Light element and lithium isotope signatures of the emii reservoir - the society islands, french polynesia: Geochemical results and an educational application

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Light Element and Lithium Isotope Signatures of the EMII Reservoir - The Society Islands, French Polynesia: Geochemical Results and an Educational Application

by

Judy Ann Harden

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
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Keywords: Boron, geochemistry, mantle, ocean island basalts, quantitative literacy

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Dedication

I would like to dedicate this thesis to a husband and children who constantly encouraged and supported me, to parents who instilled a love for travel and a fascination for rocks and volcanoes, to the professors at Hillsborough Community College that helped launch my dreams, and to the faculty and staff at the University of South Florida who helped make those dreams come true.
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Light Element and Lithium Isotope Signatures of the EMII Reservoir - the Society Islands, French Polynesia: Geochemical Results and an Educational Application

Judy Ann Harden

ABSTRACT

The purpose of this thesis is to examine the abundance systematics of Li, Be and B, and Li isotopic systematics in lavas from the Society Islands, an enriched mantle (EMII) intraplate site, to further characterize the chemical signatures in the sources for ocean island basalts that may result from subduction-related processes and mantle entrainment. The goal is to see how light-element and Li-isotope systematics vary during ocean-island volcanic evolution and during tropical weathering.

B/K, B/Be and Li/V ratios in basaltic Moorea lavas are 0.0001-.0002, 0.6-2.0 and 0.01-0.05 respectively, and the more evolved samples are somewhat higher. These ratios are similar to those for other Society Island lavas, and lower than those for lavas from St. Helena, Erebus, Hawaii, Gough and Reunion, as well as analyzed mid-ocean ridge basalts (MORBs). $\delta^7$Li values for Moorea cluster at $+3 - +5\%$ for the freshest lavas, and $0 - +2\%$ for more weathered rocks.

These new data from Moorea are consistent with earlier survey results from the Society Islands and indicate a mantle source that includes B-poor (subducted?) materials. $\delta^7$Li values for the freshest Moorea samples are similar to those of other Society Island lavas, suggesting that the EMII isotopic end-member records a Li-isotopic signature
similar to that of MORBs. Dilution by entrainment of upper mantle material is unlikely due to differing B/K ratios and similar $\delta^{7}$Li values for the Society and Hawaiian plumes. A more likely explanation is that recycled crust or sediments have minimal influence on the Li isotope signatures of hotspot plumes.

Using the Moorea data and geochemical data from other sources, I created a set of Power Point instructional modules for use in petrology classes to aid in teaching students about the effects of fractional crystallization and partial melting. I tested the module on fractional crystallization in two upper-level geology classes to assess its value in increasing student understanding. Both classes received a lecture about fractional crystallization. One class worked through the module as a homework exercise, while the other did not use the module. Students who worked through the module in addition to the lecture showed an increased understanding of the concept of fractional crystallization.
This thesis consists of two parts. The first section is a geochemical examination of ocean island basalts from the island of Moorea, French Polynesia, and other islands of the Society Islands chain. The second part uses this collected data to produce a set of instructional modules for use in classrooms to further student understanding of processes of fractional crystallization and partial melting in the Earth’s mantle.
PART I

B, Be, Li and Li isotopic systematics of the Society Islands: Insights into the nature of EMII Mantle sources

Introduction

Radiogenic isotope ratios have been used for the past 40 years to answer questions about processes within the Earth’s interior. Questions posed by Hart (1988), Hofmann (1988) and others include: How many discrete geochemical domains exist in the mantle? How do these domains form? Where are they located within the Earth?

The deep mantle plumes responsible for the generation of ocean island basalts globally have been characterized in terms of four main “end-members” defined by Pb, Sr, and Nd, isotope signatures. DMM is the depleted mantle source for mid-ocean ridge basalts (MORBs). HIMU mantle has elevated U/Pb ratios (µ), as indicated by high \(^{206}/^{204}\text{Pb}\) and \(^{207}/^{204}\text{Pb}\). EMI is enriched mantle with very unradiogenic \(^{206}\text{Pb}/^{204}\text{Pb}\) and the lowest \(^{143}\text{Nd}/^{144}\text{Nd}\) present in the oceans. EMII is enriched mantle and contains the highest \(^{87}\text{Sr}/^{86}\text{Sr}\) in the ocean and intermediate \(^{206}\text{Pb}/^{204}\text{Pb}\) and \(^{143}\text{Nd}/^{144}\text{Nd}\) (Hart, 1988). Because radiogenic isotope ratios are not modified during partial melting and magma chamber processes, data for lavas can be used to characterize the mantle source regions of basaltic magmas.

The HIMU and the EM isotopic reservoirs have been attributed to subduction-related origins in the past (Hofmann and White, 1982; Zindler and Hart, 1986; Hart,
1988; Hauri and Hart, 1993; Reisberg et al., 1993; Thirwall, 1997). However, such inferences are not equivocal because the processes of subduction profoundly modify the composition of slab materials as they descend into the mantle, invalidating comparisons with the original surface materials (i.e. sediments and ocean crustal rocks) that are carried into trenches (Bebout et al., 1993; 1999; Schmidt and Poli, 2003). Tracers are required that are both sensitive to the process in question and well documented in terms of their terrestrial distribution to confirm the role of subduction or any other terrestrial geochemical process in creating a mantle domain.

The systematics of the light elements Li, Be, and B are well understood in subduction-zone processes and are used to characterize volcanic rocks in all tectonic settings (see Ryan and Langmuir, 1987; 1988; 1993; Ryan et al., 1996; Leeman and Sisson, 1996; Ryan, 2002; Morris and Ryan, 2003; and references therein). Boron systematics in intraplate lavas globally point to a substantial B depletion in these mantle sources and boron isotopic ratios lower than those of MORBs (Ryan et al., 1996; Chaussidon and Marty, 1995). In contrast, Be abundances in intraplate lavas are markedly elevated (Ryan, 2002).

Recently the stable-isotope system of lithium (consisting of its two isotopes $^6$Li and $^7$Li), expressed as per-mille variations of $\delta^7$Li from the value of the NIST standard reference material L-SVEC ($^7$Li/$^6$Li = 12.01), has been used successfully to characterize a variety of Earth reservoirs and processes (Chan et al., 1992, 1994, 1999; 2003; Tomascak et al., 2000; 2002; Pistiner and Henderson, 2003; Rudnick and Nakamura, 2004). This system is useful in studying geologic processes involving low- to moderate-temperature fluid-rock exchanges because of the large mass difference between $^6$Li and $^7$Li (~17%).
(Tomascak et al., 1999) and the potentially large mass fractionations of the two Li isotopes in nature ($\delta^7$Li oceans = +32.3‰; sediment up to +20 ‰; mantle rocks: -17‰ to +12‰, Chan and Edmond, 1988; Chan et al., 1992; Nishio et al., 2004, Rudnick and Nakamura, 2004). The ongoing development of multi-collector inductively coupled plasma-source mass spectrometry (ICP-MS) has facilitated the study of this isotopic system, as it permits the relatively rapid determination of $\delta^7$Li values on large numbers of samples.

Lithium isotopic compositions of lavas accurately represent their sources because isotope fractionation does not appear to occur during high-temperature crystal-liquid fractionation processes (Tomascak et al., 1999). Lithium isotopes have been used in defining the role of subducted sediment (Chan et al., 1999; 2002), basaltic crust (MORB or eclogites) (Chan et al., 2000; Tomascak et al., 2002; Zack et al., 2004; Bouman et al., 2004), seawater, continental crust (Teng et al., 2004) and combinations of these in arc magma sources.

As a step in more rigorously assessing the role of subduction in intraplate mantle sources, I characterized a suite of samples from the island of Moorea, of the Society Islands in French Polynesia, for their B, Be, Li abundances and Li-isotope signatures. I also analyzed alkali basalts from the other Society Islands to define the overall light-element signature of the Society chain and to see if temporal variations are evident. The radiogenic-isotope signatures of these EMII-type, hotspot-derived lava suites preserve a signature of past subduction (specifically a subducted sediment signature; White et al., 1982, 1996). Because the behaviors of light elements during subduction are known in
great detail, we may be able to say with greater confidence that an enrichment or
depletion in B/Be or $\delta^7\text{Li}$ in these lavas is related to a process that happened during an
ancient subduction event.
Geologic Setting

The Society Islands lie in the south-central Pacific Ocean at 15-18°S latitude and 148-155°W longitude (Figure 1). The Society Island chain, along with the Australs, Tuamotus, and the Marquesas, make up French Polynesia. These four linear chains are arranged parallel to each other in the direction of motion of the Pacific Plate and are approximately perpendicular to the East Pacific Rise. All four island chains represent the passage of Pacific Ocean plate lithosphere over a set of volcanic hotspots.

Figure 1. Location map showing study area of Society Islands, French Polynesia.
Islands, seamounts, and atolls comprise the Society Chain. The islands extend over 700 km with the youngest island, Mehetia, lying to the southeast and the oldest island, Maupiti, to the northwest. Radiometric dating shows that the islands of the Society chain become progressively older to the northwest (4.5Ma – present; Okal, 1987). The land area of the Society Islands is 2,095 km². Each island is highly dissected and consists of a basaltic volcanic core that has undergone erosion and denudation (Williams, 1933).

Geographically, the Society Islands form two groupings. Tahiti, Moorea, Maiao, Mehetia and the atoll of Tetiaroa make up the Windward Islands. The older islands Raiatea, Tahaa, Huahine, Borabora, Maupiti and the atoll of Motuiti constitute the Leeward Islands.

Moorea is the second largest island in the Society chain, with an area of 132 km² (Stearns, 1978). This island, like the others, represents the summit of a large, eroded, alkali-basalt shield volcano that rises approximately 4,000 m from the ocean floor. Mt. Tohiea, the highest peak of Moorea, has an elevation of 1,207 m (or ~5,200 m above the ocean floor). The island includes a deeply eroded caldera, the northern rim of which has largely collapsed, with only an isolated remnant preserved, Mt. Rotui. Two large bays, Opunohu and Cook’s, on the north side of the island, give the island its tooth-shaped appearance.

Age/Plate Movement

The volcanism of Moorea and the other Society Islands is classically intraplate in nature. Samples collected by Dymond (1975) indicate an age of 1.65 ± 0.13 Ma for
Moorea and 0.65 ± 0.22 Ma for Tahiti. The difference in ages of these two islands correlates with the proposed movement of the Pacific Plate (Figure 2) at 11 cm/yr over a fixed hot spot or deep mantle plume (Dymond, 1975).

![Figure 2. Society Island positions, age, and distance from hot spot (after Maury, 2000).](image)

**Volcanism**

There is no historical record of volcanic activity for any of the Society Islands. However, from March to December, 1981, Mehetia (the island over current hotspot) experienced over 3,500 earthquakes associated with underwater eruptions at a depth of 1,600 m (Binard et al., 1993).

Until recently, the common assumption about Pacific hotspot volcanism was that it is dominated by effusive basaltic lava flows (Figure 3) with occasional fire fountains. Recent discoveries, however, indicate that explosive volcanism has occurred during the formation of ocean islands. One such pyroclastic deposit near the top of Kulanaokuaiki Pali covers approximately 450 km² of the summit area of Kilauea (Fiske et al., 1999).
With similar geochemistry, tectonic setting, and form, the possibility exists that explosive volcanism did occur during the formation of the Society Islands. Neither the rock record nor collected samples from Moorea, however, show evidence of explosive volcanism. Evidence for explosive volcanism on Moorea may no longer exist due to the much older age of this island and the amount of erosion that has taken place.

There is, however, a unit described as a thick, columnar pyroclastic formation on the island of Tahiti, in the upper stage of its second shield. Eroded blocks from this unit, sampled in the Vaitamanu River, constitute an ignimbrite facies (Hildenbrand, 2003). Although most of the Society Islands probably formed by effusive volcanism, explosive activity can no longer be ruled out.
Eruptive Products and Lava Composition

Moorea lavas are typically thin-bedded pahoehoe and aa flows, usually 6 meters or less in thickness, and dip 5-10 degrees seaward from the eruptive centers (Stearns, 1978). The lavas are alkali basalts with olivine, pyroxene, and plagioclase phenocrysts. Dikes that cross-cut the flows range between 10 and 40 cm in thickness.

Compositionally the lavas range from primitive magnesian basalts to trachytes (Figure 4). The presence of abundant intermediate-composition lavas (mugearites and benmoreites) may reflect magma-mixing events (Maury et al., 2000).

Figure 4. Total Alkali-Silica classification of volcanic rocks collected from the island of Moorea. Samples range in composition from primitive basalts to Hawaiites, Mugearites, Benmoreites, and trachytes.
**Previous Work**

*Mantle Plumes and Hotspot Volcanism*

Mantle plumes that produce intraplate volcanism appear to be around 200°C hotter than ambient upper-mantle temperatures (Okal, 1987). Assumed plume viscosities are only slightly lower than those of the surrounding mantle, meaning that a vertical, axisymmetric plume cannot ascend freely through the mantle (Duncan et al., 1994). The surrounding mantle will instead be viscously coupled to the plume and ascend with it as a sheath-like boundary layer that can be hundreds of kilometers thick. Further reduction in the viscosity contrast between plume and mantle is caused by conductive heat loss from the plume into this boundary layer material, which also has the effect of increasing the buoyancy of the boundary layer.

Duncan et al. (1994) suggest that the plume continuously entrains surrounding mantle as it ascends, such that the material closest to the center of the plume will ascend from the deepest levels, while the outer parts of the plume will be entrained at relatively shallow levels. The “hotspot”, then, is concentrically zoned with deep, hot plume material at its core and progressively shallower and cooler mantle material approaching its margins. When this rising structure encounters temperature/pressure conditions for melting in the upper mantle, the entrained materials melt to a lesser degree than the core plume mantle because the entrained material temperature is lower. Given that the upper mantle is chemically more depleted than the plume core (i.e. it has lower abundances of
incompatible elements and volatiles), it should melt to far lower extents at a given temperature than the core of the plume.

The highest extents of melting observed in intraplate settings correlate with the passage of the plume core beneath the hotspot volcano – thus the highly voluminous eruptions observed at Kilauea and Mauna Loa, which sit above the core of the Hawaiian hotspot. As volcanoes are carried away from the plume core by plate motion, smaller-degree melts of cooler outer plume rocks are increasingly dominant, and volcanic activity fades. This pattern has been observed in the eruptive histories of other intraplate sites and is considered a reasonable model for the volcanic history of an island in the Society chain.

Until now, no one has conducted a comprehensive examination of the petrology of Moorea lavas. However, lavas from Tahiti have been studied in some detail (Duncan et al., 1994). Mean Nd concentrations increase with time in Tahitian lavas, which means that the mean degree of melting must therefore have decreased with time. Based on $\varepsilon_{\text{Nd}}$ abundance and isotope systematics, Duncan et al. (1994) suggest that 5-15% melting produced the earliest magmas, while as little as 1-2% melting produced late-shield and late-stage magmas. These late-stage samples with the highest Nd are believed to be derived from a source consisting predominantly of depleted mantle with less than a 10% admixture of material from the Society plume.

As noted by Duncan et al. (1994) and others, the Society Islands are dominated by alkali basalts, which are poorer in SiO$_2$ and richer in alkalis than tholeiites, consistent with lower extents of melting (Green and Ringwood, 1966). Pb/Ce ratios in Society basalts are typical to slightly higher than the values of other oceanic basalts and appear to
be a feature of their mantle source. Hofmann and White (1982) used this parameter to suggest that the incompatible-element enrichments which characterize the Society plume are due in part to deep recycling of continental-crustal material, such as subducted continental sediments. Elevated Sr and Pb isotopic ratios are also consistent with the hypothesis.

Geochemistry of Hotspot Volcanics

Hotspot volcanics can preserve extreme variability in Sr, Nd, and Pb radiogenic isotopic ratios and noble gas isotopes (i.e. radiogenic isotopic ratios of He, Ar, and Xe) within a chain and even within different magma stages of a given island (Zindler and Hart, 1986; Hart, 1988; Kurz and Jenkins, 1982; Staudacher and Allegre, 1981). Explanations of radiogenic isotopic systematics in ocean islands require multiple isotopic reservoirs in their mantle sources. As many as eight reservoirs (Zindler and Hart, 1986) and as few as four (Hart, 1988) are described in the literature. Hofmann and White (1982) were early proponents of the idea that subducted ocean crustal materials incorporate into one or more of these isotopic reservoirs. Subsequent studies focused on the possible subduction origins of three reservoirs, named (originally by Zindler and Hart, 1986) HIMU, EMI and EMII.

Hart (1988) and others contend that the “enriched” radiogenic isotope signature of the EMII reservoir (i.e., high $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{143}\text{Nd}/^{144}\text{Nd}$, high $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$) is consistent with the likely signatures of subducted sediments. The EMII signature is largely limited to the southern Pacific ocean (i.e., Dupre and Allègre, 1981), and studies
suggest that it originates from a “graveyard” of subducted slabs in the mantle beneath the SE Pacific region (i.e. Castillo et al., 1996).

**Previous Work on B, Be, Li in Ocean Islands**

The relatively broad support for a subducted sediment origin for some ocean island sources aside, workers focusing on the geochemistry of downgoing slabs warn that metamorphic changes associated with progressive subduction profoundly impact the incompatible-element and isotopic ratios of subducted materials. Direct comparisons of the compositions of surficial materials and the geochemical signatures of hotspot lavas are unlikely to lead to useful conclusions, which is particularly true for the “fluid mobile” elements (e.g., Leeman, 1996) including B, Cs, Pb and (in some cases) Li.

Boron is one of the most powerful indicators for slab involvement used in studies of arc petrogenesis (Ryan and Langmuir, 1993; Ryan et al., 1996). Ryan et al. (1996), suggest that devolatilization of subducting plates segregates B into crustal reservoirs and returns large volumes of B-depleted material to the deep mantle. Materials from the deep mantle may preserve a distinctly depleted B signature and record the effects of ancient subduction events. B content ranges between 3 and 6 ppm in the majority of ocean island alkali basalts and shows greater relative variation than Be, Ce, or K, indicating that it behaves less compatibly during melting and crystallization (Ryan et al., 1996). Primitive mantle abundance estimates for B range between ~0.5 and <0.1 ppm (Leeman and Sisson, 1996).

Dostal et al. (1996) studied Li, Be, and B variations in submarine lavas from various islands in French Polynesia. Their results show that OIBs from this region have
higher B contents than MORBs. Looking at Li/Be and B/Be ratios, Dostal et al. (1996)
concluded that Li and B are most likely removed from down-going slabs during
subduction-related metamorphism and are not involved in deep-level mantle recycling.
Boron values greater than 5 ppm for intraplate lavas as reported by Dostal et al. (1996)
are suspect. Because seawater contains ~4.5 ppm B, the use of submarine lava samples
may skew the range of B contents to higher values.

While B contents are higher in MORBs than OIBs, uniformly lower B/K and
B/Nb ratios in the lavas indicate that all intraplate source regions, regardless of their
isotopic characteristics, experienced boron depletion (Ryan et al., 1996). Chaussidon and
Marty (1995) examined the B-isotope systematics of submarine intraplate lavas, finding
values between -14.6 and -4.3‰ (light compared to MORBs with values of -6.5 to -1.2
‰). They presumed these light values were “primitive” and suggested that assimilation
of small amounts of altered basaltic crust may account for the higher boron ratios of
MORBs and back-arc basin basalts (BABBs -8.0 ± 1.5 to +7.5 ± 1.5 ‰). Similar ranges
of values have not been encountered in studies of subaerial intraplate whole rocks
(generally δ^{11}B in subaerial lavas are somewhat higher: S. Tornarini, unpubl.), and the
lack of reference samples determined both via TIMS and ion microprobe makes this
dataset problematic to integrate.

In contrast to Chaussidon and Marty (1995), Ryan et al. (1996) suggest that all
OIBs show B depletions related to a global event (probably continental crust formation)
that generated two mantle reservoirs with distinct B abundances. It is likely that fine
distinctions between OIB sources developed episodically as more B-depleted subducted
materials were added to the mantle (Ryan et al., 1996).
Lithium is a moderately incompatible trace element that is concentrated in sediments and altered oceanic crust relative to mafic igneous rocks, is soluble in hydrothermal fluids, and behaves similarly to Yb during fractional crystallization and V during melting present in ocean ridge settings. Peridotite and basalt data suggest a mantle content of 1.9 ppm Li and indicate that significant Li resides in olivine and orthopyroxene (Ryan and Langmuir, 1987; Seitz and Woodland, 2000). The Li content for MORBs, from the most picritic to the most evolved, ranges from 3 to 15 ppm. Basalts usually contain less than 8 ppm Li (Ryan and Langmuir, 1987).

Lithium isotopic signatures ($\delta^{7}$Li) distinguish seawater from oceanic basalts and are elevated in altered crustal rocks (Chan and Edmond, 1988; Chan et al., 1992). Subduction may fractionate Li isotopes, such that deeply subducted slabs of isotopically light Li generate distinct reservoirs that can be sampled by plume-related magmas (Zack et al., 2003). While $\delta^{7}$Li in altered MORBs ranges from +4.5 to +14 ‰, eclogites studied by Zack et al. (2003) have dramatically lower values, from -11 to +5 ‰. Low $\delta^{7}$Li in eclogites is inferred to be produced by Rayleigh distillation-style isotope fractionation during the early stages of metamorphism (Zack et al., 2003). Processes that may also contribute to low $\delta^{7}$Li in these eclogites are seafloor alteration of their basaltic protoliths, fluid exchanges between the eclogites and their surrounding garnet mica schist during high-grade metamorphism, and fluid loss during prograde metamorphism (Zack et al., 2003).

Samples of ultramafic xenoliths presumed to reflect an EMII mantle source have $\delta^{7}$Li of +4 to +7 ‰ (Nishio et al., 2004). These values are comparable to those reported for terrestrial volcanic rocks. Anhydrous ultramafic samples presumed to represent EMII-
type mantle (based on radiogenic isotopes) have $\delta^{7}\text{Li}$ of \(<-17\%\) (Nishio et al., 2004). Serpentinites of the Mariana forearc studied by Benton et al. (2004) range in $\delta^{7}\text{Li}$ from -6 to +10\%, indicating complex processes of Li isotopic exchange during slab-fluid/mantle exchanges in shallow subduction systems.

Ocean-island basalts studied for Li isotopes include samples from Mt. Erebus and other sites examined by Ryan and Kyle (2004) and lavas from several Hawaiian volcanic centers (Tomascak et al., 1999; Chan and Frey, 2003). $\delta^{7}\text{Li}$ in these lavas range from +3 to +7\%, values nearly indistinguishable from MORBs. No OIB sample studied thus far shows the low values inferred by Nishio et al. (2004) as indicative of the EMI reservoir. An explanation for the MORB-like Li isotopic values offered by Ryan and Kyle (2004) is mixing between plume material and the MORB-like upper mantle results in the dilution of whatever “plume signature” may have been present.

The bulk solid/liquid distribution coefficient for beryllium during melting of the mantle and crystallization of basalts is 0.03-0.06 making Be a strongly incompatible trace element, similar in its behavior to neodymium (Ryan and Langmuir, 1988). Be abundances in alkaline intraplate basalts (1-10 ppm) are up to five times greater than those of MORBs (0.15-2.5 ppm) and correlate with higher abundances of Zr, Nd and other incompatible lithophile elements. Ratios of Be/Nd and Be/Zr in intraplate basalts are very similar to those of MORBs. More evolved alkaline basalts show larger variations in Be/incompatible element ratios with progressive differentiation (Ryan, 2002).
Sampling and Analysis

Sample Collection

In August 2001 and March 2003, I collected over 40 different samples on Moorea, mostly along the coastal road that encircles the island but a few further inland (Figure 5). Dr. William White at Cornell University provided characterized basalt samples from other islands in the Society chain.

Figure 5. Island of Moorea with sample names and locations (small red dots). Rock types are noted if they differ from digitized geology. Black stars indicate points of interest on the island.
Petrology/Petrography

The following descriptions are from twenty thin sections from the freshest samples representing all the different rock types.

Primitive and evolved basalts are aphyric to moderately porphyritic and contain phenocrysts of olivine and pyroxene in a groundmass of olivine, pyroxene, opaques (magnetite, ilmenite) and microphenocrysts of plagioclase. Inferred order of crystallization is olivine+plag, followed by clinopyroxene and later opaques. Olivine and pyroxenes range from euhedral to anhedral depending on alteration; some have distinct reaction rims, and some are zoned (Figure 6). Microscopic zeolite crystals (natrolite, phillipsite, analcime, etc.) are present in some samples.

Figure 6. Primitive basalt (M01Fish2D) with subhedral olivine and euhedral pyroxene with reaction rim phenocrysts. Zeolites line the rim of vesicles (40X).
Hawaiites and mugearites contain ~1-mm plagioclase phenocrysts in a fine
groundmass (60% plagioclase, 30% opaques, 10% pyroxene for hawaiites, predominantly
plagioclase in mugearites). Some contain clinopyroxenes and zeolites. Textures range
from subophitic to intersertal or felty (Figure 7).

Figures 7. M01 B2B hawaiite in plain & crossed-polarized light, plagioclase
microphenocrysts with euhedral olivine glomerocryst intergrowth (40X).
The benmoreites (intermediate lavas) are massive and variably vesicular with a trachytic texture (Figures 8). Zeolites are present in the vesicles of a few of the benmoreite samples, indicating hydrous alteration.

Figures 8. M01 PK 25N Benmoreite with trachytic texture (plagioclase, spinel, pyroxene microphenocrysts) 40X.
One benmoreite sample, M01PK-19N, contained a pyroxene xenolith, 2 cm x 3 cm (Figures 9). I observed a similar xenolith measuring 6 cm x 8 cm in the area where I collected the sample.

Figures 9. Pyroxene xenolith on left, right side is groundmass with microphenocrysts of plagioclase, olivine, and pyroxene, plain & crossed-polarized (40X).
Although samples appear fresh, in thin section most samples show some degree of alteration due to weathering (i.e. olivine oxidation and removal, or reddening of the groundmass).
**Geochemical Methods**

I prepared and analyzed samples collected in Moorea in 2001 for major and trace elements as part of a senior thesis project. I used similar methods for samples collected in 2003.

**Major and Trace Elements**

I utilized a LiBO$_2$ fluxed, fusion digestion procedure modified from that of Tenthorey et al. (1996) to prepare samples for major and some trace-element measurements. For samples collected in 2001, I diluted a 5-ml aliquot of the lithium/beryllium solution with an equal amount of 2M HNO$_3$ + 2000 ppm LiCO$_3$. I added a germanium spike to dilution acids to serve as a performance monitor for the plasma spectrometry measurements and performed the analyses for major and trace elements using the Direct Current Plasma-Atomic Emission Spectrometer (DCP-AES) at the University of South Florida.

**Light Elements**

I selected 20 of the freshest Moorea samples for Li, Be, and B analysis along with 13 well-characterized basalt samples from other Society Islands (White et al., 1996; Table 3). I prepared samples for Li and Be analysis following the HF-HClO$_4$ acid digestion method outlined in Ryan and Langmuir (1987). I used two boron digestion protocols: an HF-HCl-mannitol acid digestion method modified from Ishikawa &
Nakamura (1992) for samples collected in 2001, and a Na$_2$CO$_3$ fluxed fusion technique modified from that of Ryan and Langmuir (1993) for samples collected in 2003. The two methods yielded comparable results for the very low B concentrations of the samples. I used standard additions methods to determine all light-element abundances. Samples were measured for B, Li and Be abundances by the (DCP-AES) at the University of South Florida. Analytical precision for Li and Be measurements are routinely ±5%; uncertainties for boron measurements at the low abundance levels of these samples are in the ±10-25% range.

**Lithium Isotopes**

I analyzed six samples from Moorea and six samples from other islands in the Society chain for Li isotopes. The Moorea samples reflect both the range of differentiation represented in the suite and some variation in degree of weathering, based on the presence/absence of zeolite phases and other indicators. The other Society Islands samples chosen were the most primitive samples available (based on high MgO contents), with the intent of trying to define both the "mantle" signature for Li isotopes, and any temporal variation in the signature that may have occurred.

Sample preparation for Li isotopic analysis was at the Department of Geology at the University of Maryland and followed an HF:HNO$_3$:HCl digestion. Samples dripped through a three-column separation method modified from that of Moriguti and Nakamura (1998), in particular in that the third column is pressurized with N$_2$ to facilitate separation. On occasion, samples are passed through the third cation column a second time to improve separation of Na from Li, as excess Na in samples results in spurious Li
isotopic measurements. Typically, only samples with qualitative Na/Li intensity ratios of 5 or less are analyzed for isotopic ratios: for my samples, the Na/Li ratios were 3 or less.

Lithium-isotopic-ratio measurements were conducted using the NU Plasma doubly focusing multi-collector-inductively coupled plasma source mass spectrometer (MC ICP-MS). Sample measurements are bracketed by measurements of the Li isotopic standard L-SVEC to correct for isotopic fractionation and further calibrated to determinations of in-house standards UMD-1 (+55‰) and IRMM-1 (-0.7‰). Lithium isotope values are expressed as per-mille variations from the L-SVEC Li isotopic standard ($\delta^{7}\text{Li}$) based on the following formula:

$$\delta^{7}\text{Li} = \left(\frac{^{7}\text{Li}}{^{6}\text{Li}}\right)_{\text{sample}} \times \frac{^{7}\text{Li}}{^{6}\text{Li}}_{\text{LSVEC}} \times 1000$$

Typically, measured Li isotopic ratios for L-SVEC lie between 13.1 and 13.5, ~10% higher than the accepted $^{7}\text{Li}/^{6}\text{Li}$ value of 12.01. As the measured values for L-SVEC vary by less than 2‰ during the course of a run, it is possible to correct directly to determine $\delta^{7}\text{Li}$ values for bracketed unknowns.

The accuracy of the measurements is assessed through measurements of reference samples JB-2 (+4.5‰) and BHVO-2 (+5‰). In all cases, the measurements are within 1‰ of accepted values in all runs.
Results

The elemental and isotopic data for the Moorea and Societies samples are in Tables 1-4 and Figures 10-17.

Major Element variations

Based on the McDonald and Katsura classification scheme (1964), the samples from Moorea plot within the Hawaiian alkalic basalt field (Figure 10). SiO$_2$ ranges from 46 to 60 wt %. TiO$_2$ contents increase steadily with decreasing MgO contents up to 5 wt %; however, in the most evolved rocks (Benmoreites and Mugearites), TiO$_2$ is less than 1.5 wt % indicating crystallization of magnetite within the magma chamber (Figure 11).

![Figure 10. All Moorea samples plot within the alkalic field (Modified from McDonald & Katsura, 1964).](image-url)
Figure 11. TiO$_2$ contents increase with decreasing MgO. At ~5% Magnesium, titanium decreases sharply indicating the crystallization of magnetite in the magma chamber.

Trace Elements

Concentrations of trace transition metals are consistent with those of alkali basalts. Ni and Cr abundances correlate positively with MgO. Zn abundances range from 95 to 115 ppm. Cu abundances range from 57 to 82 ppm. The Cu/Zn ratio is < 1 (characteristic of alkali basalts; Table 1-2).

Magmas with Ni of 200-300 ppm have likely experienced little olivine crystallization or accumulation (Hart and Davis, 1978; Sun and Hanson, 1975). Ni analyses of the Moorea samples lie within this range and confirm their primitive character. The Moorea samples form a continuous spectrum from primitive basalts to trachytes. As indicated on a plot of Ni vs. TiO$_2$, fractional crystallization appears to be the dominant magmatic process of the formation of the suite of rocks (Figure 12).
Figure 12. Samples from Moorea and other Society islands follow a predicted model for fractional crystallization for a range of $F$ from 1.0 to 0.5. The most evolved Moorea sample erupted when approximately 50% of the magma chamber had crystallized.

*B-Be-Li Concentrations*

Lithium abundances vary from 2.9 to 13.2 ppm and Be contents from 1.0 to 3.0 ppm. Both elements increase with progressive differentiation. (Figure 13). Boron contents are 1.0 – 3.2 ppm. Excluding samples with zeolite alteration, the range in boron abundances is even narrower (1.0 – 2.4 ppm).
Figure 13. Li vs MgO (a) and Be vs MgO (b) contents for Moorea (turquoise squares), and Society Islands (navy squares) with similar trajectories suggestive of similar parental source. Both Li and Be increase with progressive differentiation.
Lithium and beryllium abundance systematics in the Society lavas are similar to those reported for other ocean island basalts. Li and Be abundances both increase with increasing SiO$_2$ and decrease with increasing MgO contents, suggesting that both elements behave incompatibly during differentiation processes that occur at ocean islands. Samples from Moorea and the other Society Islands show broadly similar trajectories, perhaps indicating a similar parental source.

The Li/V ratios average ~0.02 consistently, indicating that Li and V behave similarly in OIBs, just as they do in MORBs and that the Li/V ratios of primitive MORBs and OIBs are similar (Ryan and Langmuir, 1987: Table 3).

B/K$_2$O and B/Be ratios for basaltic lavas are 0.7—1.4 and 0.6—1.3, respectively, while more-evolved samples have somewhat higher values. Comparison to other ocean island basalts (Dostal et al., 1996; Ryan et al., 1996) shows that the ratios are similar to those for other Society Islands lavas and lower than those for St. Helena, Hawaii, Gough and Ascension, as well as analyzed MORB. These low B/Be and B/K ratios are consistent with a mantle source that includes boron-poor subducted materials (Figures 14 and 15).
Figure 14. B/Be ratios range from 0.6-2.0. Primitive Moorea and Society samples have lower B/Be ratios than other ocean island basalts. (Marquesas data are from Dostal et al., 1996. Other OIB data are from Ryan et al., 1996).
Figure 15. B/K₂O ratios range from 0.7-2.0. Moorea values are similar to other Society Islands and lower than those for St. Helena, Hawaii, Reunion and Ascension. Ascension, Gough, St. Helena, Hawaii and Reunion data are from Ryan et al., 1996.
Lithium Isotopes

Samples show an overall range of $\delta^7\text{Li}$ from $+1.5\%$ to $+5.5\%$, with the Moorea sample subset showing the same range in values as that of the other Society islands. These samples all fall within the range of samples from other ocean island basalts from Hawaii, Erebus, Crary, St. Helena, Reunion and Iceland (Tomascak et al., 1999; Chan and Frey, 2003; Ryan and Kyle, 2004) and are similar to values for MORBs (Tomascak and Langmuir, 1999)(Figure 16).

Figure 16. Society samples fall within a range of values for $\delta^7\text{Li}$ similar to those of MORBs, Erebus, and other OIBs. Pribilof, Erebus, MORB, and Reunion from Ryan (2004). Bullenmerri from Nishio (2004).
Society Island samples do not exhibit the range observed in the data for the EMI reservoir by Nishio et al., (2004) or for the forearc serpentinite data from Benton et al. (2004) and have neither exceptionally low or high $\delta^7$Li signatures (Figure 17).

Figure 17. Society samples fall within the upper values of Nishio et al., (2004) data for the EMI reservoir and the serpentinites of Benton et al., (2004) but do not exhibit any range variation.
Discussion and Conclusions

No simple correlations between Loss On Ignition (LOI) and Li isotopes are evident, although it is noted that weathering processes preferentially tend to remobilize and leach out $^7$Li resulting in overall lower $\delta^7$Li values (Pistiner and Henderson, 2003; Huh et al., 2004; Rudnick et al., 2004). The Moorea samples are from a tropical island with high relief, so it is reasonable to assume that all samples have been exposed to some weathering. Oddly, the sample with the most noticeable alteration, M01AIR1A, has one of the highest $\delta^7$Li values at +4.6 ‰. M01FISH2D, one of the most primitive samples, appears to be very fresh with some surface zeolites, but it has a $\delta^7$Li value of only +1.8 ‰. As zeolite formation and associated alteration is highly localized, it may be that even visibly weathered samples contain fresh horizons, which may be preferentially sampled during cutting, crushing and powdering; while ostensibly fresh sample segments may nonetheless preserve evidence of concealed alteration. Clearly, the presence of any zeolites in such samples is cause for concern in terms of obtaining a "magmatic" Li isotopic signature. The relatively limited range of values for the Moorea samples, and their similarity to those of fresh Society Island basalts, indicates that absent fresher samples, older lavas may be used to define Li isotopic minima.

As with other OIBs, boron and boron ratios are very low (the lowest compared with all other OIBs examined thus far) for Moorea and other Society Island samples.
indicating a source region that is depleted in B. Li and Be abundances are also similar to other OIBs pointing to similar behavior and source abundances.

Li isotope ratios in fresh lavas are similar to Hawaii, Erebus and several other ocean islands sites, but not to St. Helena or the Pribilof Islands. The total $\delta^7$Li range of measured intraplate lavas, at $\sim$4‰, is similar to that observed in MORBs, and offset to only slightly higher values. My samples from the Society Islands are very similar in their $\delta^7$Li to MORBs.

A question inherent in these data is why Li isotopes suggest little difference between the source regions of the Society Islands and MORBs, while B data (in particular B/K ratios) point to significant differences between the Society Islands source mantle and that of MORBs or other intraplate lavas, such as Hawaii (Figure 18).

Entrainment of upper mantle material into the plume (see Duncan, 1994) is a viable means for producing largely similar $\delta^7$Li values in such volcanic systems. The mean $\delta^7$Li is +3‰ for Society Island samples, while published data for Hawaiian lavas are around +5‰ (Tomascak et al., 1999; Chan and Frey, 2003). Both are within error of average MORB values (at +4‰: Tomascak and Langmuir 1999). Entrainment means that variable amounts of a MORB source mantle is sampled during hotspot melting. The more upper mantle material entrained, the greater the dilution of the plume signature in the resultant melts, and the more MORB-like the lavas become.
Figure 18 A) Basalts erupted at the Society Island plume are alkalic in composition due to lower temperatures, higher pressure, and/or smaller degree of partial melting. B) Typically, tholeiitic basalts are erupted from the Hawaiian plume due to higher temperatures, lower pressure and/or higher degrees of partial melting. The similar \( \delta^{7}{\text{Li}} \) values imply that the upper mantle and deep mantle have similar Li isotopic compositions. Whereas, the differing B/K ratios imply that these plumes are sampling mantle sources with different B/K signatures.
Farnetani and Richards (1995), however, suggest that mantle plumes derived from the deep mantle entrain only a very small fraction of surrounding mantle into the region of the plume that undergoes partial melting. Vertical plume tails with a strong viscosity contrast can entrain only a very small percentage of surrounding mantle (Stacey and Loper, 1983; Davies, 1999).

The boron data on the Society Island samples also make the entrainment explanation problematic. B/K ratios for the Society Islands are ~1. Hawaii B/K ratios are ~5, and MORBs are ~10. Dilution of the plume signal by entrainment and melting of upper mantle material should also cause B/K ratios to become similar to those of MORBs. The differing B/K ratios of these two plumes thus imply that these plume sources are sampling mantle sources with very different B/K signatures.

Instead of dilution by entrainment, a more viable explanation may be that the two possible mantle sources for both the Society and Hawaii plumes and the upper mantle have relatively similar Li isotopic compositions. Thus, it may be that recycled oceanic crust or sediments have only a minimal influence on the Li isotope signatures of the Society Island lavas. Data from the Society Islands suggest that δ7Li values for subducted altered crust reported by Bouman et al. (2004) may be a more accurate representation of the subducted δ7Li signature than original heavy values for altered crust reported by Chan et al. (1994). The relatively low δ7Li (~+5‰) seen in high-boron lavas from Panama (Tomascak et al., 2000) and in the serpentinite muds from the Mariana forearc (~+6‰; Benton et al., 2004) also support a modest δ7Li signature coming from subducted slabs.
PART II

Instructional Modules

Introduction

Quantitative literacy as described by the International Life Skills Survey is an aggregate of skills, knowledge, beliefs, dispositions, habits of mind, communication capabilities, and problem solving skills that people need in order to engage effectively in quantitative situations arising in life and work (Briggs, 2004). Hyman Bass, American Mathematical Society President and former chair of the Mathematical Sciences Education Board, has noted that quantitative literacy must be taught across the curriculum, stating “while mathematics and statistics contribute central knowledge and skills, other disciplines provide the contexts which are so important for quantitative literacy (Steen, 2004).” During workshops for geoscience educators, however, it is repeatedly said that students have poor mathematical skills and tend to avoid mathematics whenever possible (Vacher, 2001). Developing material that contains mathematics to increase the quantitative literacy of students, therefore, should be a goal for all geoscience educators.

In my experience as a student and teaching assistant, I found that one of the larger challenges for students in undergraduate petrology classes is learning how to think quantitatively about magmatic processes in the context of multiple geochemical variables. This ability is necessary to understanding how major and trace elements vary among petrogenetically related igneous rocks. It is also crucial in distinguishing igneous...
students trying to understand the rationale underlying the interpretive procedures.

I have prepared a series of Power Point modules for use in Petrology classes to aid in teaching fractional crystallization and partial melting processes in the mantle. These modules are patterned after modules of geological/mathematical problem solving developed by H.L. Vacher and posted on the website of the Washington Center for Improving the Quality of Undergraduate Education (The Evergreen State College) and the Science Education Resource Center (Carleton College).

The modules I have developed are intended for use in junior/senior level petrology or mineralogy/petrology courses where magmatic processes are normally covered. The modules are designed to be performed by students as self-paced lab activities or homework assignments. The goal of the modules is to help students grasp concepts that are not easily understood through lecture or reading. The modules ask the student users to graph geochemical data for a suite of rocks and determine whether partial melting, fractional crystallization, or some other process dominated the formation of the suite.

Excel spreadsheets are embedded in the modules to show students the value of solving a problem once, then using the same spreadsheet for rapid recalculations. Use of spreadsheets does not require any computer programming skills; therefore, only basic computer literacy is needed. A study by Smith (1992) suggests three possible outcomes
for students using Excel: (1) Reversal of lack of interest in mathematics; (2) improvement of technological literacy and enhancement of career preparation; (3) revitalization of mathematical skills through problem solving. The content of these modules sharpens mathematical skills by integrating algebra, logarithms, unit conversion, and graphing.

Available geochemical modeling software, such as the Geochemist’s Workbench, can be expensive. Such software is typically designed for researchers knowledgeable of geochemistry, as opposed to undergraduates learning geochemistry for the first time. Even more advanced students may be challenged in becoming proficient with these geochemical programs. This software, along with web-based tools such as the MELTS program, is best suited to train students to become geochemists. Excel, on the other hand, is available on most computers, and students are often already acquainted with its operation. The use of Excel in the modules I have developed not only helps students to understand magmatic processes, but also helps students to develop skills that they can use across a variety of courses and disciplines.

A study by Fratesi and Vacher (2004) of articles in the *Journal of Geoscience Education*, the principal journal of earth-science teachers in the US, identified 38 articles using spreadsheets, while less than a handful discuss the use of more sophisticated mathematics-oriented computer programs such as MATLAB or *Mathematica*. Geology provides the context needed to sharpen and develop mathematical skills. One of the earliest articles by Ousey (1986) introduces the idea of spreadsheets for modeling groundwater flow, an important geologic phenomenon. Spreadsheets allow students to concentrate on the subject matter rather than the software (Beare, 1993). Students who
are proficient with Excel and the mathematics within the modules attain life-long skills that transfer to other fields in geology and even other disciplines.
Module JAH1A and JAH1B

Fractional Crystallization

Part JAH1A of the fractional crystallization module introduces the process of fractional crystallization through a series of explanations and calculations of partition coefficients, bulk distribution coefficients, compatible vs. incompatible elements, and the Rayleigh fractionation equation. The goal is to develop a way by which one can evaluate whether progressive fractional crystallization relates the samples in a suite of volcanic rocks and, if it does, to calculate for each sample the extent of fractional crystallization that occurred before the lava erupted.

Module calculations use trace-element data. Trace elements simplify looking at magmatic processes quantitatively, because their low concentrations (in the ppm range) mean they do not play a role in the stoichiometry of crystallizing mineral phases. Trace elements, therefore, substitute into crystals that are forming as a function of temperature, pressure, and the overall chemical compositions of the mineral and melt. Some minor elements, such as Ti, Mn, and K, behave as trace elements in basaltic rocks and are not major stoichiometric constituents of the minerals that are forming (Best, 1982). It is possible to constrain the nature of the source rock, identify what minerals (and how much of each) melted to form a magma, and/or identify the proportions of different minerals that may have crystallized by looking at trace-element variations in a suite of volcanic igneous rocks.
The data set used in the module draws partly from the collected geochemical data in Part I of this thesis because it is important that a suite of rocks from the same source is used when using geochemical data to look at magmatic processes. The module begins by defining fractional crystallization and discussing partition coefficients \((D_{\text{mineral/melt}})\) and bulk distribution coefficients \((D_{\text{solid/melt}})\) and incorporates a \(D_{s/l}\) calculation in a spreadsheet (slides 1-7). With the introduction of the Rayleigh fractionation equation and a spreadsheet calculation (slides 8-10), students determine if a single rock has undergone fractional crystallization in its formation. Calculating the percentage of fractionation for each element in a rock, however, is extremely time consuming. Looking at the geochemistry of a suite of rocks, presumably from the same source, is a much better idea.

In slides 11 and 12, students read a discussion about the compatibility of elements. Whether an element is compatible or incompatible depends completely on what minerals are present in the melt. For example, when olivines and pyroxenes are crystallizing, Sr is an incompatible element. However, as soon as plagioclase begins to crystallize, it incorporates Sr into its crystal structure and Sr then becomes a compatible element. The students design a spreadsheet and create a graph to help them visualize the effects of compatibility.

The last section of part 1A of the module (slides 13-16) discusses forward modeling. The students design a spreadsheet to calculate predicted values for a model of fractional crystallization and then plot the given data on the model. A list of questions posted at the end of the module can be used as a homework assignment.

Part B introduces graphical techniques as a means of identifying and calculating fractional crystallization without making some assumptions that are necessary in part A.
Graphical methods rather than repetitive calculations are an excellent way to test for fractional crystallization in a given suite of samples, and so students learn to examine graphs to determine if fractional crystallization is the dominant process in the formation of the suite.

In a closer look at the Rayleigh fractionation equation (slides 3-6), the module applies logarithms and a little algebra to show students that this equation can be configured as a line in $\log x$ vs. $\log y$. Students then plot the data on a log-log graph. Another spreadsheet calculates the predicted values of fractional crystallization and plots them on the same graph showing that the samples not only fall along a straight line, but a line that can be predicted.

The end of the module includes three data sets with instructions for students to plot the data and determine from the plots if fractional crystallization is the dominant process in the formation of the suite of samples. Included is a set of questions that can be used for assessment to determine student understanding of the process of fractional crystallization and its identification from scrutinizing graphs.
Module JAH2A and JAH2B

Partial Melting

Part JAH2A of the module introduces the process of magma generation due to partial melting. Part JAH2B introduces the Shaw equation and ways to identify partial melting. The goal is to develop a way by which one can evaluate whether partial melting is the dominant process in a suite of volcanic rocks and, if it is, to calculate how much melting has occurred. A statement at the beginning of the module urges students to first work through the fractional crystallization module (JAH1) and to have a basic understanding of phase diagrams.

Once again, the module uses trace elements because they are an excellent means of looking at magmatic processes due to their low concentrations. Therefore, it is possible to constrain the nature of the elements in the partial melt.

The module uses data from the geochemical analyses in part I of this thesis along with other geochemical data from the literature. The module begins by discussing how decreased pressure, increased temperature and change in chemical composition can each produce partial melting (slides 3-6). A small animation (slide 7) helps students visualize the process by which incompatible elements are enriched in the melt and compatible elements are enriched in the mantle.

Slides 8-10 ask students to recall their knowledge of phase diagrams and calculate the percent composition by using the lever rule. This part of the module aims for
students to see that melting does not move very far off the eutectic; a slight increase in temperature produces a large increase in melt.

The second part of the module (JAH2B) introduces the Shaw equation for partial melting. Graphs walk students through the concept of compatibility but in much less detail than in the module on fractional crystallization. Several slides explain the type of samples to analyze, the elemental data to use, and how to determine graphically whether partial melting is the dominant process for a given suite of rocks. The module ends with a few questions. Particularly instructive are questions that refer the students to new data sets. The students must review these data sets and determine if partial melting is an appropriate interpretation for each of them. Students must then calculate the percent of melting for any data set that represents partial melting.
Evaluation of Fractional Crystallization Modules

Laura Wetzel of Eckerd College tested modules with similar design but different geological content during the Fall 2003 semester. (Wetzel et al., 2003). During the Fall 2004 semester, I tested modules JAH1A and JAH1B at the University of South Florida to assess improvements in student understanding of the subject of fractional crystallization. I chose two upper-level Geology courses, Solid Earth 1 (Mineralogy/Petrology) and Computational Geology (a course specifically designed to develop quantitative literacy).

At the beginning of the semester, each class of students answered ten questions, four of which we used to evaluate the effectiveness of the module. The students of the Solid Earth class (control group) received a lecture on fractional crystallization, but did not review the module or complete any assignments. The students in Computational Geology received the same lecture as preparation but had to work through the module and write a paragraph evaluating its contents. I informed both classes that they would be held responsible for the material on future exams.

One week after the lecture/assignment, I asked the same questions posed pre-lecture to assess improvements in student understanding of the concepts and application of fractional crystallization. Results are as follows:
Question 1: What is fractional crystallization?

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Question 2: What is the difference between an incompatible element and a compatible element?

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Question 3: What is the difference between a partition coefficient and a bulk distribution coefficient?

<table>
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</table>
Question 4: When plotting a suite of samples that are dominated by fractional crystallization, what type of trend would you expect to see on a linear graph? on a logarithmic graph?

<table>
<thead>
<tr>
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Comments on Evaluation Design

Students in the control group (Solid Earth I) are mostly sophomores and juniors. Three students in the Solid Earth class simultaneously enrolled in Computational Geology. Their participation in the evaluation was limited strictly to their responses on the questions posed in Solid Earth; I did not use their responses in Computational Geology in the evaluation.

Of the 14 students in Computational Geology, only one had not yet taken Solid Earth I. Most of the students in this class are at a senior level, and all of them have worked through several modules on various subjects. They are not only familiar with module design, but also with Excel spreadsheets.

Only students that attended all three classes for the pre-questions, lecture, and post-questions were included in this study. I told both classes at the beginning of each lecture that they would be responsible for knowing the material for upcoming exams. I designed the lecture to cover the material presented in the modules and presented the material in the same manner for both classes.

The students in Computational Geology worked through the module and evaluated it, but I did not require them to turn in a homework assignment. I told the students to contact me if they had any questions while working through the module. Only one student asked for assistance.

A problem in the approach with the Computational Geology class arose when several students commented that they had not had time to work through the module prior
to taking the exam. Consideration had to be taken that we inadvertently tested the seriousness of the students rather than the module. I addressed this issue by asking the students to fill out a questionnaire that included a check box stating that they had not worked through the module prior to taking the test. Of the sixteen students that filled out the questionnaire, 11 admitted that they had not worked through the module. Of the five students that did work through the module, two were in the Solid Earth I class and their results were not considered. So, only three students actually worked through the module.
Results

Students in Solid Earth I showed only a slight increase in understanding the material presented in the lecture, while students in Computational Geology demonstrated a higher increase in understanding (Figure 19). The module will be tested further, explicitly in a Min/Pet class with the same approach as the Computational Geology class, to see how students at this level benefit from the information.

Figure 19. Results of questions posed to students both pre- and post-lecture regarding the process of fractional crystallization.

The results of the data above suggest that working through a module can greatly enhance student knowledge of concepts that are hard to understand through lectures or readings. However, as I later found out, only three of the students worked through the module. On the other hand, two of these did not answer any questions correctly pre-lecture but answered all four questions correctly after working through the module. The third student answered 50% of the questions correctly. Results for the three students who carried out the experiment as it was intended are certainly encouraging.
Conclusions

The fractional crystallization module appears to increase understanding of the subject matter. However, further testing of the module is required. When retested, students should be given more time to work through the module and an assignment should be given to make the students more accountable. Telling them that the material would be covered on an exam did not seem to motivate them enough to work through it.

Because the modules are designed to be self-paced and worked through individually outside the classroom, they can be an excellent supplement to lectures and may replace textbook readings.

Another aspect noticed during the testing of the module is that modules may be a valuable tool in exposing the deficiencies in student knowledge of basic mathematical skills.

I did not test the partial melting module, but it is scheduled to be tested in Solid Earth I at the University of South Florida in the Fall of 2005 along with an additional test of the fractional crystallization module. Other modules that may be appropriate for Petrology courses are magma mixing (in the works) and assimilation.
References


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### Appendix I

Table 1. Major and trace element data from senior thesis (Harden, 2002 unpublished) for Moorea samples collected in 2001.
<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂ (wt%)</th>
<th>Al₂O₃ (wt%)</th>
<th>FeO (wt%)</th>
<th>MgO (wt%)</th>
<th>MnO (wt%)</th>
<th>CaO (wt%)</th>
<th>K₂O (wt%)</th>
<th>Na₂O (wt%)</th>
<th>TiO₂ (wt%)</th>
<th>Total (wt%)</th>
<th>Sr (ppm)</th>
<th>Cr (ppm)</th>
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<th>Ni (ppm)</th>
<th>Sc (ppm)</th>
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Table 2. Major and trace element data for Moorea samples collected in 2003.
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<th>Be (ppm)</th>
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Table 3. Li, Be, and B analysis for 20 samples from Moorea and 13 samples from other Society Islands as indicated.

Table 4. δ⁷Li values for 6 samples from Moorea and 6 samples from other Society Islands. The samples from Moorea were chosen based on increasing SiO₂ to see temporal variations of δ⁷Li within the formation of an island and to note the affects of weathering. Samples from the other Society Islands were chosen based on low SiO₂ to see temporal variation within the formation of an island chain.
When magma cools and crystallizes in the Earth’s interior, the growing crystals incorporate selected chemical elements of the magma into their structure. As a result, the magma is depleted in those elements. On the other hand, elements that are not incorporated in the growing crystals are enriched in the magma. Separation of crystals from the liquid by settling, floating, or adhering to the magma chamber walls produces a magma with a different chemical composition. This process is called fractional crystallization.

Fractional crystallization causes basaltic magmas to evolve into basaltic-andesitic magmas. Further crystallization pushes the magma toward an even more silicic composition.

Quantitative Concepts and Skills
Manipulating equations
Weighted average
Forward modeling

Judy Harden, University of South Florida
Part A introduces the process of fractional crystallization through a series of explanations and calculations of partition coefficients, bulk partition coefficients, compatible vs. incompatible elements, and the Rayleigh fractionation equation. The goal is to develop a way by which we can evaluate whether fractional crystallization has occurred in a suite of volcanic rocks and, if it has, to calculate how much fractional crystallization has occurred.

Part B introduces graphical techniques as a means of identifying and calculating fractional crystallization without making some assumptions that are necessary in part A.

About this module

This module consists of two parts, A and B.

Part A

Part B

About this module

This module consists of two parts, A and B.

Part A introduces the process of fractional crystallization through a series of explanations and calculations of partition coefficients, bulk partition coefficients, compatible vs. incompatible elements, and the Rayleigh fractionation equation. The goal is to develop a way by which we can evaluate whether fractional crystallization has occurred in a suite of volcanic rocks and, if it has, to calculate how much fractional crystallization has occurred.

Part B introduces graphical techniques as a means of identifying and calculating fractional crystallization without making some assumptions that are necessary in part A.

PREVIEW

Data in this module are from samples collected from the island of Moorea. Moorea is part of the Society Island Chain, French Polynesia. Two of the better-known islands of the chain are Tahiti and Bora Bora.

Slides 4-7 explain the difference between partition coefficients and bulk partition coefficients.

Slides 8-10 introduce the Rayleigh fractionation equation.

Slides 11-12 explain compatibility.

Slides 13-16 use forward modeling to look for fractional crystallization.
Partition coefficients

The composition of crystallizing minerals changes continuously as the composition of the remaining melt changes. Using major element geochemistry to calculate the effects of fractional crystallization is complicated due to the changing composition of the melt. Different phases of mineral growth preferentially incorporate or exclude trace elements to a greater extent than they do major elements. Therefore, trace elements provide a useful fingerprint to constrain origins of melt systems and their evolutionary processes.

Trace elements are elements that represent <1wt.% of the rock composition and are typically in the ppm range.

The concentration of a trace element in a mineral is proportional to the concentration of the trace element in the liquid from which it grew. This principle is represented by the partition coefficient ($K_D$), which is defined as follows:

$$K_D = \frac{\text{concentration of trace element in mineral}}{\text{concentration of trace element in melt}}$$

Partition coefficients in a mineral

Trace elements are incorporated into some minerals more than they are into others. This phenomenon is addressed by the concept of compatibility. Compatibility results from the effects of the structure of the mineral and the ionic radius and charge of the element. For example:

$K_D$ of nickel in olivine is 10, meaning that nickel is compatible and will fit into the structure of olivine. In contrast, the $K_D$ for nickel in plagioclase is 0.07, meaning that nickel is incompatible and will likely not fit into the structure of plagioclase.

Suppose you have a huge caldron of vegetables (magma chamber) and you decide to make cucumber and onion salad (olivine). When you pull chopped cucumber and onion from the caldron, you may likely mix in some cherry tomatoes (Nickel) because they fit well (compatible) into the structure of what you are making. Later, however, you decide to make succotash (plagioclase). You pull corn and lima beans from the caldron, and it is unlikely that you will mix in any cherry tomatoes (Nickel) because they just don’t fit as well (incompatible) into the structure of succotash. Sufferin’ Succotash!

$K_D$ relates to the concentration of a trace element in a mineral. What about rocks?
Bulk Partition Coefficient - $D$

The bulk partition coefficient addresses the amount of trace element in a rock.

$$D = \frac{\text{concentration of trace element in mineral assemblage}}{\text{concentration of trace element in melt}}$$

To calculate $D$, you need to know the mass fraction ($X$) of the element in each mineral and the $K_D$ value for the element in each of the minerals.

$$D = X_a K_{D,a} + X_b K_{D,b} + X_c K_{D,c}$$

where $a, b, c$ are different minerals in the assemblage. $D$ is the sum of the weighted average of each element in the mineral assemblage.

$K_D$ values are derived empirically. A good website to find these values is the Geochemical Earth Reference Model (GERM):


### Calculating $D$

Calculate the bulk partition coefficient for nickel ($D_{Ni}$) in a rock that contains 10% olivine, 42% clinopyroxene, 45% plagioclase, and 3% magnetite. $K_D$ values are 10, 3, 0.07, and 48 respectively.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
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<tr>
<td>8</td>
<td></td>
<td>$D =$</td>
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</table>

According to your answer, will Ni stay in the melt or be incorporated into the crystal composition of the rock?

Use the sumproduct function in this cell.

Once you have set up the spreadsheet to calculate $D_{Ni}$ for the mineral assemblage, use the GERM website to find the values for titanium ($K_{D,Ti}$) in the same mineral assemblage and calculate $D_{Ti}$. Will Ti stay in the melt or be incorporated into the crystal? Save this spreadsheet, because you will use a similar calculation later in the module.
Rayleigh Fractionation

To see how trace-element concentrations change as a result of crystallization, we use the Rayleigh fractionation equation shown below. Minerals that crystallize out of a melt and the trace elements they contain are removed from chemical contact with the residual liquid. Therefore, the concentration of the trace element in the remaining liquid \( (C_I) \) is lower than the original concentration \( (C_o) \) of the trace element. \( C_o \) is sometimes called the **parental source**. \( C_I \) depends on \( C_o, D, \) and the fraction of remaining liquid \( (F) \). Geochemical data of rock samples are the values we use for \( C_I \).

\[
C_I = C_o F^{(D-1)}
\]

Suppose we want to track the concentration of a trace element in a rock formed during fractional crystallization. We can show this variation on a graph as a function of crystallization progress using a ratio of \( C_I/C_o \). To see how, rearrange the equation to:

\[
\frac{C_I}{C_o} = F^{(D-1)}
\]

See what happens when we insert values for \( D \).

<table>
<thead>
<tr>
<th>( D )</th>
<th>( C_I/C_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1/( F )</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>( F )</td>
</tr>
<tr>
<td>3</td>
<td>( F^2 )</td>
</tr>
</tbody>
</table>

Calculating \( F \)

We know \( C_I \) from geochemical analyses of our rocks. We calculated \( D \). Often one assumes a value for \( C_o \) by using calculated values for spinel peridotites (representative of the Earth’s mantle). One can find these values on the GERM website. For this module, we set \( C_o \) equal to the value of \( C_I \) in our most magnesium-rich sample. With this assumption, we can develop a spreadsheet to calculate \( F \).

**Problem**

A sample collected from Moorea contains 61 ppm Copper \( (Cu) \) and 389 ppm Nickel \( (Ni) \). Assume the parental basalt contained 56 ppm Cu and 517 ppm Ni. What is the value for \( F \) if \( D_{Cu} = 0.17 \) and \( D_{Ni} = 3.73 \)?

<table>
<thead>
<tr>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Cu</td>
<td>Ni</td>
</tr>
<tr>
<td>3</td>
<td>( C_I )</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>( C_o )</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>( D )</td>
<td>0.17</td>
</tr>
<tr>
<td>6</td>
<td>( D-1 )</td>
<td>-0.83</td>
</tr>
<tr>
<td>7</td>
<td>( F )</td>
<td></td>
</tr>
</tbody>
</table>
Calculating $F$

The answer reflects the portion of the original melt present in the magma chamber when the fractionated magma erupted to form this sample.

When $F = 1$, no crystallization has occurred (100% of the melt remains). In contrast, $F = 0.1$ means that 90% of the original melt has crystallized.

You should not expect every element to be exactly 0.90. Why?

Identical values testify that (a) fractional crystallization has occurred and (b) your geochemical analysis is accurate.

Calculating a value of $F$ for each element in each sample that you have collected would be very time consuming. There is a better way of finding the percent of fractionation for your samples.

Compatibility

Before we try to find $F$ for a suite of rocks, we must fully understand compatibility. Create a spreadsheet now to see how $C_i/C_o$ changes with different values of $D$ and $F$. Then plot your results as a function of $F$ for each $D$ value. Make the $y$-axis a logarithmic scale.

The values you calculate are the predicted values for fractional crystallization for any given $D.$

<table>
<thead>
<tr>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Cu</td>
<td>Ni</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$C_i$</td>
<td>61</td>
<td>389</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$C_o$</td>
<td>56</td>
<td>517</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$D$</td>
<td>0.17</td>
<td>3.73</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$D-1$</td>
<td>-0.83</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$F$</td>
<td>0.90</td>
<td>0.90</td>
<td></td>
</tr>
</tbody>
</table>
Compatibility

What you should discover with your graph is that compatible elements \( (D > 1) \) show depletion in the melt \( (C_i/C_o < 1) \). Depletion occurs more rapidly the higher the value for \( D \). Incompatible elements \( (D < 1) \) show enrichment in the melt \( (C_i/C_o > 1) \).

![Graph showing depletion and enrichment of elements](image)

Compatible elements preferentially enter the solid phase while incompatible elements preferentially remain in the liquid phase.

Using previously designed spreadsheets to calculate ratios

Now we are ready to analyze a suite of samples to test whether fractional crystallization is the dominant process of their formation. The process we use here illustrates forward modeling where values are predicted and then tested to see if real data fit the model.

Use the spreadsheet you created in Slide 11 to predict the \( C_i/C_o \) values for Ti and Ni with \( D \) values of 0.32 and 3.73 respectively. (Just type the new values for \( D \) in your chart and let Excel do the work!)

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>Ti</td>
<td>Ni</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>D</td>
<td>0.32</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>D-1</td>
<td>-0.68</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>Ti/Ti_o</td>
<td>Ni/Ni_o</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

After you obtain the values for \( Ti/Ti_o \) and \( Ni/Ni_o \), plot them on a graph with the Ni ratio on the \( y \)-axis and the Ti ratio on the \( x \)-axis.

To see the maximum compositional variation, we use a compatible element and an incompatible element.
What the graph tells us.

Your graph should produce a curve that indicates that Ti increases in abundance while Ni decreases.

At this point, 90% of the original melt remains, while 10% of the original melt has crystallized.

Now we’re ready for our suite of samples!

Adding real data

Create a new spreadsheet as shown to the right to calculate the concentration ratios for real samples collected from Moorea. The samples were analyzed on a Direct Current Plasma – Atomic Emission Spectrometer (DCP-AES) to obtain the values of major and trace elements for each sample.

Now plot the calculated sample ratios on the graph that you just made with the predicted ratios. Samples that plot on the curve confirm a dominant process of fractional crystallization. Which samples appear to be affected by some process other than fractional crystallization?
Samples that plot off the curve owe their origins to some other process.

This plot allows you to see what samples were erupted after a percentage (blue dots) of fractional crystallization took place.

End of the module questions

1. Calculate $F$ for a rock that contains 3.03 (wt %) Ti and 392 ppm Ni with a composition of 10% olivine, 45% pyroxene, and 45% plagioclase. Assume that the parental source contained 2.56 (wt %) Ti and 517 ppm Ni. Is Ti a compatible or incompatible element?

2. Suppose you calculate values for $F$ on slide 10 and they don’t match. What could be some possible explanations for the discrepancy?

3. How sensitive is $D$ to changing rock composition?

4. What happens when $D = 1$?

5. Since $F$ represents the amount of remaining liquid, $(1-F)$ is the amount of crystallization that has occurred. Add a column to the spreadsheet from slide 11 to calculate $(1-F)$. Plot each of the D values vs. $(1-F)$. What observations can you make regarding this graph?

6. What are some possible explanations for the Moorea samples that do not plot anywhere on the predicted fractionation curve (green dots on graph of slide16)?

7. On the graph of Slide 16, the samples end at the point where ~45% of the original magma had crystallized. Would you expect to find erupted rocks further down the curve? Explain your answer.

8. Look through geologic literature and find geochemical data for a suite of rocks from another island in a chain such as Hawaii, Canaries, Galapagos. Show whether fractional crystallization was a dominant process in the formation of those rocks.
In module 1A we demonstrated various ways of determining whether fractional crystallization was a dominant process in the formation of a suite of rocks. This module introduces the use of logarithms as a shortcut method of testing for fractional crystallization.

This module should be worked only after working through module 1A.

Quantitative Concepts and Skills
Manipulating equations
Logarithmic graphing

PREVIEW
Slides 3-6 Manipulate the Rayleigh fractionation equation to produce the equation of a straight line on a log-log graph

Slide 7 provides data for use on a log-log graph.

Slides 8-10 show a means of double checking your assumptions about fractional crystallization.

Slides 11-16 contain end-of-module questions in the form of data sets.

Slide 17 Pre- and Post-module questions

Note: To save time and to minimize errors, the data sets in this module are in Excel format. This means that when you are in Power Point in normal view (not in the slide show), you can double click on the data and Excel will open. You can then copy the data to a new Excel spreadsheet rather than re-type the entire data set. At that point, you can manipulate the data by sorting or any other process.
Graphical methods rather than repetitive calculations are an excellent way to test for fractional crystallization in a given suite of samples. Using the graph made in slide 16 of module 1A requires that we know $C_o$ and $D$ for the trace elements in order to see if our samples follow a predicted curve for fractional crystallization. By using the technique in this part of the module, we no longer need to know $C_o$ and $D$.

Logarithms and a little algebra make it possible to test whether fractional crystallization is a dominant process in the formation of a suite of rocks. It’s as easy as plotting the data on a log-log graph. Always use a compatible and incompatible element with the largest range in concentration.

Using logarithms for graphing purposes

To see how the method is going to work, we start with the Rayleigh fractionation equation.

$$C_f = C_o F^{(D-1)} \quad (1)$$

Using logarithms for graphing purposes

Take the logarithm of equation 1.

$$\log C_f = \log C_o + (D - 1) \log F \quad (2)$$

Substitute the element of interest into equation 2, and do the same for the second element of interest.

$$\log Ti_i = \log Ti_o + (D_{Ti} - 1) \log F \quad (3a)$$
$$\log Ni_i = \log Ni_o + (D_{Ni} - 1) \log F \quad (3b)$$

Now, solve equations 3a and 3b for $\log F$.

$$\log F = \frac{\log Ti_i - \log Ti_o}{D_{Ti} - 1} \quad (4a)$$
$$\log F = \frac{\log Ni_i - \log Ni_o}{D_{Ni} - 1} \quad (4b)$$

Set equations 4a and 4b equal to each other and solve for $\log Ni_k$.

Before proceeding, write down your equation.
Using logarithms for graphing purposes

Does your equation look like the equation below? If it doesn’t, review the rules of logarithms and try again.

\[
\log N_i = \left( \frac{D_{Ni}}{D_{Ti}} - 1 \right) \log T_i + \log N_o - \left( \frac{D_{Ni}}{D_{Ti}} - 1 \right) \log T_o
\]  \hspace{1cm} (5)

The website listed below offers easy to understand explanations of logarithm rules.

http://www.purplemath.com/modules/logrules.htm

Using logarithms for graphing purposes

Although this equation 5 may look complicated, it is merely the equation of a straight line.

\[
\log N_i = \left( \frac{D_{Ni}}{D_{Ti}} - 1 \right) \log T_i + \log N_o - \left( \frac{D_{Ni}}{D_{Ti}} - 1 \right) \log T_o
\]

Because of this relationship, we can say that the dominant process of formation for a suite of samples that produce a straight line trend on a log-log graph is consistent with fractional crystallization.
Using the following samples from Moorea, create a plot of the samples on a log-log graph. You can see that a straight line trend occurs and we can say that the samples are consistent with fractional crystallization processes during the formation of this suite of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti (wt%)</th>
<th>Ni (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FISH2D</td>
<td>2.70</td>
<td>395</td>
</tr>
<tr>
<td>LIN-049</td>
<td>2.56</td>
<td>517</td>
</tr>
<tr>
<td>FISH1 A</td>
<td>2.93</td>
<td>389</td>
</tr>
<tr>
<td>T1A</td>
<td>2.93</td>
<td>298</td>
</tr>
<tr>
<td>FISH2B</td>
<td>2.89</td>
<td>385</td>
</tr>
<tr>
<td>FISH1B1</td>
<td>3.06</td>
<td>369</td>
</tr>
<tr>
<td>FISH2A</td>
<td>3.03</td>
<td>383</td>
</tr>
<tr>
<td>PK19N</td>
<td>2.74</td>
<td>464</td>
</tr>
<tr>
<td>B2C</td>
<td>3.00</td>
<td>338</td>
</tr>
<tr>
<td>AIR 1A</td>
<td>3.24</td>
<td>284</td>
</tr>
<tr>
<td>T2A</td>
<td>2.51</td>
<td>482</td>
</tr>
<tr>
<td>20</td>
<td>2.56</td>
<td>498</td>
</tr>
<tr>
<td>11</td>
<td>2.62</td>
<td>491</td>
</tr>
<tr>
<td>10</td>
<td>2.74</td>
<td>508</td>
</tr>
<tr>
<td>B1A</td>
<td>3.18</td>
<td>190</td>
</tr>
<tr>
<td>B2A</td>
<td>3.96</td>
<td>325</td>
</tr>
<tr>
<td>PK9N</td>
<td>3.44</td>
<td>100</td>
</tr>
<tr>
<td>B2B</td>
<td>4.01</td>
<td>105</td>
</tr>
<tr>
<td>G9</td>
<td>3.59</td>
<td>285</td>
</tr>
<tr>
<td>T2A</td>
<td>3.34</td>
<td>235</td>
</tr>
<tr>
<td>PK20N</td>
<td>3.69</td>
<td>112</td>
</tr>
<tr>
<td>QA</td>
<td>2.71</td>
<td>277</td>
</tr>
<tr>
<td>LIND</td>
<td>3.71</td>
<td>100</td>
</tr>
</tbody>
</table>

We can also do a simple calculation to check if our samples follow a predicted trend.

Log-log graphs

Modify the spreadsheet you created for slide 13 in part 1A of this module to include the Co values for Ni and Ti concentrations. You have already calculated F(D-1) (same as C/Co); now multiply it by the given Co values to solve for C. This will allow you to see the predicted sample values (not ratios) for the given parental concentrations that you can then compare with real sample values.

The parental magma (Co) is the most primitive (highest magnesium, lowest silica) found in an area. It is the one from which we assume all others have been derived.

Now, plot the predicted sample values on a logarithmic graph.
Log-log graphs

From the graph, we can see that the Moorea samples not only form a straight line trend, but they also fall along a line that we predict for fractional crystallization processes.

The Moorea samples all plot along the trend of this line except for the six samples that you have already discovered have been affected by some other process.

What about the slope of the line?

Calculating slope of logs

Using the predicted values you calculated, or picking two points from the line on your logarithmic graph (we used the second and third points), calculate the slope of the line. The logarithmic form of the Rayleigh equation says the slope is \( \frac{D_{\text{Ni}} - 1}{D_{\text{Ti}} - 1} = \text{slope} \). Using the \( D \) values from slide 8, you should calculate a slope of -4.0.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>x</td>
<td>2.75</td>
<td>2.98</td>
</tr>
<tr>
<td>4</td>
<td>y</td>
<td>387.77</td>
<td>281.14</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>m</td>
<td></td>
</tr>
</tbody>
</table>

Remember the rules of logarithms in your calculation!

If your slopes don't match, double check your graph points and your math. They must match!

Now you're ready to plot data and decide whether fractional crystallization is the dominant process for the suite of rocks that you are working with!
1. You may plot samples on a log-log graph and two different trajectories may be evident as in the graph below of additional data from Moorea. What are some explanations?

2. Add a trend line to the graph you made for slide 9. Display the equation and the R² value. What is the slope of the line?

3. The following slides contain data for several different suites of rocks. For which of the suites of rocks, if any, are the chemical data consistent of fractional crystallization? For which suites of rocks, if any, do the chemical data contradict fractional crystallization as the dominant process?

Sample set 1: The following data from Hawaiian Volcano Observatory represent basalts from Kilauea on the Big Island of Hawaii. This volcano has been erupting from the Pu‘u O‘o crater almost continuously since 1983 adding over 220 hectares to the island.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>MgO</th>
<th>TiO₂</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-5</td>
<td>46.68</td>
<td>19.52</td>
<td>1.8</td>
<td>542</td>
</tr>
<tr>
<td>S-15</td>
<td>46.82</td>
<td>18.87</td>
<td>1.86</td>
<td>525</td>
</tr>
<tr>
<td>S-7</td>
<td>48.22</td>
<td>13.67</td>
<td>2.27</td>
<td>296</td>
</tr>
<tr>
<td>S-9</td>
<td>48.41</td>
<td>13.34</td>
<td>2.3</td>
<td>293</td>
</tr>
<tr>
<td>F-17</td>
<td>48.77</td>
<td>13.13</td>
<td>2.42</td>
<td>289</td>
</tr>
<tr>
<td>S-8</td>
<td>49.12</td>
<td>10.46</td>
<td>2.53</td>
<td>170</td>
</tr>
<tr>
<td>F-12</td>
<td>49.34</td>
<td>10.58</td>
<td>2.69</td>
<td>191</td>
</tr>
<tr>
<td>S-25</td>
<td>49.44</td>
<td>8.85</td>
<td>2.67</td>
<td>130</td>
</tr>
<tr>
<td>S-14</td>
<td>49.45</td>
<td>8.55</td>
<td>2.62</td>
<td>149</td>
</tr>
<tr>
<td>S-3</td>
<td>49.62</td>
<td>8.85</td>
<td>2.56</td>
<td>168</td>
</tr>
<tr>
<td>S-1</td>
<td>49.91</td>
<td>8.08</td>
<td>2.62</td>
<td>104</td>
</tr>
<tr>
<td>10</td>
<td>50.53</td>
<td>6.33</td>
<td>3.23</td>
<td>94</td>
</tr>
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<td>6</td>
<td>50.55</td>
<td>6.19</td>
<td>3.31</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>50.61</td>
<td>6.61</td>
<td>3.12</td>
<td>92</td>
</tr>
<tr>
<td>F-5</td>
<td>50.76</td>
<td>6.09</td>
<td>3.37</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>50.99</td>
<td>5.42</td>
<td>3.57</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>51.06</td>
<td>5.44</td>
<td>3.65</td>
<td>68</td>
</tr>
<tr>
<td>1</td>
<td>51.24</td>
<td>5.12</td>
<td>3.74</td>
<td>87</td>
</tr>
</tbody>
</table>

Note that Ni decreases in concentration with increasing SiO₂ and that TiO₂ increases in concentration with increasing SiO₂.

Effusive flow during March 2003 at Kilauea, Hawaii (photo by Judy Harden).

Click on the link below to see exciting pictures of current eruptions and to learn more about Kilauea and other Hawaiian Volcanoes.

Sample set 2: The data set on the following slide is from Colima, Mexico. The Colima volcano complex is one of the most active volcanic systems in North America and has recently experienced dome-growing eruptions and Vulcanian type explosions.

Sample set 2: Colima, Mexico. You will need to sort the data before choosing the elements you want to look at. What can you determine about the formation of these samples?


<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO2</th>
<th>MgO</th>
<th>V</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Rb</th>
<th>Zr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-8.0</td>
<td>59.02</td>
<td>4.01</td>
<td>143</td>
<td>101</td>
<td>40</td>
<td>27</td>
<td>57</td>
<td>16</td>
<td>124</td>
<td>473</td>
</tr>
<tr>
<td>S-8.1</td>
<td>55.67</td>
<td>5.7</td>
<td>189</td>
<td>163</td>
<td>77</td>
<td>35</td>
<td>59</td>
<td>12</td>
<td>121</td>
<td>387</td>
</tr>
<tr>
<td>Col-204</td>
<td>57.07</td>
<td>5.73</td>
<td>111</td>
<td>330</td>
<td>138</td>
<td>40</td>
<td>61</td>
<td>20</td>
<td>114</td>
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Sample set 3: The following data set is from Soufriere Hills, Montserrat in the Caribbean. After 8 years of activity the volcano has recently quieted but only after destroying the main city of Plymouth and the only airport on the island.

Small eruption with a pyroclastic flow at Soufriere Hills, Montserrat on April 20, 2003 (photo by Judy Harden).


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Pre- and Post- module questions

Geology related questions:

- What rock types or features of rocks do we see at the surface of the Earth that give us insight about the composition of the Earth’s mantle?
- What is fractional crystallization?
- What is the difference between an incompatible and a compatible element?
- What is the difference between a partition coefficient and a bulk partition coefficient?
- When plotting a suite of samples that are dominated by fractional crystallization, what type of trend would you expect to see on a linear graph? On a logarithmic graph?
- Would a magma that undergoes fractional crystallization be depleted or enriched in incompatible elements?

Quantitative Literacy related questions:

- What are the basic rules of logarithms?
- What is forward modeling?
- What is a weighted average?
Partial Melting Module JAH2A

"Igneous rocks are those which have been ejected in a melted state, as from volcanic vents, or from fissures opened to some seat of fires within or below the earth’s crust." – New Textbook of Geology (Dana, 1863)

We have gained much insight about the interior of the Earth since 1863. We now know that some Dante-like “seat of fires” does not exist and that volcanic eruptions occur when certain processes cause the rocks in the mantle to melt.

Students should work through module 1A and 1B (fractional crystallization) and have a basic understanding of phase diagrams before working through this module.

PREVIEW

This module is the first part of a set of two (JAH2A and JAH2B). JAH2A was developed to illustrate current ideas of how melting occurs within the mantle. JAH2B introduces ways to identify partial melting using geochemistry. It is highly recommended that each module be worked through for a better understanding of partial melting.

Slides 3-6 discuss the various known means of melting in the Earth’s interior: decreasing pressure, increasing temperature, and changing the composition of the mantle.

Slide 7 contains a simple animation of current ideas of how partial melting occurs and how the concentration of incompatible elements decreases as melting increases.

Slides 8-10 present a binary phase diagram and asks students to use the lever rule to calculate the percentage of a melt.

Slide 11 presents a calculation illustrating how much melting must occur to completely melt a mineral and change a phase.

Slide 12 – end-of-module questions.

See module JAH2B for an introduction of the Shaw equation and data sets to look for indications of partial melting.
The Processes of Melting

As with fractional crystallization, it is important to look at a suite of samples from the same source, rather than at a single sample, to identify partial melting.

Seismic data indicate that melting does not occur in the mantle under normal circumstances. Although various estimates have been calculated for the oceanic geothermal gradient, none of them approach the solidus of the mantle. Melting, therefore, is not a product of the geothermal gradient.

However, melting must occur or we would not have basalts erupted at the surface of the Earth.

There are only three known ways to cause melting in the mantle:
1. Lower the pressure
2. Raise the temperature
3. Change the composition

Before looking at samples, let’s take a look at these processes.

Lowering pressure

Melting can occur by a decrease in pressure at a constant temperature. One way is to raise mantle rocks rapidly enough to minimize heat loss to the surroundings. Diverging plates are the prime location for this process to occur. Mantle material flows upward to fill in areas that have been vacated from erupting Mid-ocean ridge basalts (MORB).

This process is known as decompression melting. It occurs not only where plates are rifted apart. It also occurs at hot spots.

The material inside the area of the bold black lines is typically called “mush” by geologists. It consists of some solid and some melt.

Increasing temperature

Melting could occur if the mantle was heated beyond the normal geotherm by the decay of radioactive elements such as K, U, and Th. Radioactivity is the only known source of heat in the interior of the earth other than that from the primordial differentiation process.

The radioactive elements can produce only $\sim 10^{-8} \text{ J g}^{-1} \text{ a}^{-1}$.

The specific heat of a typical rock is $\sim 1 \text{ J g}^{-1} \text{ deg}^{-1}$.

With these values, it would take over $10^7$ years for radioactivity in the mantle to increase the temperature in a mantle rock 1°C, making radioactivity an unlikely source for melt.

Changing composition

Although the mantle is much more hydrated in subduction zones, amphibole and phlogopite have been found in mantle xenoliths. Water, therefore, is present in the mantle. Other fluid inclusions contain liquid CO$_2$.

At high pressure, water can dramatically decrease the solidus temperature of the mantle. The water content of “normal” mantle is only $\sim 0.1$ weight %. In order to produce melting, however, additional volatiles need to be added to the mantle.

The following slide has a simple animation to show the process of changing the composition of the mantle.

Melts within the mantle are thought to be merely droplet sized.
Melting begins when a flux is added to the system (mantle). Flux is a substance that reduces the melting point of the mixture when it is added to a mixture. Water is one of the most dominant fluxes. It is added to the mantle during subduction processes.

Initial melts are contained within the intergranular space in a rock and are adsorbed to grain surfaces. Press the enter key now to begin the animation.

Water added
Melting begins containing highest concentration of incompatible elements
Liquid rises due to density difference
As drops of melt accumulate, concentration of incompatible elements decreases
Residue depleted in incompatible elements

The binary phase diagram below will help us see that melting in the mantle happens at the solidus, above which crystals and melt exist together for a large range of temperatures.

At the eutectic point (A), the temperature is 1542°C. For a different phase to occur, the temperature needs to increase to 1557°C (point B).

This diagram is an enlargement of part of the previous one. Print this page and use the lever rule to calculate the percent of enstatite (MgSiO₃) and quartz present at the location of the red dot. Only solids exist at this point.

By increasing the temperature by a degree or two, we have shifted the position of the red dot from a solid into an area of solid and melt. Now use the lever rule again to calculate the percent of enstatite and liquid present at the new location. You should see that a slight increase in temperature will greatly increase the amount of liquid present.
How much melting occurs?

Consider a mantle rock with a composition of 74% olivine, 15% orthopyroxene (opx), 10% clinopyroxene (cpx), and 1% spinel.

From Bowen’s reaction series, we know that the pyroxenes will be the first to melt. If they melt equally at 50% cpx to 50% opx, how much melting must occur before all of the cpx is consumed and a phase change takes place?

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<td>6</td>
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<tr>
<td>7</td>
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<tr>
<td>8</td>
<td>% melt</td>
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A value larger than 20% melting is much higher than can occur according to experiments. This means that real-world melts do not get past the eutectic point and that an entire mineral phase will not melt.

We know that olivine forms as orthopyroxene melts, but the amount is small enough to disregard it in this calculation.

End-of-module questions

1. How can we obtain mantle-derived samples such as the one described on slide 5? (ophiolites, dredge samples, xenoliths in basalts, xenoliths in kimberlites, possibly stony meteorites.)
2. Define the terms liquidus and solidus.
3. Determine the temperature in °F for the eutectic (point A) on slide 8.
4. Can hotspots be a means of adding heat to the mantle? (They can add heat to the mantle, but they are local perturbations and cannot produce all the basalt seen at the surface of the Earth.)
5. How do we know the mantle is predominantly solid? (Geophysical studies show that S-waves cannot propagate through a liquid; therefore, we know that the mantle is predominantly solid and the outer core is liquid.)
6. Using the values on slide 5, how long would it take for radioactivity in the mantle to increase the temperature in mantle rock 1°C? (1J/g deg / 10⁻⁸J/g a = 1 deg C / 10⁷a)

Continue with partial melting module JAH2B.
The advances in geochemistry, geophysics, and volcanology have increased our understanding of the earth and the processes that shape and form it.

It is recommended that students work through JAH2A before working through this part of the module.

---

PREVIEW

Slide 3 introduces the Shaw equation used for partial melting.

Slides 4-6 ask the students to develop a spreadsheet to calculate the $C/C_0$ ratio for given $D$ values and then to graph those values versus $F$ to see the range of concentration of incompatible and compatible elements.

Slide 7 uses a spreadsheet mentioned in the Fractional Crystallization module (JAH1A) to calculate bulk partition coefficients.

Slides 8-9 ask students to use the Shaw equation to calculate and graph $C/C_0$ values for incompatible trace elements to see how concentrations vary with progressive melting.

Slides 10-11 offer some guidelines on what type of samples to choose, what elements to plot, and how to determine if partial melting has played a role in the formation of a given suite of rocks.

Slides 12-17 end-of-module questions and related data.
Because the concentration of trace elements with $D'$s=0 vary inversely with the amount of liquid diluting it, their concentration in the liquid reflects the proportion of liquid at a given state of melting.

The batch-melting equation listed below was derived by H. R. Shaw:

$$\frac{C_l}{C_o} = \frac{1}{D(1-F) + F}$$

$C_o$ = trace element concentration in original assemblage
$C_l$ = trace element concentration in the liquid
$D$ = bulk partition coefficient
$F$ = weight fraction of melt produced

Because the concentration of trace elements with $D'$s=0 vary inversely with the amount of liquid diluting it, their concentration in the liquid reflects the proportion of liquid at a given state of melting.

Now that we’ve looked at processes of melting in the mantle, we can study a model that detects when samples have been affected by partial melting.

The batch-melting model is a simple model in which the melt and solid remain in equilibrium until it is released and ascends as an independent system.

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$F$ = weight fraction of melt produced

Because the concentration of trace elements with $D'$s=0 vary inversely with the amount of liquid diluting it, their concentration in the liquid reflects the proportion of liquid at a given state of melting.
When $D >> 1$, the concentration of compatible elements in the melt show only small ranges in abundance during initial melting. For small values of $F$ (low degrees of melting), the concentration of highly incompatible elements ($D << 1$) varies greatly. The highly incompatible elements concentrate in the first few drops of melt and become progressively more dilute as $F$ increases.

When $D >> 1$, the concentration of compatible elements in the melt show only small ranges in abundance during initial melting.

PARTIAL MELTING

If we know the concentration of a trace element in a magma ($C_l$) and $D$, we can use the Shaw equation to calculate $C_o$ enabling us to characterize and constrain the source region of magmas. When $F$ approaches zero, the equation reduces to:

$$\frac{C_l}{C_o} = \frac{1}{D}$$

Only those elements with $D$'s <<1 show a wide range in abundance for a given range of $F$. For example, the maximum enrichment for an element with $D = 0.01$ is 100 while an element with $D = 0.3$ the maximum enrichment is 3.3.

By knowing the concentration of a highly incompatible element ($D \rightarrow 0$) in the magma and the source rock, we can calculate $F$, the fraction of partial melt produced.

$$\frac{C_l}{C_o} = \frac{1}{F}$$

Let's see how this technique works.
Suppose we have a sample of basalt derived from melting in the mantle with a composition of 70% olivine, 17% orthopyroxene (opx), 12% clinopyroxene (cpx), and 1% spinel. Use the spreadsheet you created in slide 7 of module 1A and $K_D$ values for Rb and Li from the Geochemical Earth Reference Model (GERM) website listed below to calculate $D$ for each element.


You should discover that Rb is highly incompatible and that Li is only slightly more compatible than Rb (moderately incompatible).

Now we can calculate $C/C_0$ for different $F$ values.

Using the Shaw equation, calculate the $C/C_0$ ratio for Rb and Li. Add another column to calculate the Rb/Li ratio.

After completing the spreadsheet, plot the $C/C_0$ ratios for the two elements vs $F$ on a linear graph with arithmetic scales on both axes.
You should see from your graph (1) that Rb, a highly incompatible element, is concentrated in the earliest stages of melting; (2) that it is strongly partitioned from the source rock; and (3) that the Rb/Li ratio decreases as melting increases.

Li on the other hand, is only moderately incompatible and does not vary much with progressive melting.

The concentration of incompatible elements becomes more dilute as melting continues.

When looking at a data set, we don’t know what process formed the suite of rocks. They may have formed from fractional crystallization or partial melting. So, what must we do to identify partial melting?

IDENTIFYING PARTIAL MELTING

CHOOSING SAMPLES

1. You must look at a suite of rocks, not just one rock.
2. The rocks should have MgO contents > 7 wt. %. However, MgO contents > 15 wt % are probably due to olivine accumulation.
3. The rock should be glassy and should not contain excess olivine phenocrysts.

EXAMINING THE GEOCHEMISTRY

1. The major element compositions should not vary much among the samples.
2. Incompatible elements will vary significantly. Highly incompatible elements will vary even more.
3. Compatible elements will show at most a slight variation.
What elements are the best to plot?

Because the concentration of highly incompatible elements has such a large range, and moderately incompatible elements vary only slightly, a plot on a linear graph of the ratio of a highly incompatible element to a moderately incompatible element vs the moderately incompatible element is best (Example: Be/Li vs. Be)

EXAMINING THE GRAPHS

A steeply-sloped, tight linear trend (A) indicates partial melting as a dominant process while a shallower slope with a more scattered trend (B) indicates some other process such as fractional crystallization (but not necessarily).

End-of-module questions

1. As $F$ approaches 1, what can we say about the $C_i/C_o$ ratio in the Shaw equation? (The concentration of every trace element in the melt equals the concentration in the source rock, it approaches 1.)

2. Make plots of the data from various settings on the following slides (You will need to use the spreadsheet and rock compositions from slide 7 and $K_D$ values from the GERM website to calculate $D$ values so that you will know which trace elements to plot). Which suite of rocks, if any, indicates that partial melting was a dominant process of formation.

3. After plotting all the data, create a spreadsheet like the example below to calculate $F$ for each sample in any suite of rocks that appears to have been formed from partial melting. Be sure to use element(s) with a $D$ value close to zero (see slide 6):

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<thead>
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<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
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</tr>
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<td>4</td>
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<tr>
<td>5</td>
<td>C_i</td>
<td>F</td>
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</tr>
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<td></td>
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<tr>
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</tr>
<tr>
<td>8</td>
<td>0.207</td>
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<td>9</td>
<td>0.207</td>
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<td>10</td>
<td>0.104</td>
<td>12</td>
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</tr>
<tr>
<td>11</td>
<td>0.242</td>
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</tr>
<tr>
<td>12</td>
<td>0.346</td>
<td>5</td>
<td></td>
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</table>

$C_o$ for Be ~ 0.01
$C_o$ for Ba ~ 1.1
$C_o$ for Li ~ 1.9
$C_o$ for Zr ~ 9.0
$C_o$ for Y ~ 4.0
The East Pacific Rise is a divergent boundary.


http://www.pmel.noaa.gov/vents/acoustics/shipops.html Basalt photos:
http://imager.ldeo.columbia.edu/courses/subgeol/mid_ocean_landscape.html

The FAMOUS (French American Mid-Ocean Undersea Study) was performed in an area around the 45°N latitude where ALVIN could be used to collect samples.

DATA:

PHOTOS:
Upper right: http://www.pmel.noaa.gov/vents/acoustics/shipops.html
Left: http://www.cliffshade.com/colorado/images/mid_atlantic.gif

The FAMOUS Area MORBS (Mid-Atlantic Ridge)

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<th>sample</th>
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<th>MgO</th>
<th>FeO</th>
<th>Cr</th>
<th>Ni</th>
<th>Ca</th>
<th>TiO2</th>
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The Juan de Fuca ridge is a divergent boundary off the coast of western Canada.

The Society Islands, French Polynesia, were formed by a hot spot like the islands of Hawaii.

The Juan de Fuca Ridge

<table>
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<tr>
<th>Sample</th>
<th>SiO2</th>
<th>MgO</th>
<th>TiO2</th>
<th>Li</th>
<th>Be</th>
<th>Ba</th>
<th>Zr</th>
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The Society Islands, French Polynesia, were formed by a hot spot like the islands of Hawaii.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO2</th>
<th>MgO</th>
<th>TiO2</th>
<th>Li</th>
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<th>Ba</th>
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Moorea is the third youngest island in the Society Chain.

To the right are thin sections of basalts from the island. The middle photo is of a xenolith.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO2</th>
<th>MgO</th>
<th>TiO2</th>
<th>Li</th>
<th>Be</th>
<th>Ba</th>
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