

Lithium isotope evidence for light element decoupling in the Panama subarc mantle

Paul B. Tomascak* Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, D.C. 20015, USA
Jeffrey G. Ryan } Department of Geology, University of South Florida, Tampa, Florida 33620, USA
Marc J. Defant }

ABSTRACT

The systematics of fluid-mobile trace elements in arc lavas from Panama, relative to their Li isotopic compositions, provide unique evidence for the fertilization and subsequent differential extraction of mobile species from the subarc mantle. Calc-alkaline lavas that crystallized between 20 and 5 Ma (Old Group) that possess $\delta^7\text{Li}$ as high as +11.2 have low B/Be. Otherwise identical (and similarly old) calc-alkaline lavas with high B/Be (to 23), have mid-ocean ridge basalt (MORB) like $\delta^7\text{Li}$ (+4.7 to +5.6). Adakite lavas (<3 Ma; Young Group) possess $\delta^7\text{Li}$ from +1.4 to +4.2 and have consistently lower B/Be than Old Group lavas, consistent with derivation from melting of a devolatilized MORB slab. If Li and B had comparable fluid mobility in the subarc mantle, then slab fluids would carry both high B concentrations and elevated $\delta^7\text{Li}$ signatures into arc sources, and samples with the highest $\delta^7\text{Li}$ would also have the highest B/Be. Our data suggest that although both Li and B are initially derived from the slab, older $\delta^7\text{Li}$ signatures may be preserved in the mantle beneath arcs. As a result, regions of the lithospheric mantle will develop Li isotope signatures that are heavier than typical MORB mantle.

Keywords: lithium isotopes, boron, adakites, MORB, subduction.

INTRODUCTION

Boron and Li have been shown naturally (Ryan and Langmuir, 1987, 1993; You et al., 1994; Ryan et al., 1995) and experimentally (Seyfried et al., 1984; Brenan et al., 1998) to be soluble elements released from subducting slabs in aqueous fluids during the breakdown of hydrous minerals. Recent experiments demonstrate that the bulk fluid-clinopyroxene partition coefficients of B, Li, and Be are 50, 5, and 0.5, respectively (Brenan et al., 1998). Thus, whereas data from subduction-zone igneous and metamorphic rocks indicate efficient B removal from slabs at shallow depths (Moran et al., 1992; Bebout et al., 1993, 1999; Ryan et al., 1996), Li may be retained on slabs to greater depths. This further suggests that substantial Li may partition out of slab fluids during transit through the mantle without reaching the zone of melting beneath arcs. The extent to which Li, Be, and B are removed from the lithosphere during subduction-zone processes should have direct impact on their abundance, and perhaps on the isotopic constitution of Li and B, in the deep mantle sources of ocean island basalts (OIB).

Our understanding of Li isotope systematics is hampered by limited data on mantle and crustal reservoirs. Nevertheless, owing largely to the work of L.H. Chan and coworkers, several features of terrestrial Li isotope distributions are clear. The upper mantle, as characterized by mid-ocean ridge basalts (MORB), has $\delta^7\text{Li}$ between +1.5 and +4.7 (Chan et al., 1992; Moriguti and Nakamura, 1998; $\delta^7\text{Li} = 1000 \times [{}^7\text{Li}/{}^6\text{Li}_{\text{sample}}/{}^7\text{Li}/{}^6\text{Li}_{\text{standard}}] - 1$, using the National Institute of Standards and Technology standard L-SVEC [Flesch et al., 1973]). The oceans are the primary sink for ${}^7\text{Li}$, with $\delta^7\text{Li} \sim +32$ (Chan and Edmond, 1988). Sediments and basaltic ocean crust take up seawater Li during low-temperature alteration, elevating the $\delta^7\text{Li}$ of ocean crust (Seyfried et al., 1998; Chan et al., 1992, 1994). The vast majority of upper crustal materials analyzed to date have $\delta^7\text{Li}$ considerably higher than MORB but lower than seawater (Huh et al., 1998; Zhang et al., 1998;

*Current address: Lamont-Doherty Earth Observatory of Columbia University, Route 9W, Palisades, New York 10964, USA.

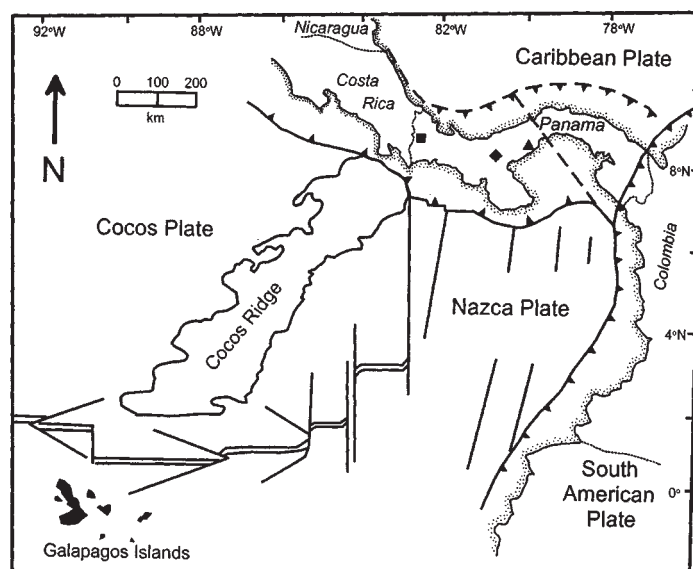


Figure 1. General tectonic features of southern Central America, adapted from Defant et al. (1992). Heavy lines are major faults (dashed are inferred), except for outline of Cocos Ridge, which is 2000 m bathymetric contour. Volcanic centers in Panama examined in this study include El Valle (triangle), El Barú (square), and La Yeguada (diamond). These symbols are used in geochemical plots.

Bottomley et al., 1999). Hence, the Li isotope budget of material being introduced to the mantle during subduction will be predominantly heavier than MORB, by 5% or more.

The purpose of this study is to characterize the light element and Li isotope systematics of a suite of subduction-related lavas from Panama. The samples show sharply contrasting petrogenetic histories: the older calc-alkaline lavas (ages 20–5 Ma; termed Old Group) show evidence for variable slab fluid inputs to a subarc mantle source, whereas the younger lavas (ages <3 Ma; termed Young Group or adakite lavas [Drummond and Defant, 1989]) suggest the direct melting of a basaltic or eclogitic source region (Fig. 1). This change in volcanic style, indicated in the lavas by dramatically different Sr/Y and La/Yb (Sr/Y <20 in Old Group lavas and >100 in Young Group lavas), is associated with a recent transition to high heat flow in the downgoing plate, and with a change to shallower subduction angles beneath Panama, both due to the subduction of a younger, hotter slab. We have looked at these geochemical differences over time at three Panamanian volcanic centers to examine how the transfer of elements from slab to mantle to arc lava changes. We also present the first Li isotope data from adakites, lavas interpreted as arising from the melting of metamorphosed slabs (Defant and Drummond, 1990). Our results demonstrate the applicability of Li isotope and light element systematics to the study of elemental transport processes in arcs.

RESULTS

The Old Group calc-alkaline lavas have $\delta^7\text{Li}$ that range from +3.9 to +11.2 (Table 1; Fig. 2). The Li isotopic composition does not correlate with B/Be in a simple way. The Young Group adakites have $\delta^7\text{Li}$ of +1.4 to +4.2, and low B/Be.

TABLE 1. ELEMENTAL AND ISOTOPIC DATA FROM PANAMA LAVAS

Sample number	Locality	Age* (Ma)	$\delta^7\text{Li}$	SiO_2 (wt%)	MgO (wt%)	Li (ppm)	Be (ppm)	B (ppm)	B/Be
Young Group, adakites									
23-3-88	La Yeguada	1.58	+3.4	66.5	1.18	19.0	1.29	9.9	7.7
27-2-86	El Valle	1.54	+4.2	68.7	0.97	11.9	0.37	2.7	7.3
	replicate analysis		+4.6						
27-1a-86	El Valle	---	+3.8	68.2	0.95	15.2	1.12	6.0	5.4
9-2b-86	El Baru	---	+1.4	57.0	6.36	16.6	0.40	2.7	6.8
Old Group, calc-alkaline									
15-1-88	La Yeguada	---	+11.2	63.3	1.73	9.29	0.69	4.4	6.4
13-13-88	La Yeguada	---	+4.7	52.3	4.23	20.9	0.59	6.7	11.4
23-2-88	La Yeguada	---	+8.2	54.8	3.38	9.00	0.71	6.3	8.9
11-10-88	La Yeguada	9.73	+4.7	74.6	0.45	27.5	1.12	26	23.0
27-6b-86	El Valle	10.19	+3.9	68.9	1.35	14.8	1.33	10	7.5
9-5b-86	El Baru	---	+5.6	61.8	1.86	4.45	1.33	14	10.5

Note: Ages (by conventional K-Ar) and SiO_2 , MgO , and Y concentrations are from Defant et al. (1991a, 1991b). Concentrations of Li, Be, and B were measured by direct current plasma emission spectroscopy at the University of South Florida (precision: Li $\pm 2\%$; Be $\pm 5\%$; B $\pm 5\%$ for >5 ppm, $\pm 10\%$ for <5 ppm). Lithium isotopes were measured by multicollector sector ICP-mass spectrometry, Carnegie Institution of Washington (see Tomascak et al., 1999a). Estimated precision is $\pm 1.1\%$ (2σ , population).

* --- = sample not analyzed.

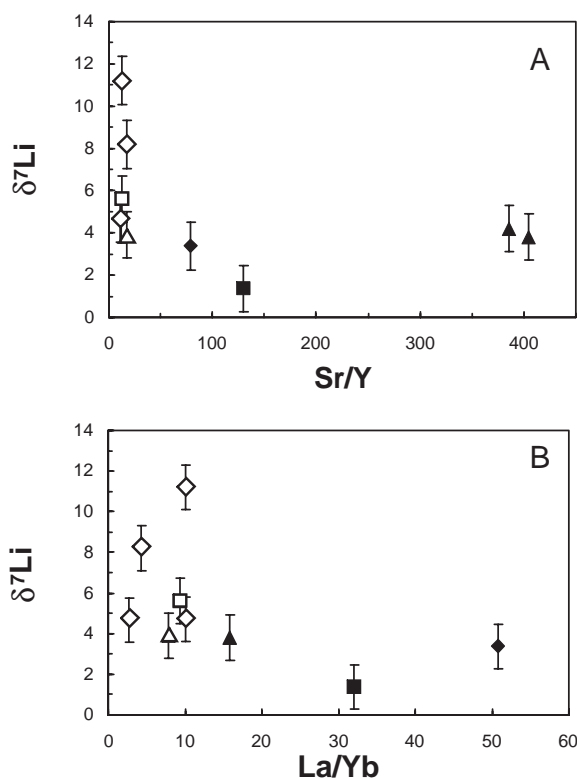


Figure 2. A: Sr/Y vs. $\delta^7\text{Li}$. B: La/Yb vs. $\delta^7\text{Li}$. Symbols as in Figure 1. Filled symbols are Young Group samples (adakitic), open symbols are Old Group (calc-alkaline) lavas. Adakite lavas have characteristic high Sr and La, and low Y, resulting in extremely high Sr/Y and La/Yb. Young Group adakites have Li isotopic compositions consistent with derivation from melting of devolatilized mid-ocean ridge basalt slab.

LITHIUM ISOTOPES IN ADAKITES

Melting of a devolatilized MORB slab should produce magmas with MORB-like $\delta^7\text{Li}$, especially because Li isotopes do not fractionate during melting or crystallization at high temperatures (Tomascak et al., 1999b). Thus, along with high Sr/Y and low $^{87}\text{Sr}/^{86}\text{Sr}$ (see Drummond et al., 1996),

MORB-like $\delta^7\text{Li}$ values may be characteristic of adakites. The absence of $\delta^7\text{Li} > \text{MORB}$ in the adakites (Fig. 2) indicates that these magmas did not react appreciably with the subarc mantle during their transit to the surface. It is also possible that by the time adakite genesis took place, the subarc mantle had to some degree been purged of its slab-derived, isotopically heavy Li by extensive Old Group volcanism. Vigorous subarc mantle convection could also help to obliterate a high $\delta^7\text{Li}$ signal in the mantle, given that subduction of the Cocos-Nazca ridge after ca. 7 Ma led to the development of a slab window (Johnston and Thorkelson, 1997).

The adakite data from Panama argue that the Li that is returned to the deeper mantle is unlikely to be isotopically lighter than MORB. It is also probable that less thoroughly devolatilized slabs (e.g., those in cold subduction zones) could transport isotopically heavy Li into the deep mantle. The interesting finding of $\delta^7\text{Li}$ as low as -3 in backarc lavas elsewhere (Chan et al., 1999) demonstrates that Li isotopic heterogeneity of an unknown nature exists in the upper mantle. Further studies are required to test if slab materials with $\delta^7\text{Li} < \text{MORB}$ can be produced by low-temperature reactions. Retention of such material could supply isotopically light Li to the deeper parts of arcs and to the deep mantle.

SOURCES OF ELEVATED $\delta^7\text{Li}$ AMONG OLD GROUP LAVAS

As noted here, the $\delta^7\text{Li}$ of the continental crust is predominantly higher than MORB, so crustal materials may be called upon to explain the high $\delta^7\text{Li}$ of some of the Old Group lavas. If the elevated $\delta^7\text{Li}$ signature is continental in origin, it is necessary to assess the extent of crustal assimilation required to produce these signatures. No specific data exist to define the $\delta^7\text{Li}$ of likely crustal assimilants in Panama. Assimilation has been used to explain some major element variations in some lavas from La Yeguada (Defant et al., 1991a), but in general crustal assimilation does not appear to control the trace element systematics of the Panama suites (Defant et al., 1992). Crustal thicknesses in Panama are the lowest along the Central American arc. Lack of correlations between Li/Yb, B/Be, $\delta^7\text{Li}$, and SiO_2 contents of samples within each volcanic complex is taken as further evidence that crustal assimilation does not exert a strong control on $\delta^7\text{Li}$ in the Panama lavas.

The presence of an enriched OIB mantle component (e.g., from the Galapagos hotspot; Johnston and Thorkelson, 1997) has been called upon to explain Nd and Sr isotopic compositions and major and trace element systematics among calc-alkaline lavas from Panama to Nicaragua (Leeman et al., 1994; Herrstrom et al., 1995). Would such an enriched component lead to elevated $\delta^7\text{Li}$ among the Old Group lavas? Lithium isotope data for OIB

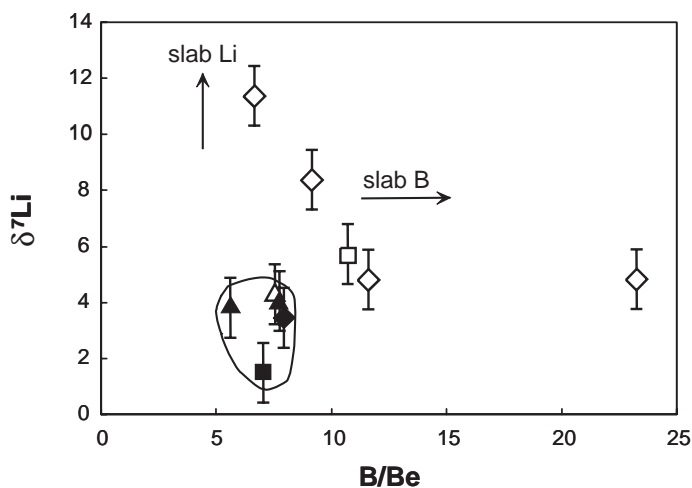


Figure 3. B/Be vs. $\delta^7\text{Li}$. Symbols as in Figures 1 and 2. Old Group samples do not show simple correlation between B enrichment and $\delta^7\text{Li}$, interpreted to result from elemental decoupling, from reaction of slab fluids with subarc mantle. Because of this, samples rich in slab-derived B show little evidence of slab-derived heavy Li. Samples with slab Li isotope signature derive from portions of mantle from which slab B has been extracted previously. Field highlights uniform basaltic crust character of adakite lavas.

lavas are limited to a handful of samples from Hawaii (Tomascak et al., 1999b, 1999c). The highest $\delta^7\text{Li}$ in Hawaiian lavas ($\sim +6.0$) is considerably lower than the extreme values of some of the Old Group lavas. In addition, Li isotope data from some primitive mantle rocks indicate the existence of regions that are isotopically lighter than MORB (Chan et al., 1999). Hence, the available data imply that the extreme enrichment in ^7Li in the Panama subarc mantle does not result from an enriched, OIB-like mantle component.

Although much of the Li in subducting slabs is sequestered in primary mafic silicate minerals, the upper ~ 1 km of the slab, including its sedimentary veneer, is rich in Li derived from weathering reactions in the presence of seawater. The Li-rich hydrous minerals of the uppermost slab decompose with progressive subduction metamorphism (Domanik et al., 1993; Bebout et al., 1999), which means that the recycling of subducted materials should provide slab-derived Li to the subarc mantle. Several lines of evidence are consistent with slab-derived Li possessing $\delta^7\text{Li} > \text{MORB}$. Fluids from the downgoing Pacific crust at Conical Seamount have an estimated minimum $\delta^7\text{Li} \sim +17$. Lavas from Nicaragua and Costa Rica with high B/La and Li/Y, indicators of significant slab-fluid input, also have elevated $\delta^7\text{Li}$, to $+7.8$ (Chan et al., 1999). The estimated slab fluid composition in the Izu arc has $\delta^7\text{Li} \sim +9$ (Moriguti and Nakamura, 1998).

SIGNIFICANCE OF LIGHT ELEMENT-Li ISOTOPE DECOUPLING

In arcs where their systematics have been examined, there is a prevalent coupling between the elemental systematics of B and Li, such that lava that shows B enrichment also shows Li enrichment (Ryan and Langmuir, 1987, 1993). If elevated $\delta^7\text{Li}$ characterizes slab fluids, as suggested here, it would be expected that samples with the highest B/Be would have the highest $\delta^7\text{Li}$. The lack of such a correlation in the Old Group lavas from Panama (Fig. 3) thus requires an alternate explanation.

Given the compatibility of Li in olivine and other Mg-silicates, equilibration of slab fluid with mantle peridotite should strongly increase the B/Li of the fluid. Much of the slab-derived, isotopically heavy Li should thus be preferentially retained in mantle rocks, with only a fraction of the initial fluid inventory reaching the zone of melting. Such chromatographic effects have been argued for other settings, and with other elements (e.g., Stolper and Newman, 1994; Tatsumi and Eggins, 1995; Hochstaedter et al.,

1996), but the impact on Li distributions in the mantle should be profound. Further episodes of fluid flux and melting should generate further Li isotopic heterogeneity in the mantle, as subsequent fluid inputs equilibrate with both modified and unmodified mantle domains. Data from forearc mantle rocks (e.g., Benton et al., 1999) demonstrate that slab Li releases can occur at very shallow depths, which means that the modification of the mantle may begin very early in subduction, and cannot be effectively washed away by wedge convection.

The correlation of B/Be with $\delta^7\text{Li}$ in Old Group lavas from Panama (Fig. 3) is similar to that observed between B/Be and radiogenic isotopes in Sunda arc lavas (Edwards et al., 1993). Isotopic variations in Sunda were attributed to mantle heterogeneity beneath Indonesia, whereas the signature of the slab was identified in lavas with the highest B/Be. In view of the likely sources of high $\delta^7\text{Li}$, we reach a different conclusion for Panama. The highest B/Be lavas we have examined are associated with a $\delta^7\text{Li}$ signature of $+5$ to $+6$, only slightly elevated relative to our adakite samples, or to MORB. This modestly elevated $\delta^7\text{Li}$ signature makes sense in light of the thermal characteristics of this arc segment over time (i.e., the downgoing plate is overall warmer and more devolatilized than in other segments of Central America), and is consistent with the lower overall B/Be signatures of the Old Group Panama lavas as compared to the rest of the arc. The variable and high $\delta^7\text{Li}$ values observed in Old Group lavas with lower B/Be reflect the time-integrated Li isotopic signature of each packet of melted mantle, signatures that developed as a function of variable histories of subduction-related fluid-mantle exchanges. We see these effects strongly in Panama because of the marked changes in thermal structure and magma source regions that have occurred here since the Miocene. In arcs where cool slabs can transport Li and B to great depths (i.e., Izu-Bonin: Moriguti and Nakamura, 1998), the signature of slab-fluid-derived Li may dominate in the lavas. Our data from Panama suggest that in the case of Li isotopes, enriched mantle reservoirs can be produced through the processes of slab-mantle chemical exchange. Thus, $\delta^7\text{Li}$ signatures may be a powerful tool for addressing the role of subduction processing in the genesis of intraplate magma sources.

SUMMARY

The Li isotope and B/Be elemental systematics of Old Group and Young Group Panama lavas are consistent with a process whereby magmas generated via fluid-fluxed melting of the mantle preserve Li isotopic differences that stem from elemental decoupling during fluid-mantle exchange. Subduction of the Nazca-Cocos ridge ca. 7 Ma changed the thermal state of the arc and eventually permitted partial melting of the devolatilized basaltic (eclogite) slab, yielding melts with adakite major and trace element characteristics and MORB-like $\delta^7\text{Li}$.

The results demonstrate that the combination of Li isotope and B and Be abundance systematics offers a means for more accurately describing slab fluid inputs in volcanic arcs. Interpretations of slab fluid flux based solely on B/Be or Li/Y are shown to be potentially faulty without Li isotope information from the same samples. In addition, our results offer insights into the important role that subduction may play in generating Li isotopic variability in the subcontinental lithosphere and deep mantle. Fluid-modified mantle convected to depth, as opposed to deeply subducted slabs, may play a significant role in creating Li isotopic heterogeneity. This work supports the contentions of geochemical studies based on a variety of tracers (Weaver, 1991; Hauri and Hart, 1993), that in many different ways subduction may act as a primary control on the geochemical evolution of Earth's mantle.

ACKNOWLEDGMENTS

Lithium isotopes were measured during the Carnegie Postdoctoral Fellowship of Tomascak at the Department of Terrestrial Magnetism, to whose staff we are indebted for their magnanimous support. The Carnegie Plasma 54-30 multicollector sector ICP-mass spectrometer was purchased with funds from the Carnegie Institution of Washington and the National Science

Foundation (NSF), Major Research Instrumentation Program (EAR-9724409). This work was partially supported by NSF grant EAR-9205804 to Ryan, Defant, and A.G. Hochstaedter. The Li, Be, and B concentration analyses were performed by Suzie Norrell. We thank Julie Morris, Alberto Saal, and Liz Widom for beneficial discussions, and Julie Morris and an anonymous reader for helpful reviews.

REFERENCES CITED

- Bebout, G.E., Ryan, J.G., and Leeman, W.P., 1993, B-Be systematics in subduction-related metamorphic rocks: Characterization of the subducted component: *Geochimica et Cosmochimica Acta*, v. 57, p. 2227–2237.
- Bebout, G.E., Ryan, J.G., Leeman, W.P., and Bebout, A.E., 1999, Fractionation of trace elements by subduction-zone metamorphism—Effect of convergent-margin thermal evolution: *Earth and Planetary Science Letters*, v. 171, p. 63–81.
- Benton, L.D., Savov, I., and Ryan, J.G., 1999, Recycling of subducted lithium in forearcs: Insights from a serpentine seamant [abs.]: *Eos (Transactions, American Geophysical Union)*, v. 80, p. S349.
- Bottomley, D.J., Katz, A., Chan, L.H., Starinsky, A., Douglas, M., Clark, I.D., and Raven, K.G., 1999, The origin and evolution of Canadian Shield brines: Evaporation or freezing of seawater? New lithium isotope and geochemical evidence from the Slave craton: *Chemical Geology*, v. 155, p. 295–320.
- Brenan, J.M., Ryerson, F.J., and Shaw, H.F., 1998, The role of aqueous fluids in the slab-to-mantle transfer of boron, beryllium, and lithium during subduction: Experiments and models: *Geochimica et Cosmochimica Acta*, v. 62, p. 3337–3347.
- Chan, L.H., and Edmond, J.M., 1988, Variation of lithium isotope composition in the marine environment: A preliminary report: *Geochimica et Cosmochimica Acta*, v. 52, p. 1711–1717.
- Chan, L.H., Edmond, J.M., Thompson, G., and Gillis, K., 1992, Lithium isotopic composition of submarine basalts: Implications for the lithium cycle in the oceans: *Earth and Planetary Science Letters*, v. 108, p. 151–160.
- Chan, L.H., Gieskes, J.M., You, C.F., and Edmond, J.M., 1994, Lithium isotope geochemistry of sediments and hydrothermal fluids of the Guaymas Basin, Gulf of California: *Geochimica et Cosmochimica Acta*, v. 58, p. 4443–4454.
- Chan, L.H., Leeman, W.P., and You, C.F., 1999, Lithium isotopic composition of Central American volcanic arc lavas: Implications for modification of the sub-arc mantle by slab-derived fluids: *Chemical Geology*, v. 160, p. 255–280.
- Defant, M.J., and Drummond, M.S., 1990, Derivation of some modern arc magmas by melting of young subducted lithosphere: *Nature*, v. 347, p. 662–665.
- Defant, M.J., Richerson, P.M., De Boer, J.Z., Stewart, R.H., Maury, R.C., Bellon, H., Drummond, M.S., Feigenson, M.D., and Jackson, T.E., 1991a, Dacite genesis via both slab melting and differentiation: Petrogenesis of La Yeguada volcanic complex, Panama: *Journal of Petrology*, v. 32, p. 1101–1142.
- Defant, M.J., Clark, L.F., Stewart, R.H., Drummond, M.S., De Boer, J.Z., Maury, R.C., Bellon, H., Jackson, T.E., and Restrepo, J.F., 1991b, Andesite and dacite genesis via contrasting processes: The geology and geochemistry of El Valle Volcano, Panama: Contributions to Mineralogy and Petrology, v. 106, p. 309–324.
- Defant, M.J., Jackson, T.E., Drummond, M.S., De Boer, J.Z., Bellon, H., Feigenson, M.D., Maury, R.C., and Stewart, R.H., 1992, The geochemistry of young volcanism throughout western Panama and southeastern Costa Rica: An overview: *Geological Society of London Journal*, v. 149, p. 569–579.
- Domanik, K.J., Hervig, R.L., and Peacock, S.M., 1993, Beryllium and boron in subduction zone minerals—An ion microprobe study: *Geochimica et Cosmochimica Acta*, v. 57, p. 4997–5010.
- Drummond, M.S., and Defant, M.J., 1989, A model for trondhjemite-tonalite-dacite genesis and crustal growth via slab melting: Archean to modern comparisons: *Journal of Geophysical Research*, v. 95, p. 21,503–21,521.
- Drummond, M.S., Defant, M.J., and Kepezhinskas, P.K., 1996, Petrogenesis of slab-derived trondhjemite-tonalite-dacite/adakite magmas: *Royal Society of Edinburgh Transactions, Earth Sciences*, v. 87, p. 205–215.
- Edwards, C.M.H., Morris, J.D., and Thirlwall, M.F., 1993, Separating mantle from slab signatures using B/Be and radiogenic isotope systematics: *Nature*, v. 362, p. 530–533.
- Flesch, G.D., Anderson, A.R., Jr., and Svec, H.J., 1973, A secondary isotopic standard for $^6\text{Li}/^7\text{Li}$ determinations: *International Journal of Mass Spectrometry and Ion Processes*, v. 12, p. 265–272.
- Hauri, E.H., and Hart, S.R., 1993, Re-Os isotope systematics of HIMU and EMII oceanic island basalts from the South Pacific Ocean: *Earth and Planetary Science Letters*, v. 114, p. 353–371.
- Herrstrom, E.A., Reagan, M.K., and Morris, J.D., 1995, Variations in lava composition associated with flow of asthenosphere beneath southern Central America: *Geology*, v. 23, p. 617–620.
- Hochstaedter, A.G., Ryan, J.G., Luhr, J.F., and Hasenaka, T., 1996, On B/Be in the Mexican Volcanic Belt: *Geochimica et Cosmochimica Acta*, v. 60, p. 613–628.
- Huh, Y., Chan, L.H., Zhang, L., and Edmond, J.M., 1998, Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget: *Geochimica et Cosmochimica Acta*, v. 62, p. 2039–2051.
- Johnston, S.T., and Thorkelson, D.J., 1997, Cocos-Nazca slab window beneath Central America: *Earth and Planetary Science Letters*, v. 146, p. 465–477.
- Leeman, W.P., Carr, M.J., and Morris, J.D., 1994, Boron geochemistry of the Central American volcanic arc: Constraints on the genesis of subduction-related magmas: *Geochimica et Cosmochimica Acta*, v. 58, p. 149–168.
- Moran, A.E., Sisson, V.B., and Leeman, W.P., 1992, Boron depletion during progressive metamorphism: Implications for subduction processes: *Earth and Planetary Science Letters*, v. 111, p. 331–349.
- Moriguti, T., and Nakamura, E., 1998, Across-arc variation of Li isotopes in lavas and implications for crust/mantle recycling at subduction zones: *Earth and Planetary Science Letters*, v. 163, p. 167–174.
- Ryan, J.G., and Langmuir, C.H., 1987, The systematics of lithium abundances in young volcanic rocks: *Geochimica et Cosmochimica Acta*, v. 51, p. 1727–1741.
- Ryan, J.G., and Langmuir, C.H., 1993, The systematics of boron abundances in young volcanic rocks: *Geochimica et Cosmochimica Acta*, v. 57, p. 1489–1498.
- Ryan, J.G., Morris, J.D., Tera, F., Leeman, W.P., and Tsvetkov, A., 1995, Cross-arc geochemical variations in the Kurile arc as a function of slab depth: *Science*, v. 270, p. 625–627.
- Ryan, J.G., Morris, J.D., Bebout, G.E., and Leeman, W.P., 1996, Describing chemical fluxes in subduction zones: Insights from “depth-profiling” studies of arc and forearc rocks, in Bebout, G.E., et al., eds., *Subduction: Top to bottom: American Geophysical Union Geophysical Monograph 96*, p. 263–268.
- Seyfried, W.E., Jr., Janecky, D.R., and Mottl, M.J., 1984, Alteration of the oceanic crust: Implications for the geochemical cycles of lithium and boron: *Geochimica et Cosmochimica Acta*, v. 48, p. 557–569.
- Seyfried, W.E., Jr., Chen, X., and Chan, L.H., 1998, Trace element mobility and lithium isotope exchange during hydrothermal alteration of seafloor weathered basalt: An experimental study at 350 °C, 500 bars: *Geochimica et Cosmochimica Acta*, v. 62, p. 949–960.
- Stolper, E., and Newman, S., 1994, The role of water in the petrogenesis of Mariana Trough magmas: *Earth and Planetary Science Letters*, v. 121, p. 293–325.
- Tatsumi, Y., and Eggins, S., 1995, *Subduction zone magmatism: Cambridge, Massachusetts, Blackwell Science*, 211 p.
- Tomascak, P.B., Carlson, R.W., and Shirey, S.B., 1999a, Accurate and precise determination of Li isotopic compositions by multi-collector sector ICP-MS: *Chemical Geology*, v. 158, p. 145–154.
- Tomascak, P.B., Tera, F., Helz, R.T., and Walker, R.J., 1999b, The absence of lithium isotope fractionation during basalt differentiation: New measurements by multi-collector sector ICP-MS: *Geochimica et Cosmochimica Acta*, v. 63, p. 907–910.
- Tomascak, P.B., Hauri, E.H., and Lassiter, J.C., 1999c, Lithium isotope constraints on Hawaiian plume components [abs.]: *Eos (Transactions, American Geophysical Union)*, v. 80, p. S354.
- Weaver, B.L., 1991, The origin of ocean island basalt end-member compositions—Trace element and isotopic constraints: *Earth and Planetary Science Letters*, v. 104, p. 381–397.
- You, C.F., Butterfield, D.A., Spivack, A.J., Gieskes, J.M., Gamo, T., and Campbell, A.J., 1994, Boron and halide systematics in submarine hydrothermal systems: Effects of phase separation and sedimentary contributions: *Earth and Planetary Science Letters*, v. 123, p. 227–238.
- Zhang, L., Chan, L.H., and Gieskes, J.M., 1998, Lithium isotope geochemistry of pore waters from Ocean Drilling Program Sites 918 and 919, Irminger Basin: *Geochimica et Cosmochimica Acta*, v. 62, p. 2437–2450.

Manuscript received October 18, 1999

Revised manuscript received March 3, 2000

Manuscript accepted March 14, 2000