Li and mantle wedge peridotite (Tomascak et al., 2002; Halama et al., 2009). Recent experimental data on fluid partitioning suggests that Li carried in slab fluids would indeed not make it through the mantle wedge if the fluids move via porous flow (Caciagli et al., 2011). However, these scenarios fail to explain why arc lavas are generally enriched in Li (low Y/Li) relative to MORB (Plank, 2014). An alternative possibility is that Li from the slab is not isotopically distinct from MORB in most arcs (Halama et al., 2009).

Due to the large quantities of highly weathered terrigenous materials delivered to the sea floor by the Orinoco River, Site 543 and Site 144 sediments have the lightest Li isotopes (concentration weighted mean $\delta^7\text{Li} = -0.5 \pm 1.8$, 1σ) among global trench sediments (Figs. 6 and 7). Plank (2014) reports a new global subducting sediment estimate (GLOSS-II) with a δ^7Li of $+2.4 \pm 0.2$ (the uncertainty represents the maximum difference in the global weighted mean for 90 out of 100 trials using Monte Carlo simulation). To emphasize the variability of δ^7Li from trench to trench, we calculated the mean value and standard deviation for 28 sedimentary columns from 26 trenches reported by Plank (2014): 3.9 ± 2.3 (1σ). This average is indistinguishable from the average MORB with δ^7Li of $+3.7 \pm 1.0$ (Tomascak et al., 2008). Therefore, the Li isotopes in subducting sediments from other trenches that may be the source of the Li enrichment in arc lavas (Plank, 2014), may not generate measurable or systematic isotopic shifts in the δ^7Li of the lavas, thus explaining why arc lavas, in general, do not have δ^7Li that is distinct from MORB. As a counter example to the Martinique lavas, arc lavas from Nicaragua are isotopically heavier than MORB, possibly due to the incorporation of high δ^7Li sediments in the source region (Chan et al., 2002b; Plank, 2014). The slab Li signatures observed in Lesser Antilles and Nicaragua lavas support the view that the slab derived Li may survive mantle chromatographic processes and reappear in arc lavas.

6. CONCLUSIONS

1. Lithium isotopes in Martinique lavas are significantly lighter, on average, than those in MORB and other arc lavas. δ^7Li in the lavas is independent of SiO_2, $(La/Sm)_N$, Y/Li, and radiogenic isotopes, and thus does not appear to be influenced by crustal contamination or igneous differentiation.
2. Subducting sediments to the northeast (Site 543) and southeast (Site 144) of Martinique Island have the lightest Li isotopes (mean $\delta^7\text{Li} = -1.0$) observed for global subducting sediments. The Li isotopic variation is also decoupled from other geochemical indices in these sediments.
3. A δ^7Li–Y/Li two end-member mixing model indicates that the average Li isotopic composition in the Martinique lavas can be reproduced by ~2% sedimentary input to the mantle source.
4. Slab Li derived from subducted sediments may explain the Li enrichment seen in arc lavas, as suggested by Plank (2014); the MORB-like δ^7Li in many arcs may simply reflect the isotopic compositions of the sediments being subducted. Our work demonstrates that if isotopically distinct sediments are subducted, the signature reappears in the arc lavas.

ACKNOWLEDGEMENTS

This work was supported by NSF Grant EAR 0948549. We thank Richard Ash for help in the plasma lab, and Xiao-Ming Liu for help with lithium chemistry procedures. Thoughtful reviews by Terry Plank, Paul Tomascak and Tomas Magna, and the comments of Associate Editor Shichun Huang helped us to strengthen the manuscript. This work also benefited from discussions with William F. McDonough.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2014.09.003.

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Associate editor: Shichun Huang