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TITLE OF PROPOSED PROJECT **Collaborative Research: The role of the Slab and the Mantle in Volcanic Arc Petrogenesis: A B-Be-Li and Li Isotope Study of Off-Axis Arc Centers in Mexico and Central America**

REQUESTED AMOUNT	PROPOSED DURATION (1-60 MONTHS)	REQUESTED STARTING DATE	SHOW RELATED PREPROPOSAL NO., IF APPLICABLE
$ 147,567	36 months	03/01/03	

CHECK APPROPRIATE BOX(ES) IF THIS PROPOSAL INCLUDES ANY OF THE ITEMS LISTED BELOW

- ☐ BEGINNING INVESTIGATOR (GPG I.A)
- ☐ DISCLOSURE OF LOBBYING ACTIVITIES (GPG II.C)
- ☐ PROPRIETARY & PRIVILEGED INFORMATION (GPG I.B, II.C.6)
- ☐ HISTORIC PLACES (GPG II.C.9)
- ☐ SMALL GRANT FOR EXPLOR. RESEARCH (SGER) (GPG II.C.11)
- ☐ VERTEBRATE ANIMALS (GPG II.C.11) IACUC App. Date ________
- ☐ HUMAN SUBJECTS (GPG II.C.11) Exemption Subsection ________ or IRB App. Date ________
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PI/PD DEPARTMENT	PI/PD POSTAL ADDRESS
Department of Geology	4202 East Fowler Avenue Tampa, FL 33620 United States
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CERTIFICATION PAGE

Certification for Authorized Organizational Representative or Individual Applicant:

By signing and submitting this proposal, the individual applicant or the authorized official of the applicant institution is: (1) certifying that statements made herein are true and complete to the best of his/her knowledge; and (2) agreeing to accept the obligation to comply with NSF award terms and conditions if an award is made as a result of this application. Further, the applicant is hereby providing certifications regarding debarment and suspension, drug-free workplace, and lobbying activities (see below), as set forth in Grant Proposal Guide (GPG), NSF 02-2. Willful provision of false information in this application and its supporting documents or in reports required under an ensuing award is a criminal offense (U. S. Code, Title 18, Section 1001).

In addition, if the applicant institution employs more than fifty persons, the authorized official of the applicant institution is certifying that the institution has implemented a written and enforced conflict of interest policy that is consistent with the provisions of Grant Policy Manual Section 510; that to the best of his/her knowledge, all financial disclosures required by that conflict of interest policy have been made; and that all identified conflicts of interest will have been satisfactorily managed, reduced or eliminated prior to the institution's expenditure of any funds under the award, in accordance with the institution's conflict of interest policy. Conflicts which cannot be satisfactorily managed, reduced or eliminated must be disclosed to NSF.

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By electronically signing the NSF Proposal Cover Sheet, the Authorized Organizational Representative or Individual Applicant is providing the Drug Free Work Place Certification contained in Appendix A of the Grant Proposal Guide.

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Is the organization or its principals presently debarred, suspended, proposed for debarment, declared ineligible, or voluntarily excluded from covered transactions by any Federal department or agency? Yes ☐ No ☒

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Certification Regarding Lobbying

This certification is required for an award of a Federal contract, grant, or cooperative agreement exceeding $100,000 and for an award of a Federal loan or a commitment providing for the United States to insure or guarantee a loan exceeding $150,000.

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The undersigned certifies, to the best of his or her knowledge and belief, that:

(1) No federal appropriated funds have been paid or will be paid, by or on behalf of the undersigned, to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with the awarding of any federal contract, the making of any Federal grant, the making of any Federal loan, the entering into of any cooperative agreement, and the extension, continuation, renewal, amendment, or modification of any Federal contract, grant, loan, or cooperative agreement.

(2) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with this Federal contract, grant, loan, or cooperative agreement, the undersigned shall complete and submit Standard Form-LLL, ''Disclosure of Lobbying Activities,'' in accordance with its instructions.

(3) The undersigned shall require that the language of this certification be included in the award documents for all subawards at all tiers including subcontracts, subgrants, and contracts under grants, loans, and cooperative agreements and that all subrecipients shall certify and disclose accordingly.

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AUTHORIZED ORGANIZATIONAL REPRESENTATIVE	SIGNATURE	DATE
NAME **Judy Erickson**	**Electronic Signature**	**May 31 2002 2:09PM**

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Project Summary

We are proposing to assess the geochemical role of the mantle wedge vs. that of the slab in the petrogenesis of volcanic arc lavas using a combination of B-Be-Li abundance and Li isotope ratio systematics. The combination of light element systematics with isotopic signature has been an effective tool for resolving mantle inputs from those of the slab in other arcs, and Li isotopes additionally afford an opportunity to constrain the origins of sub-arc mantle chemical signatures. We will target two different but comparable subduction systems for study: the Trans-Mexican Volcanic belt (TMVB), where documented overall low B/Be ratios and abundant off axis volcanism related to crustal extension offers a great opportunity to assess the role of the mantle, and careful petrologic studies of several arc centers allow for the assessment and resolution of crustal assimilation effects; and the Guatemala segment of the Central American arc, which like the TMVB has abundant off-axis volcanism associated with extension, but is associated with more vigorous subduction and significant B enrichment at the volcanic front.

The project is collaborative between the University of South Florida and Appalachian State University, and will be conducted in two parts: 1) an undergraduate summer research experience, where students from the PI school + other participating institutions take part in the collection, characterization and B-Be-Li abundance studies of TMVB suites, and 2) MS/PhD. student research on the Li isotope systematics of lavas from the TMVB, Guatemala, and key intraplate volcanic sites. Our ultimate goal is to use light element abundance and isotopic systematics to define the chemical variability of the sub-arc mantle, and to constrain how this variability may have developed.

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For font size and page formatting specifications, see GPG section II.C.

Appendix Items:

*Proposers may select any numbering mechanism for the proposal. The entire proposal however, must be paginated. Complete both columns only if the proposal is numbered consecutively.

Results from Previous NSF Support - Ryan

Grant OCE9977306: The Role of the Forearc in Subduction Zone Geochemical Cycles: Insights from Forearc Serpentinite Seamounts, ODP Leg 125: Conical Seamount samples have now been characterized for alkaline elements, rare-earth elements, As, Pb, Th, and U and Sr and Li isotopes. O isotopes will be measured at Lehigh University this calendar year, and Pb isotopes will be measured at Florida State University. The overall story is one of an H2O-dominated fluid outflux in forearcs that mobilizes only a limited menu of elements. B isotopes document this unique fluid signature. Li isotopes provide insights both into the fluid outfluxes, and into the chemical heterogeneity of sub-arc mantle source regions.

Presentations and Publications

Benton, L.D., J.G. Ryan, and F. Tera (2001) The boron isotopic ratio of slab fluids inferred from Mariana Forearc serpentinites. *Earth and Planetary Science Letters*, v.187, p. 273-282.

Tomascak, P.B., E. Widom, L. D. Benton, S.J. Goldstein, and J. G. Ryan (2002) The Control of Lithium Budgets in Island Arcs. *Earth and Planetary Science Letters*, v. 196, p. 227-238.

Savov, I.P., J.G. Ryan, P. Mattie, and J. Schijf (2000) Fluid-mobile element systematics of ultramafic xenoliths from the Izu-Bonin-Mariana forearc: implications for the chemical cycling in subduction zones. Presented at the 2000 AGU Fall Meeting.

Ryan, J.G., Benton, L. and Savov, I. (2001) Isotopic and elemental signatures of the forearc, and its impacts on subduction recycling: evidence from the Marianas. Presented at the 2001 AGU Fall Meeting, San Fransisco, CA.

Ryan, J.G., Savov, IP, and Benton, LD (2002) B, Li and Be Insights into forearcs, arcs and beyond. Submitted for the 2002 AGU Spring Meeting, Washington, DC

Guggino, S., Savov IP, and Ryan, JG (2002) Light element systematics of metamorphic clasts from ODP Legs 125 and 195, South Chamorro and Conical Seamounts, Mariana forearc. Submitted to the 2002 AGU Spring Meeting, Washington, DC

Papers in Preparation:

Savov, I.P., J.G. Ryan, P. Mattie, P. et al. Forearc chemical fluxes inferred from the geochemistry of erupted serpentinites, Conical Seamount, ODP Leg 125. In preparation for *G3*.

Benton, L.D., Ryan, J.G. and Savov, I.P. The lithium isotope systematics of slab fluids and the mantle wedge as inferred from Mariana forearc serpentinites. In preparation for *G3*.

Educational Outcomes: This grant supports the Ph.D. dissertation research of Ivan Savov at USF. As a result of his work on this project, Ivan participated as a Shipboard Scientist on ODP Leg 195 to the South Chamorro Seamount, and JOIDES support has been obtained to contrast the Leg 195 suite with that of Leg 125. Mr. Steve Guggino has completed an REU Supplement project on the geochemistry of entrained mafic clasts from Legs 125 and 195, which he will be presenting at the 2002 AGU Spring Meeting.,

Grant OPP9980421: The Search for Subducted Components in the Mantle: B and Li Isotope, and Fluid-Mobile Element Systematics in Lavas from Mt. Erebus: Samples were characterized for Li isotopes during Ryan's sabbatical term at DTM, and for light element abundances during the following calendar year by REU Participant Gene Foster. Li isotopes are very consistent in less-evolved Erebus lavas at ∂^7 Li = +4‰, but range from +1‰ to +7‰ in Erebus phonolites, pointing to crustal contributions. Li isotopes in Erebus are distinct from those in HIMU center St. Helena, but lie within the range of samples from Hawaii. The total range of OIBs thus far examined, at +2‰ to +7‰, is significantly more variable than that of MORBs, or "normal" arcs, but less variable than are observed in "hot" subduction settings, such as Panama. B/K ratios show a subtle variation from island to island: EMII ocean island sites appear to have the lowest B/K ratios. An out growth of this project has been undergraduate research into the light element geochemistry of intraplate volcanic centers. The first completed project, on the Society Islands, will be presented at the 2002 AGU Fall Meeting.

Presentations/Educational Outcomes

Ryan, J.G. and P.R. Kyle (2000) Lithium isotope systematics of McMurdo Volcanic Group lavas, and other intraplate sites. Presented at the 2000 AGU Fall Meeting.

Foster, G., J.G. Ryan, and P.R. Kyle (2001) Fluid-mobile elements as tracers in intraplate volcanic Environments: Mt. Erebus, Ross Island, Antarctica. Presented at the 2001 AGU Spring Meeting, Boston, MA [An undergraduate presentation by an REU participant.]

Harden, J.A., Ryan, J.G. and Savov, IP (2002) Goechemistry and light element systematics of Moorea, Society Islands. Submitted to the 2002 AGU Spring Meeting, Washington, DC [Senior Honors Thesis project which grew out of the REU work]

Grants EAR9619932 and EAR9988077 (REU Summer Program on the Origins and Tectonic significance of Appalachian ultramafic rocks: collaborative with Dr. Virginia Peterson and colleagues, Western Carolina University: In four years we have taken 48 student participants to field sites in western North Carolina to map and sample exposed mafic-ultramafic rock complexes, and then to USF-Tampa to chemically characterize these samples, and attempt to answer questions about the petrogenesis and tectonic significance of the units. The first two years of the program focused on the Buck Creek mafic-ultramafic complex, the largest such unit in the Blue Ridge; the current incarnation of the program examined the Carroll Knob mafic complex, located ESE of Buck Creek, and last year we examined the Webster-Addie and Balsam Gap ultramafic bodies further east. The Summer projects have spawned post-summer research projects by eleven students so far, three of which have been presented at regional GSA meetings. This past year, along with use of geophysical equipment and plasma emission spectrometry, students were able to make use of the electron microprobe facility at the Florida Center for Analytical Electron Microscopy (FCAEM) in Miami, FL, to which USF has an Internet 2-based remote operation link. Two ongoing post-summer projects from the 2002 Summer program are microprobe based.

Publications:

Berger, S, Cochrane, D., Simons, K. Savov I., J.G. Ryan, and V.L Peterson (2001) Insights from rare earth elements into the genesis of the Buck Creek Complex and other Blue Ridge ultramafic bodies. *Southeastern Geology*, 40, p. 201-212.

Papers in Preparation:

Peterson, V., J.G. Ryan, S.P. Yurkovich, S. Kruse, and J. Burr, A successful collaborative NSF-REU Site Research program on the Geology of the Blue Ridge Mountains. For the *CUR Quarterly*.

Peterson, V., and J.G. Ryan, Petrology, geochemistry and Emplacement of the Buck Creek mafic-ultramafic complex, Blue Ridge Mountains, NC. For the *Geological Society of America Bulletin*.

Lang, H., Lee, A., Peterson, V. and J.G. Ryan (2002) Coexisting clinpyroxene/spinel and amphibole/spinel symplectites in metatroctolites from the Buck Creek ultramafic body, North Carolina Blue Ridge, USA. For *American Mineralogist.*

Primm, S., J.A. Schneider, S.C. Akers, C.M. Bruinsma, B. DeArmond, R.L. Shannon, S.E. Kruse, S.P. Yurkovich J.G. Ryan, V.L. Peterson, and J.Burr (2002) Geophysical imaging of mafic/ultramafic bodies within gneiss country rock, western North Carolina, USA. Submitted to *Journal of Applied Geophysics*.

Presentations

EAR9619932 - 11, 8 by undergraduate participants, two by graduate student M. Emilio.
EAR9988077 - 11 thus far, 7 by undergraduate particpants.

Educational Outcomes: Of 24 participants in the first two years of the program, 17 pursued graduate studies in Geology, three as Ph.D. candidates (at Caltech, Yale and Columbia). Three others chose to seek geoscience employment upon graduation, and are now seeking to enter geology graduate programs. Of the 12 participants in the first year of current program, four were in graduate schools the following Fall, and several more are following. Two of our participants thus far have received NSF Graduate Fellowships to support their efforts in graduate schools. This program also helped to mentor several graduate students at USF. Mr. Michael Emilio, the graduate field assistant for 97-98, completed his MS thesis on the metamorphic history of the Buck Creek complex and entered the Ph.D. program at Lehigh University. Mr. Ivan Savov, a graduate laboratory assistant in 1998, completed his MS thesis on the petrogenesis of the Balkan-Carpathian ophiolite in 1999, and stayed on for a Ph.D. degree, focusing on the geochemistry of serpentinized ultramafic rocks from the Mariana forearc (see Grant 9977306 above). Ms. Suzanne Norrell (MS 1999), Ms. Monica Palanseau (MS 2001), Mr. Livio Tornabene (MS 2001) and Ms. Megan Hendren (MS candidate, USF) have all participated as support personnel for this program.

Project Description

We are requesting funds to conduct a study focusing on the B, Be, and Li abundances and Li isotope compositions of lavas erupted off of the arc volcanic fronts in key segments of the Trans Mexican Volcanic Belt, and the Central American Arc in Guatemala. Specific goals in this work are to

- Resolve in these lavas the geochemical roles of the overriding crust, the subducting slab and mantle wedge, and
- To try and identify the geochemical "fingerprint" of the mantle wedge in these arcs.

A second key goal of this work is to further characterize the natural variation of Li isotope ratios and B-Be-Li abundance systematics, identified as "key tracers" in the Subduction Factory theme of the MARGINS Initiative. Specifically, we shall assess the value of these tracers (in particular Li abundance and Li isotope systematics) as tools for identifying and characterizing the development of mantle heterogeneity in subduction settings.

Background

Advances in our understanding of the subduction process since 1980 have led to the recognition of "subducted components", chemical inputs from downgoing slabs, in the makeup of volcanic arc and back arc lavas (Tera et al. 1986; Ryan and Langmuir 1987; 1988; Morris and Tera 1989; Morris et al. 1990; Hochstaedter et al. 1990; Fryer et al. 1990; Ryan and Langmuir 1993; Stolper and Newman 1994). The subducted component is now viewed as including several different constituents, the proportions and characteristics of which change as subduction proceeds (Plank and Langmuir 1993; Ryan et al. 1995; 1996; Elliott et al. 1997; Miller et al. 1994; Ishikawa and Nakamura 1994; Ishikawa and Tera 1996). Attempts have also been made to define both the sources and physical characteristics of the slab flux (Kepezhinskas et al (pick it!), Class, et al (2000), though such efforts are necessarily founded on assumptions as to the composition of the mantle from which arc magmas originate, and the lithospheric/crustal column through which they rise and erupt.

The abundance and isotopic systematics of B, Be, and Li have been important tools in making these discoveries . ^{10}Be isotopic variations provided the first unequivocal evidence for the involvement of subducted sediments in making arc lavas (Brown et al. 1982; Tera et al. 1986; Morris and Tera 1989). B abundance and later B isotopic systematics provided valuable insights into the role of H_2O-rich fluids in generating arc melts (Leeman 1987; Ryan and Langmuir

1993; Leeman et al. 1994), into the processes of slab devolatilization (Bebout et al. 1993; 1999; Leeman et al. 1992; Moran et al 1994, Benton et al. 2001), and were key data in developing hypotheses as to how the slab-mantle exchange process changes with progressive subduction (Ishikawa and Nakamura 1994; Ryan et al. 1995; 1996; Ishikawa and Tera 1996; 1999; Straub and Layne 2002).

The role of the mantle wedge: While the role of the slab has been aggressively investigated of late, less attention has recently been paid to the geochemical role of the mantle in subduction-related volcanism, although that role can often be significant. Feigenson, Carr and coworkers (Feigenson and Carr 1993; Carr et al. 1990) have proposed isotopically distinctive reservoirs in the mantle wedge beneath the Central American arc. Stern and others (1988; 1990; Lin et al.1989, 1990) note significant mantle-derived geochemical variation in lavas from the northern Mariana arc, and Hickey-Vargas et al (2002) using B systematics, among other tracers, documented relatively long-lived chemical heterogeneities in mantle wedge sources beneath Chile. Edwards et al (1993) used the combination of B/Be ratios and radiogenic isotopic systematics to identify the geochemical signature of the slab flux and several mantle wedge components in lavas erupted along the Sunda Arc. Two key observations from their work are a) that over large stretches of arc length (~1000+ km) the overall slab-derived flux is very homogeneous isotopically, and b) that the slab flux overwhelms other signatures in the lavas, so that only in arc volcanic centers where the magnitude of slab input is very low (i.e. in behind-the-front centers ± a few volcanic front centers) can distinct mantle contributions be recognized.

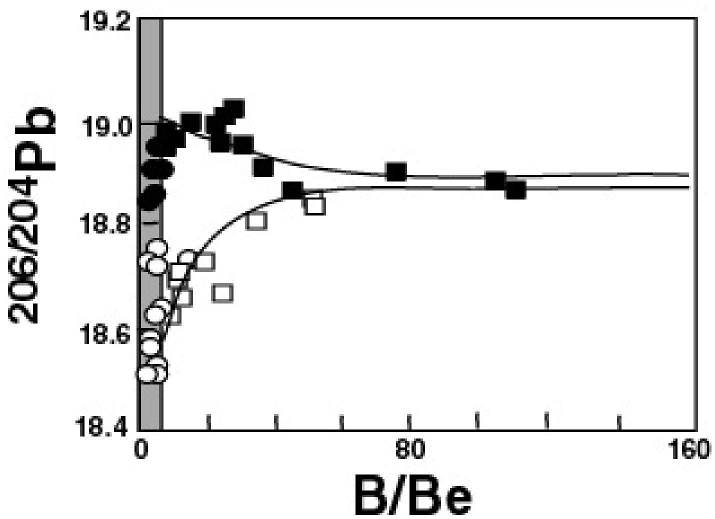

Figure 1: Plot of $^{206/204}$Pb vs. B/Be from Edwards et al. (1993). Curves are hypothetical mixing trajectories between a high B slab fluid and a mantle component. Comparing Pb and B/Be systematics allow for the identification of the slab flux, and isotopic characterization of the mantle wedge.

Li isotopes as a tracer of the slab and Mantle: Tomascak et al (2000; 2002) used an approach similar to that of Edwards et al (1993) in the study of lavas from Central America, and other arcs, though in this case their goal was to assess the variations of Li isotopes in these settings.

The stable isotope systematics of Li are a relatively new tool for the study of subduction zone processes. Due to the very large relative mass difference,natural variations in the $^{7/6}$Li ratio can be induced by geochemical exchanges. Data are reported as ∂^7Li values, based on permil variations from the $^{7/6}$Li of the NIST standard Li_2CO_3 L-SVEC:

$\partial^7 Li = (^{7/6}Li_{sample} - ^{7/6}Li_{L\text{-}SVEC})/^{7/6}Li_{L\text{-}SVEC} \times 1000‰$

The current precision reported on ∂^7Li values is ±1‰, though with the advent of multicollector ICP-MS systems, better precision appears achievable.

Seawater and other fluid phases have high ∂^7Li (+32.3‰ for oceans and lakes) while most igneous rocks tend to be lower (Chan and Edmond. 1988; Chan et al. 1992, 1993, 1999, 2001). Marine sediments and altered ocean crust, such as are carried down subduction zones globally, have elevated ∂^7Li - +10 to +15‰. (Chan et al. 1994). Thus, it seems likely that a "slab signature" in arc lavas should also show an elevated ∂^7Li signature

Interestingly, what has shown up in studies of Li isotopes in young volcanic rocks thus far is considerable uniformity. Preliminary data for the Li isotopic ratios of MORBs lie between +2 and +5‰.(Tomascak and Langmuir 2000) "Normal" island arcs (i.e., those with high B/Be ratios) overlap the MORB range almost entirely - lavas from the Kuriles, Sunda, and Aleutian arcs) completely overlap the MORB range, while in the Marianas and the Izu-Bonin arcs a few samples extend to slightly higher values (up to +7‰). Of all of these arcs, only Izu appears to show changes in lithium isotopic ratios as one moves from the volcanic front into behind-the-front arc centers, as are observed in recognized tracers of slab fluid inputs such as B isotopes, and the "fluid mobile" elements (Moriguti and Nakamura 1996; Leeman 1996; Ishikawa and Nakamura 1994; Ryan et al. 1995; 1996)

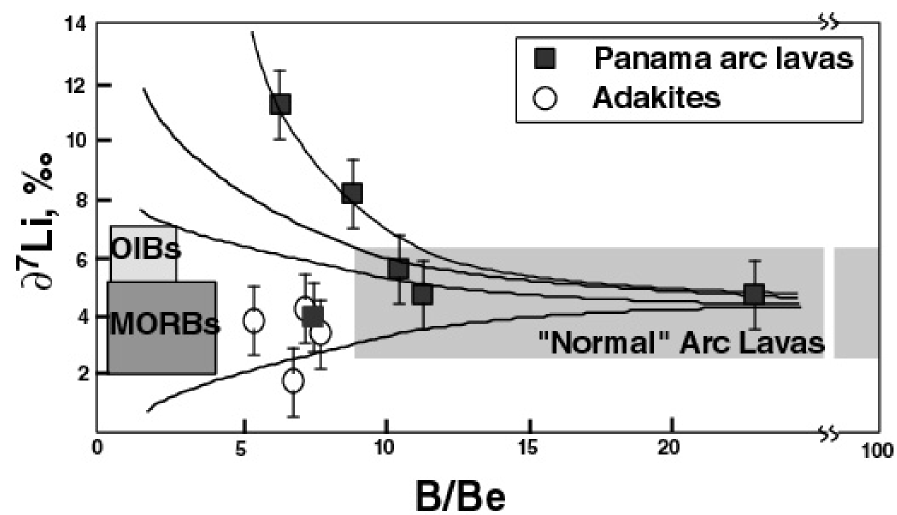

Figure 2: Plot of ∂7Li vs. B/Be for lavas of Panama. Fields for "normal" arc lavas (Central America, Kuriles, Aleutians, Sunda) and for MORBs and OIBs are shown. Curves are hypothetical mixing trajectories between slab fluids (∂7Li = +5=+6‰) and the mantle, though MORB and OIB sources do not indicate sufficient spread. Data from Tomascak et al. 2000; 2002; Chan et al. 1999; Leeman, 1994.

Why might Li isotope signatures be relatively uniform in these arcs? Because Li, unlike most of the elements of isotopic interest, is somewhat compatible in olivine and other magnesian mantle minerals (Ryan and Langmuir 1987; Brenan et al 1998). The abundance of lithium in mantle rocks is relatively high (~2 ppm) so only very large Li inputs from the slab can cause measurable changes in the mantle signature. Large degree melts of the mantle wedge, as are triggered by slab inputs at the volcanic fronts of arcs, should show Li concentrations only modestly elevated relative to MORBs (as is observed) and only modestly (possibly non-detectably) elevated ∂^7Li. (Tomascak et al. 2002)

The Mantle Signature for Li isotopes: However, not all arcs show this pattern. Tomascak et al. (2000) studied the Panama segment of the Central American arc, a setting where the subduction of the Cocos Ridge to the west has slowed subduction rates, yielding a "hot" slab, and ultimately the eruption of adakites (i.e., Defant and Drummond 1990; Defant et al. 1991)(Figure 2). Arc lavas from the Panama segment show significant Li isotopic variation - ∂^7Li ranging from +1‰ to +11‰. This variation did not correlate regularly with B/Be ratios for these lavas - in fact, the lavas with the highest B/Be ratios converge on a ∂^7Li value of +5.5‰, comparable to lavas in the rest of the Central American arc, and all other arcs. The lavas with the lowest B/Be (that is, the lowest levels of slab input) showed the greatest diversity in ∂^7Li, suggesting that this Li isotopic heterogeneity was not derived from the slab, but instead from the mantle wedge.

Possible sources of Li isotope heterogeneity in the mantle include

a) inherent long-lived mantle heterogeneities with several possible origins, as with radiogenic isotope systems
b) heterogeneous inputs of Li from the slab to the mantle wedge over time.

The database for Li isotopes in mantle-derived basaltic rocks is very limited at present, but that which has been reported suggests modest variability (Figure 3). Ryan and Kyle (2000) reported on ∂^7Li systematics of Antarctic intraplate lavas from Erebus and the Crary Mtns, along with selected samples from other OIB sites. As shown in Figure 3, basalts from St. Helena and the Antarctic (which both show HIMU isotopic affinities) may fall on a mixing array with MORB-source mantle. The HIMU reservoir appears to have elevated ∂^7Li, reaching +7‰ in St. Helena AOB's. The other OIB lavas span a limited range in ∂^7Li (+2‰ - +6‰). At this point nothing is known about EM I or EM II OIB lavas, so one cannot draw final conclusions. While one cannot currently explain the heterogeneity observed in the Panama arc lavas based on pre-existing mantle heterogeneities, the sources of intraplate lavas do appear to have greater Li isotopic variability than MORBs.

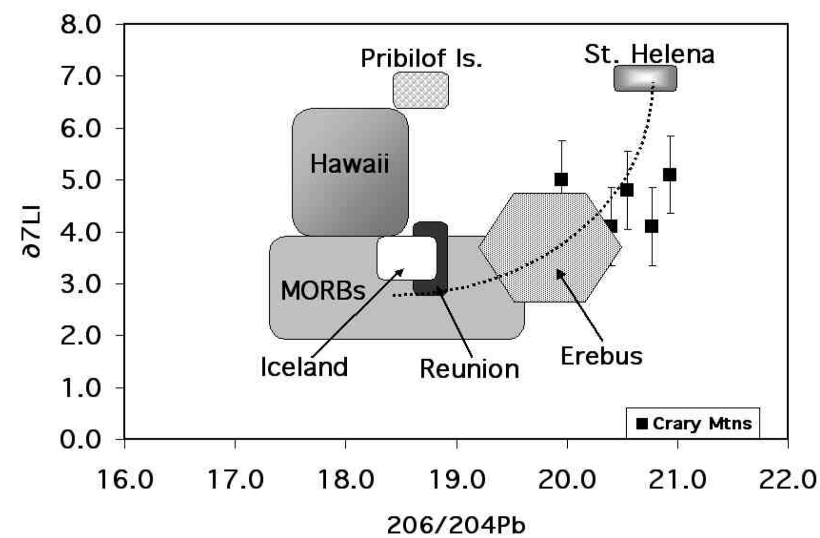

Figure 3: Li isotopes vs. $^{206/204}$Pb for OIBs. Pb Data from Zindler and Hart (1987), Sun and Hanson (1975). Li isotope data for Hawaii from Tomascak (1999)

New Li isotope data we have collected from forearc ultramafic rocks from the Mariana subduction system may provide support for option b) above (Figure 4). In these samples, erupted as muds and entrained ultramafic clasts from the active Conical serpentinite mud volcano, we see two distinct isotopic patterns:

i. the unconsolidated serpentinites all converge on a ∂^7Li of +6‰, similar to the mean Li isotope signature of the Mariana arc (Benton et al. 2000; Elliott et al 1999) and most other arcs (Tomascak et al. 2002)
ii. the serpentinized ultramafic clasts show extreme Li isotopic diversity - ∂^7Li ranges from -6‰ to +10‰, a wider range than is observed in any other known rock suite (Benton et al. 1999; Benton, Ryan and Savov, in prep).

This great range in Li isotope ratios correlates broadly with a wide range in Li abundances in these rocks (<1 to 12 ppm Li; Benton et al in prep) that itself may be related to the multistage hydrothermal veining evident in the serpentinite clasts. The variability in Li and Li isotopes suggests that in the shallow mantle wedge of forearcs, considerable low-T° hydrothermal redistribution of Li occurs. If this heterogeneous mantle is transported to arc depths and becomes part of the arc source region, as has been suggested based on the B isotope systematics of Izu-Mariana forearc and arc lavas (Benton et al. 2001; Straub and Layne 2002), then the mantle source regions of arcs may be extremely diverse in terms of Li and Li isotopes on a fine scale. The scale of sampling of this mantle via melting will then control the isotopic diversity of the erupted lavas - large extents of melting will average out this variation, while smaller degree melting events (as in hotter, drier subduction settings) may permit its expression (see also Allan et al. 1987).

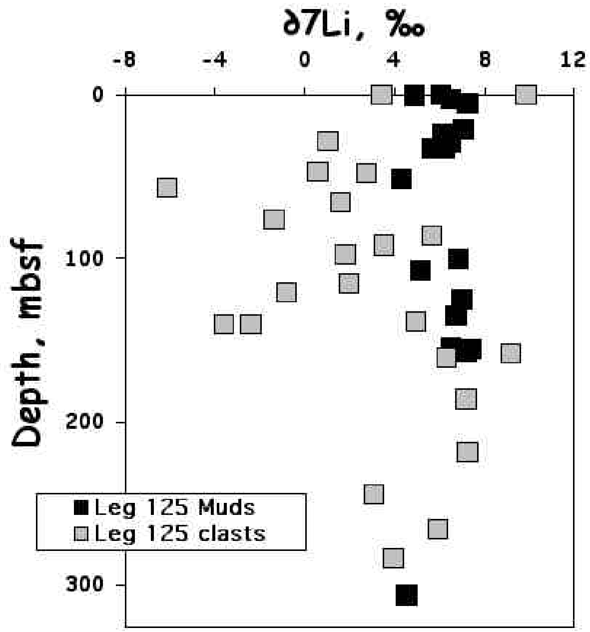

Figure 4: Plot of ∂^7Li vs. depth in core for serpentinite muds and entrained ultramafic clasts from the Conical Seamount, ODP Leg 125

Proposed Work:

To test the hypotheses for Li isotopes noted above; to try and characterize the geochemical contributions of the mantle wedge in arc petrogenesis; and to assess the origins and significance of mantle wedge Li signatures, we are proposing a combined Li isotope/B-Be study of off-axis lavas - both behind-the-front calc-alkaline centers, and monogenetic alkaline centers - from two well-studied subduction systems. The primary focus of this work will be the Trans-Mexican Volcanic Belt, a "hot" subduction system, where previous survey work indicates lower B/Be ratios overall, and particularly low B/Be in the numerous alkaline monogenetic centers (Hochstaedter et al. 1996 Chesley et al. 2002). As well, the role of crustal assimilation has been documented in several MVB centers, so we can use these results to assess the affects of assimilation on Li isotopes. Results from the TMVB will be contrasted against those from monogenetic back-arc centers in Guatemala, where Walker et al. (1995, 2000; see also Cameron et al., in press) have done careful studies (including some B/Be determinations) to define the roles of the slab and mantle wedge in magma genesis.

A) B)

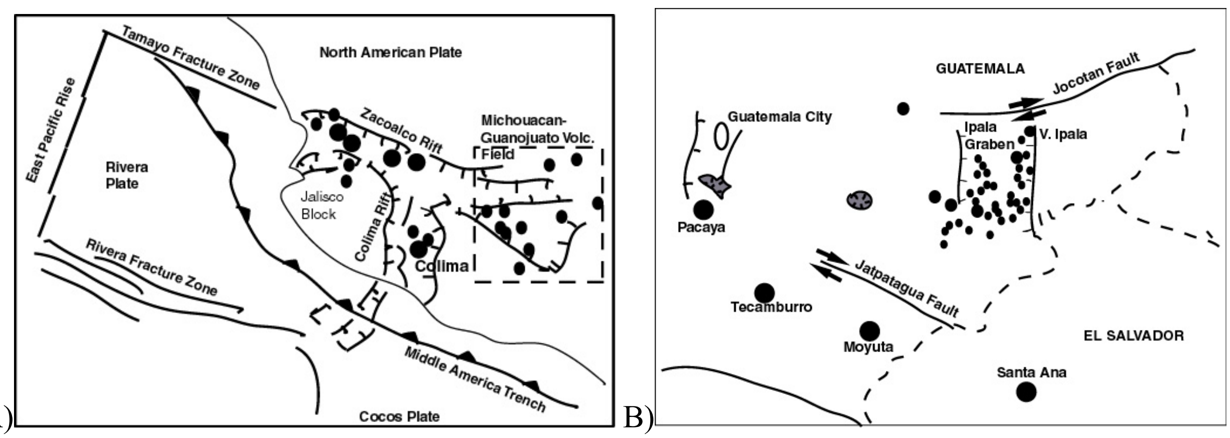

Figure 5: Schematic maps of A) the western Trans-Mexican Volcanic Belt, and B) the Central American arc in Guatemala, modified from Hochstaedter et al (1996) and Walker et al (1995), respectively. Black circles represent large and small volcanic centers in each region.

The Western Trans-Mexican Volcanic Belt (TMVB)

The Trans-Mexican Volcanic Belt (TMVB), is an ideal site for this study, as the associated calc-alkaline composite centers, cinder cones and lava cones and small-volume transitional and alkaline cinder and lava cones document both a changing slab input and a variable mantle wedge. The TMVB occurs in southwestern Mexico where the Rivera and Cocos plates subduct beneath the North American plate (Fig. 5a). Three large, tectonically active rift systems control the locations of the larger composite centers, which define the volcanic axis, and heavily influences the location of smaller centers as well (e.g. Allan et al., 1991; Luhr, 1997). These structures interect to form a rift-rift-rift triple junction south of Guadalajara (Fig. 5a; Allan, 1986; Johnson and Harrison, 1990). NW of this intersection, the the arc axis is defined by moderate-sized composite volcanoes within the Tepic-Zacoalco Fault Zone. The Zacolaco half-graben is the southeasternmost fault basin, and shows evidence for right-lateral movement in addition to listric faulting (Pacheco et al., 1999; Allan, 1986).The eastern limb of this rift-rift-rift structure is the Chapala Rift. Fault basins in the Chapala-Tula system extend over 400 km to the east and show evidence for left-lateral movement (Delgado, 1985; 1992; Johnson and Harrison, 1990). The south-trending Colima Rift extends 200km to the coast, with an offshore extension to the trench; it represents E-W extension in the arc and approximates the subducting Rivera-Cocos boundary (Allan et al., 1991; Bandy et al., 1995). Here, the volcanic axis, as defined by large, composite centers, is offset ~90 km towards the trench at Colima Volcano (Luhr and Carmichael 1980a, b; Allan et al 1986). Together, the Colima and Tepic-Zacoalco Rifts roughly outline the Jalisco Block, whch contains many extensional fault basins (Allan et al., 1991; Ferrari et al., 1994; Michaud et al., 1991; Rosas-Elguera et al., 1996).

These numerous fault basins serve as the loci for eruptions of small volume alkaline and transitional magmas, and both small and large-volume calc-alkaline magmas. During the opening of the Colima Rift (earliest Pliocene), small-volume eruptions of hydrous, LILE- and LREE-rich alkaline, transitional, and calc-alkaline lavas likely represent shallow decompression of metasomatized and hybridized mantle (Allan, 1999; Allan et al., 1991). With continued extension, decompression melting continued, but was subsequently joined by deeper-seated melting related to fluid-fluxing, or a deepening of the melting column that built the large composite volcanoes of Colima and Cantaro (Hochstaedter et al., 1996; Allan, 1999). NW of the Colima Rift in the Jalisco Block, the Mascota, San Sebastian and Los Volcanes fields occur in extensional basins and represent alkaline and calc-alkaline magmatism trenchward of the composite volcano axis (Lange and Carmichael 1990; 1991; Wallace and Carmichael 1992). These lavas mostly represent decompression melts of subduction-modified (e.g. metasomatized and hybridized) mantle, but alkaline melts erupted from the Atenguillo graben and other fault basins within the Tepic-Zacoalco Rift represent decompression melts of asthenospheric mantle apparently unmodified by subduction (Righter and Rosas-Elguera, 2001; Luhr, 1997; Righter and Carmichael, 1992; Luhr et al, 1989; Nelson and Carmichael, 1984). E and SE of the Colima Rift, the Michoacan-Guanajuato volcanic field includes over 1000 cinder and lava cones producing calc-alkaline rocks, including the recently active Paricutin volcano, where the role of crustal assimilation has been carefully documented (Hasenaka and Carmichael 1985; 1987; McBirney et al., 1987).

Convergence rates between the North American and Rivera Plates are controversial, with models of both slow subduction (about 2 cm/yr; DeMets and Stein, 1990) and faster subduction (2-5cm/yr; Kostoglodov and Bandy, 1995). Cocos Plate subduction is more rapid (5-6 cm/yr; DeMets and Stein 1990). Rivera Plate subduction is initially flat, then becomes quite steep (Pardo and Suarez, 1993), unlike the uniformally shallow dip angle of subduction for the Cocos Plate (Pardo and Suarez, 1995). The volcanic axis of the MVB seems to lie ~100 km above a poorly defined Benioff zone (Fig. 10a). Magnetic anomaly data indicates that both the Rivera and Cocos plates are relatively young (10-15 Ma)(Klitgord and Mammerickx 1982; Lonsdale, 1995), so the slabs subducting beneath the MVB are likely to be rather hot. This likelihood, along with the observed extensional features, prevalent volcanism, and the proximity of the EPR, points to a hot subduction setting, where a relatively dehydrated slab is contributing little fluid (as indicated by B/Be ratios) and melting is triggered by decompression as well as via slab fluxing. Lavas from the many monogenetic alkaline arc centers have been described as arising from veined regions of the mantle wedge (Luhr et al, 1989; Allan et al., 1991; Luhr, 1997), while the large calc-alkaline centers represent more extensive melting.

Intensive petrogenetic study in recent years by the University of California group (Ian Carmichael, Jim Luhr, and others) has generated a large set of well characterized igneous samples from the MVB. Jim Luhr is providing Pleistocene-Recent rock suites from the Colima Rift and Paricutin volcano for this study and will lend his regional expertise in the interpretation of the results. Allan will provide his well-characterized Pliocene to Pleistocene alkaline, transitional, and calc-alkaline samples from the Colima Rift and Zacoalco half-graben for the this study, as well participate in the field and laboratory research and REU programs.

The Guatemala segment of the Central American Arc:

The Central American arc in southeastern Guatemala offers a useful comparison to the TMVB. Here, subduction rates are higher and the downgoing slab is cooler, so fluid fluxing by the slab is more vigorous, and lavas with significantly elevated B/Be and other ratios indicative of slab inputs are erupted (Leeman 1994; Walker et al. 1995; 2000, Cameron et al. 2002). The active volcanic region of the Central American arc is at its widest in SE Guatemala (~100 Km), and much as in the TMVB, numerous small, monogenetic volcanic centers are observed behind the main volcanic front. The Ipala Graben, an extensional feature approximately perpendicular to the trend of the Central American volcanic front, is a locus for behind-the-front, monogenetic volcanoes. The localization of behind-the front volcanism in this region of Central America may either relate to the segmentation of the subducting and overriding plates (Stoiber and Carr 1973; Carr et al. 1982), or to interactions between the North American and Caribbean plates (Walker et al. 1995). Walker et al (1995) noted a break in the compositions of lavas across Guatemala from the volcanic front into the behind-the-front centers, which correlated with a change in the manner of magma generation - volcanic front lavas in Guatemala reflect predominantly fluxed melting of the mantle wedge due to the influx of slab fluids, while behind-the-front magmas, even as little as 20 km from the volcanic front, indicated the effects of decompression melting of a geochemically variable mantle source.

We shall examine a representative suite of well-characterized Guatemala lavas, representative of the geochemical variation across the Central American volcanic zone in this region, from the collections of Dr. James Walker at Northern Illinois Univ., who will collaborate with us scientifically, and will mentor undergraduate participants from NIU (see Work Plan below) The effects of crustal assimilation have been studied in these lavas (see Walker et al. 1995), so our samples will be chosen to a) identify the crustal signature of light elements and Li isotopes in this region, and then b) to minimize the effects of the crust. The goal of this work will be one of comparison to the MVB suite, and to assess from light element systematics the model of Walker, et al. (1995): are B/Be and Li isotopic heterogeneity in the mantle wedge resolvable through the effects of the slab in this setting? If so, are abundance patterns consistent with decompression melting, and how does this variability compare to what is observed in the MVB to the north, and Panama to the south? As slab inputs to the Central American arc have been carefully studied, and surveys of B and Li isotope systematics along the arc are available (Plank and Langmuir 1999; Patino et al. 2000 Leeman et al 1994; Chan et al. 1999; 2001) this site also may offer the best opportunity for addressing the question of how Li isotope heterogeneity may develop in the mantle wedge beneath arcs.

Work Plan:

The work in this grant will be completed predominantly by undergraduate student participants at the University of South Florida and Appalachian State University, and by MS and/or Ph.D. students at the University of South Florida,under the supervision of PI's Ryan and Allan. This collaborative approach brings together the geochemical expertise of PI Ryan in the study of light elements and Li isotopes, and the considerable field and petrologic experience in the of PI Allan, who has studied off-axis and monogenetic volcanism of the TMVB for many years. It also brings together a necessary critical mass of student participants from the participating institutions (Univ. South Florida, Appalachian State Univ. and Northern Illinois Univ.) who will complete the proposed analytical work as part of planned undergraduate summer research programs (see below), and as part of Senior theses and MS/PhD thesis efforts. Both the undergraduate participants and the graduate students will be full collaborative partners in this research effort, and they will conduct all their work toward presentation of their results at regional or national GSA (or AGU) meetings. The PI's have considerable experience in successfully mentoring students in research at all levels. PI Allan is faculty in the Geology Department at Appalachian State University, an undergraduate-only department. PI Ryan has extensive experience supervising undergraduates in geochemical research, supported both by REU Supplements an through the successful REU Site research program he has run at USF since 1997 (See Results from Previous NSF Support above).

Undergraduate Summer Research - Petrology and Li, Be, B geochemistry of lavas from the Mexican Volcanic Belt: ASU, USF, and NIU undergraduates will be recruited to participate in petrologic and light element abundance studies of lavas from monogenetic volcanic centers from the western Mexican Volcanic Belt (MVB). This work will build upon initial B-Be survey studies of MVB lavas by Hochstaedter et al (1996), and the work of Allan and others (Allan and Carmichael 1984; Allan 1986; Allan et al. 1991); and will also serve as a foundation for Li isotope studies by USF graduate student participants. Undergraduate participants (4 students/yr) will be selected from all the participating institutions (Appalachian State Univ., Univ. South Florida, and Northern Illinois Univ.). Based on Ryan's experiences with REU Site programs, this number of student participants is sufficient to establish an efficient working group in the lab, and provide a good collaborative research experience for the participants. The summer experience will consist of a short period (2 weeks) of fieldwork, to be done in concert with Dr. Hugo Delgado-Granados at the Universidad Autonoma de Mexico (UNAM), during which time students will be familiarized with the geology of the western TMVB, and collect new samples from monogenetic volcanic centers in the Colima Rift and Zacoalco half grabens. Sample collection will focus on numerous new roadcuts in the area since Allan did his original fieldwork in the 1980's, as well as on sampling previously unvisited, more remote Pliocene lava cones, made more accessible by new roads in the last decade. While in the field, the PI's will mentor and guide the student participants in defining specific scientific questions to be solved via geochemical measurements. The field experience will be followed by six weeks of laboratory analysis and interpretive work at USF, where the participants will characterize their collected samples petrographically and geochemcially, and conduct Li, Be, and B analyses on subsets of their collected samples, selected lavas from other TMVB sites from the collections of PI Allan, and others (i.e., samples from Colima and other proximal MVB stratocones from the the Smithsonian Institution; alkaline lavas of the Michouacan block from Univ. Arizona). The last week of the program will be devoted to data interpetation and the construction of abstracts for the following GSA regional meeting. Both PI's will be present for the field experience, Ryan will supervise students at USF. Both PI's will participate in the final week of the Summer project. Planned post-summer undergraduate research opportunities in which interested students may participate will include mineral chemistry studies of our new samples using the FCAEM electron microprobe facility at FIU in Miami, which Ryan operates remotely via an Internet 2 operational link.

Graduate Research: Li isotope signatures of Intraplate Mantle Sources, and Li isotope-B/Be comparisons of MVB and northern Central American off-axis lavas. All Li isotope work will be conducted by graduate students under the supervision of PI Ryan, as will B-Be-Li abundance determinations on lavas from the northern Central American arc. This work will take two directions:

Li isotope systematics of Ocean island basalts.A current graduate student at USF, Mrs. Judy Harden, is pursuing M.S. research focusing on the Li isotope systematics of intraplate lavas, which will build upon Ryan's past NSF-supported work on Mt. Erebus and other intraplate sites. A selection of characterized samples from the suite studied for B systematics by Ryan et al (1996b) will be analyzed, along with samples from the Society islands that Mrs. Harden collected and characterized for B-Be-Li abundances as part of a Senior Honor's Thesis project at USF (Harden et al. 2002). Mrs. Harden is a non-traditional student who returned to seek a Geology degree after several years in K-12 education. When she completes her MS, she will return to the education profession as an earth science instructor at the high school or community college level in Florida.

Funds are requested to conduct the necessary Li isotope measurements on these OIB suites, so that we may have a more comprehensive (if not complete) picture of the natural Li isotopic variation in oceanic mantle reservoirs.

Li isotopic comparisons of MVB and norther Central America: A future MS/Ph.D student will pursue this work, which will involve conducting Li isotope measurements on a selection of those TMVB samples previously characterized in the undergraduate program, and light element abundances and Li isotopes on a selection of samples from the off-axis centers in Guatemala. Li isotope sample preparation will occur in Ryan's light element lab at USF, while the multicollector ICP-MS isotopic measurements will occur either at the Department of Terrestrial Magnetism, or at the University of Maryland. Ryan has a standing invitation for himself and his students from both labs to do Li isotopic work on fee for sample basis. Funds are requested to cover these use fees, as well as to cover isotope sample preparation expenses at USF.

Timetable for the Program:

- Spring 1/Summer 1/Fall 1: Li isotopes on OIBs (Harden)
- Spring1/Summer 1: Petrologic and light element studies on TMVB samples collected in the field, + those available from PI Allan. Work will focus on defining the role of crust vs. mantle vs. slab in TMVB magmatism(student recruitment, setup, trip, etc, including presentation of results the following Spring)
- Fall 2/Spring 2/ Summer 2: Li isotopes on northern Central America and TMVB rocks; post-Summer microprobe/petrography of new TMVB samples (necessary to characterize and classify them).
- Spring2/Summer 2:Further petrologic al and light element studies of TMVB stratocones and off-axis lavas, to define LIL/light element variability in the TMVB mantle source.
- Summer2/Fall3/Spring 3: Complete Li isotope work and other characterization efforts on TMVB lavas.

Scientific Outcomes:

The Li isotope and B-Be-Li abundance data we propose to collect will allow us to answer the following questions:

1) ***What degree of Li isotope heterogeneity occurs in the mantle wedge?*** Our results will either confirm the observations of Tomascak et al. (2002) in hot and tectonically complex subduction settings, or (as in Panama) we will discover some degree of variability in ∂^7Li in the low B lavas of the TMVB and Guatemala.
2) ***What are the origins of Li isotope variations in the mantle?*** Our work will provide a reasonable, if not comprehensive, assessment of Li isotopic variability in intraplate settings, which we will then compare to the ∂^7Li variations in these arc settings. Our arc Li isotope data will also be compared with existing Sr, Nd, and other radiogenic isotope data for these suites, to confirm the existence of intraplate-like mantle heterogeneity in these settings, or to identify a different source for the observed ∂^7Li variations.
3) ***How does crustal assimilation impact Li isotope and B-Be-Li systematics?*** Both in the TMVB and in Guatemala, the effects of arc magma interactions with the crusthave been carefully addressed. We will use this body of data to identify the range of crustal effects on light element systematics and Li isotope variations, and to help us identify the subsets of our sample suites most likely to preserve mantle-derived geochemical signatures.
4) ***What are the origins of mantle wedge geochemical heterogeneities in arcs, and how and why do they persist?*** Several recent papers have raised the question of whether mantle chemical heterogeneities can be induced by slab-mantle exchange processes over time, and how such heterogeneities may persist, if (as many assume) the sub-arc mantle is convecting in response to subduction (see Hickey et al. 2002; Righter and Rosas-Elguara 2001; Chesley et al. 2002). A reasonable inference from the conclusions of Tomascak et al. (2000) is that at least in terms of Li isotopes, the Panama sub-arc mantle is preserving heterogeneities generated via earlier subduction inputs. Light element systematics are one of the most powerful tools we have for identifying subduction-related chemical exchanges, and because of the relative compatibility of Li, Li isotopes are well suited to record time-integrated slab input effects. Combining light element/Li isotope data with that for radiogenic isotopes should allow us to place constraints on how mantle heterogeneities, such as they may be, developed and were preserved in these two arc settings.

Dissemination of Results:

Along with the traditional dissemination of research results (abstracts, talks, papers) which the PI's have committed to herein, the outcomes of the undergraduate experience in terms of student education will also be considered and disseminated. PI Ryan is a Geoscience Councilor for the Council on Undergraduate Research, and he and PI Allan will present and publish on the student outcomes from this program in CUR outlets (education sessions at GSA annual meetings, and a publication in the *CUR Quarterly*.

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RESUME

Jeffrey G. Ryan

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Email: RYAN@CHUMA.CAS.USF.EDU

Personal Data:

Born: October 26, 1960, New York, N.Y. U.S. Citizen
Home Address: 14952 Old Pointe Rd. Tampa, FL 33613
S.S. #:239-23-9344

Education:

1978-1983: B.S. (Summa Cum Laude), Geology, Western Carolina University
1983-1989: M.A., M. Phil., Ph.D., Columbia University. Thesis Title: The Systematics of Lithium, Beryllium and Boron in Young Volcanic Rocks.   Advisor: C.H. Langmuir

Scholarships and Awards:

1989-1991: Post-Doctoral Fellowship, Department of Terrestrial Magnetism, CIW
1997: USF Outstanding Undergraduate Teacher Award
1999 Carnegie Foundation for the Advancement of Teaching/CASE Florida Professor of the Year
2000 USF Phi Kappa Phi Artist/Scholar Award

Professional History:

1/83-8/83:	Intern at DOE-Morgantown Energy Technology Center,Morgantown, West Virginia
3/89-6/91:	Postdoctoral Fellow, Department of Terrestrial Magnetism, Washington, DC.
8/91-8/96:	Assistant Professor, Department of Geology, University of South Florida
8/96-Present	Associate Professor, Department of Geology, University of South Florida
1/00-Present:	Visiting Investigator, Department of Terrestrial Magnetism
8/00–8/01	Interim Chair, Department of Geology, University of South Florida

Recent National Science Foundation Grants Received:

"The role of the Forearc in Subduction Zone Chemical Cycling: Elemental and Isotopic Signatures of Forearc Serpentinites, ODP Leg 125" $95,163. 8/15/99; REU Supplement $4925 4/1/00

"The Search for Subducted Components in the Mantle: a Boron and Lithium isotope, and Fluid-Mobile Element study of Mount Erebus." $39,640 1/1/00-6/30/01

'Collaborative Research: REU: An integrated field-laboratory experience for undergraduates: constraints on the evolution of Southern Blue Ridge mafic-ultramafic massifs." $83,585 1/10/00-3/31/02

JOI-USSSP: 'The Role of the Forearc in Subduction Zone Chemical Cycles: Fluid-Mobile Element and B-Li isotope signatures of serpentinites from S. Chamorro Seamount, ODP Leg 195." $28,275

Professional Activities:

Geoscience Councilor and Campus Representative, Council for Undergraduate Research
Panelist, NSF-MARGINS (1999) and REU-Site program (2001)

Member of: Geological Society of America, American Geophysical Union, Mineralogical Society of America, Meteoritical Society, Geological Society of Washington, New York Academy of Science, Sigma Gamma Epsilon, Sigma Xi, AAAS

Recent Publications (Students in Boldface)

Ryan, J.G. (2002) The trace-element behavior of beryllium in rocks and fluids. *Reviews of Mineralogy* series publication on the chemistry and mineralogy of beryllium, in press.

Benton, L.D., J.G. Ryan, and F. Tera (2001) Boron isotope systematics of slab fluids as inferred from a serpentinite seamount, Mariana forearc. *Earth and Planetary Science Letters*, 187, p. 273-282.

Savov, I. J.G. Ryan, I. Haydoutov, and J. Schijf. (2001) Late Precambrian Balkan-Carpathian Ophiolite - a slice of the Pan-African ocean crust? Geochemical and tectonic insights from the Tcherni Vrah and Deli Jovan massifs, Bulgaria and Serbia. *Journal of Volcanology and Geothermal Research*, 110, 299-318.

Lentz, R.C.F., H.Y. McSween, Jr., J.G. Ryan, L. Riciputi, (2001) Water in martian magmas: Clues from light lithophile elements in shergottites and nakhlites. *Geochimica et Cosmochimica Acta*, 65: 4551-4565.

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Hochstaedter, A.F., Ryan, J.G., Luhr, J.F., and Hasenake, T. (1996) On B/Be systematics of the Mexican Volcanic Belt. *Geochimica et Cosmochimica Acta*. **60**, 613-628.

Ryan, J.G., Morris J.D., Tera F., Leeman W.P. and Tsvetkov A. (1995) Cross-arc geochemical variations in the Kurile island arc as a function of slab depth. *Science*., **270**, 625-628.

Recent Collaborators:

Dr. Julie Morris, Washington University
Dr. Fouad Tera, DTM
Dr. Gray Bebout, Lehigh Univ.
Dr. Bill Leeman, Rice Univ.
Dr. Virginia Peterson, Western Carolina Univ.
Dr. John Burr, WCU.
Dr. Steven Yurkovich, Western Carolina Univ.
Dr. Robert Brinkmann, USF
Dr. Simon Turner, Univ. Bristol
Dr. Paul Tomascak, Univ. Maryland
Dr. Laurie Benton, EXPONENT Env. Grp.
Dr. Rosemary Hickey-Vargas, FIU
Dr. Gautam Sen, FIU
Dr. Rachel Lentz, Univ. Tennessee
Dr. Harry McSween, Univ. Tennessee

Academic Advisors:

Dr. Charles Langmuir, Columbia University
Dr. Julie Morris, Washington Univ.(Postdoctoral)

Past Students

Dr. Eric Tenthorey (Australian National Univ.)

Budget Justification

A.1: 1 month/ year support for two summers is requested for PI Ryan, who will oversee and mentor undergraduate participants during the summer term, and direct thesis/dissertation research of participating graduate students

B.3: Three semesters + two summers support for graduate students are requested. Graduate students will conduct all Li isotope determinations, along with additional Li, Be, B measurements as required.

C: 15.45% fringe benefit rate on faculty summer salary; 0.5% fringe rate on student stipends.

E: Domestic Travel

1a) Travel to Washington, DC to conduct Li isotope measurements. Airfare, lodging and food/incidentals for Ryan and a graduate student estimated at $900/ visit (assuming 2-3 days on the machine.), 1-2 visits/year, 5 visits, total.

1b) Travel by Ryan and graduate student to present Li isotope results at a national professional meeting (GSA Annual Mtg. or Fall AGU Mtg.) Airfare ($400/person), Lodging ($125/night, double occupancy four nights), registration (est. $350 for Ryan, $150 for student) and food/incidentals ($150 each)

1c) Travel support for Ryan to attend regional GSA meeting with undergraduate participants. Based on past REU trips to these meetings, estimated to be $300/year for the two years of the undergraduate program.

1d)Partial post-Summer travel support for undergraduates to do work at USF: $200/year in the first two years of the grant

1e) Travel to Mexico to participate in summer field trip w/ undergraduate participants and Mexican collaborators. Airfare ($1000) and daily perdiem for lodging and food, estimated at $2050/year each of the first two years of the grant.

F: Participant Support Costs:

Costs for four undergraduates fro m the participating institutions (ASU, USF, NIU) to participate in this research, following the model of my past REU Site projects. The undergraduate participants will collect of samples in the field, define specific research questions to be resolved analytically, and conduct all elemental analyses on the selected Trans-Mexican Volcanic Belt samples. They will also submit a group abstract, and conduct a poster presentation on their work at the GSA Southeastern Section meeting in the following Spring.

Stipends: 6 weeks/summer at $325/week

Travel: Round-trip travel support for off-campus participants to and from USF: $200/student/summer (student travel to and from Mexico is in ASU budget)

Subsistence: Lodging at $190/week (double occupancy); food at $75/student/week, each Summer

Other: Funds to help support undergraduates to present their Summer results at a regional GSA meeting. Additional support will be obtained from USF and ASU, as well as GSA

G: Other Direct Costs:

1. Materials and Supplies
    a) DCP analysis of Li, Be, and B abundances in Mexican and Central American volcanic rocks. \$35/sample for 120 samples overall.
    b) DCP analyses of major elements and lithophile trace elements in uncharacterized Mexican Volcanic Belt samples. \$25/sample for 60 samples overall.
    c) Expenses related to chemical preparation and separations for Li isotopes, to be done at USF. \$25/sample for 85 arc and ocean island volcanic samples.
    d) Cost for purchase of additional Pt crucibles for B, Be sample digestions, to accommodate the heavy usage in Summer by undergraduate participants - \$3000 in year 1 of grant.
    e) \$400 to support post summer projects by undergraduate participants over the life of the grant. These projects would involve further characterization of collected samples (ICP-MS trace elements, microprobe studies, etc.) such as may be necessary and relevant to the undergraduate research efforts. These projects would be supervised on the student's home campuses, by a selected on-campus research mentor. Funds requested here would support analytical expenses.
2. Publication/Dissemination. Funds for abstract fees at national meetings.
6. Other:
    a) Use charges for multi-collector ICP-MS instrument for Li isotopic analysis at the University of Maryland. \$80/sample (Univ. Md. standard academic rate). 85 samples, total.
    b) In-State tuition charges for graduate students (assuming a 9 hour/semester and 6 hour/ summer courseload for full time enrollment.

I. Indirect Costs:

- 45% full indirect on all expenses save tuition and Participant Support Costs.
- 0% indirect costs charged son Participant Support Costs
- 0% indirect costs charged on tuition.

FACILITIES, EQUIPMENT & OTHER RESOURCES

FACILITIES: Identify the facilities to be used at each performance site listed and, as appropriate, indicate their capacities, pertinent capabilities, relative proximity, and extent of availability to the project. Use "Other" to describe the facilities at any other performance sites listed and at sites for field studies. USE additional pages as necessary.

Laboratory: **At USF:**
Sample preparation and digestion labs for conducting major and trace element measurements by Direct Current Plasma Emission Spectrometry.
"Clean Lab" facility for doing digestions and preparation for Li, Be, and B abudance

Clinical:

Animal:

Computer: **Generous computing facilities in both the USF Geology Department and the College of Arts and Sciences available to students for data reduction, processing and interpretation.**

Office:

Other: ____________________

MAJOR EQUIPMENT: List the most important items available for this project and, as appropriate identifying the location and pertinent capabilities of each.

Instrumentation Relevant to this grant:
Direct Current Plasma Emission Spectrometer - the "workhorse" instrument at USF for conducting elemental analyses on rock samples. Low level Li, Be, and B abundance measurements done here routinely via DCP.

OTHER RESOURCES: Provide any information describing the other resources available for the project. Identify support services such as consultant, secretarial, machine shop, and electronics shop, and the extent to which they will be available for the project. Include an explanation of any consortium/contractual arrangements with other organizations.

For Li isotopic ratio measurements, we have access to the multi-collector ICP-MS instruments at the Department of Terrestrial Magnetism in Washington, DC, and at the University of Maryland - in both labs Li isotopes are measured routinely. PI Ryan has worked closely with Dr. Paul Tomascak at Univ. Maryland on Li isotope studies for five years, and learned the techniques himself while spending a sabbatical term at DTM in 2000.

LABORATORY FACILITIES (continued):

work, and Li isotope ratio measurements

May 23, 2002

Dr. Jeffrey G. Ryan
Department of Geology
University of South Florida
Tampa, FL 33620-5201

Dear Jeff,

This note is to confirm our collaboration in a study of the Li isotopic compositions of basaltic lavas of southeastern Guatemala, particularly those from the Ipala Graben region. We have an extensive collection of these lavas here at Northern Illinois University from some erupted close to the volcanic front to some erupted over 100 km behind the front.

In addition, I plan to act as a mentor of undergraduate students participating in this collaborative project.

It is great to finally be working together on an across-arc project.

Sincerely,

Jim Walker
Department of Geology and Environmental Geosciences
Northern Illinois University
DeKalb, IL 60115

jim@geol.niu.edu

May 20, 2002.

James F. Allan, PhD
Co-Chair, JOIDES and iSAS Scientific Measurements Panels
Professor and Chair, Dept. of Geology
Appalachian State University
Boone, NC 28608-2067

Dear Dr. Allan,

The Institute of Geophysics of the National Autonomous University of Mexico is currently carrying out a series of geological studies on volcanoes of western Mexico aimed to better understand volcanic activity in space and time and its relationship with the regional tectonic framework.

In particular, we have been studying the volcanism at the rift-rift-rift system of Chapala Colima-Sayula and Tepic-San Marcos. Our attention is also focused on the Michoacán-Guanajuato volcanic field and the Cotija half-graben structure. A key for understanding the intimate relationship among tectonics and volcanism is the study of isotopic compositions of volcanic rocks to better understand the magmatic processes and fluid flux in the mantle wedge, and therefore, the combined consequences of subduction and rifting processes on the volcanic products and tectonics.

Based on this, I am pleased to tell you that I am eager to collaborate with you and your associates in research projects that may help to throw light on the mentioned issues and especially, strength our longstanding cooperative ties.

Yours sincerely,

Dr. Hugo Delgado Granados
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From: "Paul Tomascak" <tomascak@geol.umd.edu>
To: "Ryan, Jeffrey" <ryan@chuma.cas.usf.edu>
Subject: Support for Li isotope analyses
Date: Wednesday, May 29, 2002 2:57 PM

Dear Jeff--

It was good to have you over to the lab today and talk about research projects. Now you should have a good idea of all we are capable of doing in the Plasma Lab, and how well Li isotopes are going.

It will be a pleasure to continue our collaborative work and to make available the instrumentation for Li isotope measurements of your samples. Whether it will be me doing the measurements or yourself +/- students coming up when the time permits, this should work out fine, given the degree of routineness we have reached with Li. It is especially excellent that you have set up the chemical preparations at USF, which will really make the whole process that much more efficient.

I look forward to hearing more about the progress on samples.

-paul.
. . .
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