Revision #2

Petrologic Evolution of Boninite Lavas from the IBM Fore-Arc, IODP Expedition 352: Evidence for Open-System Processes During Early Subduction Zone Magmatism

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ABSTRACT

Boninite samples from several intervals within Hole U1439C, recovered during IODP Expedition 352, show highly variable mineral chemistries that imply complex crystallization histories. Small pyroxene grains show oscillatory zoning with cores and zones ranging from pigeonite to augite. Late crystallizing augite has highly variable Al\textsubscript{2}O\textsubscript{3} contents (1.9-13.7 wt\%) and Ca-Tschermak component contents (3-13 mol\%), which reflect disequilibrium conditions. Large, euhedral, low-Ca pyroxene (i.e., enstatite/clinoenstatite) crystals exhibit complex sector and oscillatory zoning patterns. Cr-rich spinel is found as inclusions both in olivine and low-Ca pyroxene. Early-crystallized olivine phenocrysts have embayed and reacted margins, and some early-crystallized olivines exhibit zoning. A few olivines have multiple zones, with both normal and reverse zoning between Fo\textsubscript{86-92}. Olivine xenocrysts also have embayed and reacted margins; however, xenocrysts do not exhibit chemical zoning patterns and have consistent Fo\textsubscript{88} compositions. Disequilibrium crystallization of pyroxene rims reflects rapid cooling during eruption. Sector zoning in low-Ca pyroxenes is the result of crystallization during periods of moderate undercooling between mixing events. Oscillatory, normal, and reverse zoning in olivine and pyroxene appears to have formed in response to multi-stage magma mingling or
mixing processes, which introduced additional Ca, Fe, Ti, and Al into parental boninitic melts. The presence of olivine xenocrysts and orthopyroxene indicate equilibrium at 2-4 kbar (Whattam et al. 2020) indicates that boninite magma mixing events likely occurred within shallow magma chambers containing olivine-rich cumulate piles. Large mixing events probably destabilized the magma chamber, resulting in devolatilization and eruption. In contrast, small mixing events lacked the energy to destabilize the chamber, resulting in repeated compositional oscillations in minerals affected by multiple small mixing events.

Keywords: Boninite, Magma Mixing, Olivine, Pyroxene, Zoning

INTRODUCTION

Boninites are unusual, high SiO$_2$ (>52 wt%), high MgO (>8 wt%), and low TiO$_2$ (<0.5 wt%) mafic rocks that are distinctively associated with subduction processes, in particular the unusual processes and phenomena of subduction initiation (Pearce and Reagan 2019; Shervais et al. 2021). They are commonly found in the forearcs in western Pacific arc systems such as the Izu-Bonin-Mariana (IBM) system (the type locality of boninite) and Tonga-Kermadec arc system (Dietrich et al. 1978; Bloomer et al. 1979; Meijer 1980; Meijer et al. 1982; Crawford 1989; Arculus et al. 1992; Dobson et al. 2006; Meffre et al. 2012) and have been observed actively erupting in the Lau Basin (Falloon and Crawford 1991; Falloon et al. 1992; Resing et al. 2011). Boninites are also common in ophiolites such as Troodos (Cyprus), Samail (Oman), Thetford Mines (Canada), Betts Cove (Canada), and Koh (New Caledonia) (Cameron 1985; Kyser et al. 1986; Meffre et al. 1996; Bedard et al. 1998; Wyman 1999; Ishikawa et al. 2002, 2005; Page et al. 2008, 2009). "Boninite-like" veins have also been found in some mantle xenoliths from Kamchatka and the West Bismarck arc (Benard et al. 2016, 2018).
Boninites associated with the Izu-Bonin fore-arc reflect the evolution of magmatic processes associated with subduction initiation, in which the foundering of old oceanic lithosphere leads to upwelling of asthenospheric mantle (e.g., Stern and Bloomer 1992; Reagan et al. 2010; Reagan et al. 2017). Competing models exist as to how boninites form in this setting. Pearce et al. (1999) suggests that boninites result from mixing between partial melts from gabbroic veins in the shallow mantle and melts from the upwelling asthenosphere. Recent studies have contended that mantle upwelling associated with initial plate foundering results in decompression melting that produces voluminous tholeiitic basalts (fore-arc basalts (FAB); Reagan et al. 2010, 2017, 2019; Shervais et al. 2019). This basaltic melting extensively depletes this upwelling mantle, which is then fluxed with a high-temperature fluid phase from the downgoing slab, triggering continued melting and the formation of boninite magma (Li et al. 2019; Reagan et al. 2017, 2019; Shervais et al. 2021; Coulthard et al. 2021).

Past studies of western Pacific boninites have focused on their unusual whole-rock major and trace element chemistries and isotopic compositions (Hickey and Frey 1982; Bloomer and Hawkins 1987; Falloon and Crawford 1991; Arculus et al. 1992; Murton et al. 1992; Pearce et al. 1992, 1999; Dobson et al. 2006; Shervais et al. 2021; Coulthard et al. 2021). Detailed mineralogical studies of fresh boninite volcanic sections have been comparatively rare given uncommon land-based exposures and/or limited dredging or submersible recovery. As the mineralogical features in boninites can directly reflect the conditions of their crystallization and melting, understanding these features can provide important insights into the conditions of magma formation and volcanism as subduction begins. IODP Expedition 352 cored over 800 m of the volcanic basement of the Izu-Bonin forearc at two different sites, recovering over 460 m of boninite and high-Mg andesite core (Reagan et al. 2015, 2017). These samples represent the
most complete stratigraphic sequence of boninites recovered in any forearc setting. We have examined the mineralogical features of a suite of Expedition 352 boninites from Hole U1439C, using thin-section petrography and mineral chemistry, to place new constraints on the petrogenesis of these lavas. Our results point to a significant role for open-system magmatic processes, both among different boninitic lava types and spatially associated boninitic differentiates.

**Past mineralogical and petrologic studies of Izu-Bonin boninites**

Johannsen (1937) reported on high-Mg/high-Si volcanic rocks in the Bonin (Ogasawara) Islands; however, systematic petrologic and geochemical studies of these lavas did not occur until much later (e.g., Kuroda and Shiraki 1975; Hickey and Frey 1982; Cameron et al. 1983). Meijer (1980, 1982) proposed the existence of a boninite suite associated with fore-arc volcanism based on discoveries by the Deep Sea Drilling Program (DSDP) and dredging. The first full petrologic study was performed by Umino (1986), who distinguished two major types and five subtypes of boninite, and, based in part on zoned pyroxene crystals, argued for their evolution in a dynamic magma chamber, with the mixing of more- and less-evolved boninitic magmas to produce at least one of the lava subtypes. Taylor et al. (1994) examined trace element compositions in Chichijima boninite, noting their unusually low Ti/Zr and Sm/Zr ratios, which were inferred to reflect chemical inputs from amphibolitic, probably slab-related, sources. Dobson et al. (2006) conducted an extensive study of the Chichijima volcanics, documenting related rock types ranging from Mg-rich boninite to rhyolite, and the presence of high-Ca clinopyroxene in all the Chichijima volcanic rock types. Li et al. (2013) described boninite and differentiates from Hahajima seamount occurring in association with adakites, which point to high-temperature conditions on the slab. ODP Leg 125 (Hole 786A) drilled a boninitic volcanic
sequence in a basement high near the Izu-Bonin trench at Site 786, NE of Sumisu-Jima island, that appeared to be lithologically and compositionally similar to both Chichijima Island boninites, and to Mariana boninites encountered during DSDP Site 458 (Meijer et al. 1982; Arculus et al. 1992).

**IODP Expedition 352**

A primary objective of IODP Expedition 352 was to recover a complete stratigraphic section through the igneous crust exposed near the trench in the Izu-Bonin fore-arc, as identified during a series of Shinkai dive expeditions (e.g., Ishizuka et al. 2011). Four sites were drilled, two into boninites (Sites U1439 and U1442), and two into fore-arc basalts (FAB) (Sites U1440 and U1441), with 20-30% recovery in the boninites, and ≤10% in the basalts (Reagan et al. 2015; Figures 1 & 2). In one fore-arc basalt site (U1440) and one boninite site (U1439), rocks with diabasic textures were penetrated, indicating that the transition from tholeiite to boninite may reflect a shift in the locus of magmatism, at odds with the ostensibly vertical basalt-to-boninite sequences encountered in the Troodos ophiolite (Reagan et al. 2017). However, Reagan et al. (2017) state that a direct transition from FAB to boninite melt compositions at the original spreading center is the preferred hypothesis.

Sites U1439 and U1442, though less than 1 km apart, reflect remarkably different stratigraphies (Figure 1). Hole U1442A is dominated by distinctive low-Si boninite (LSB), and boninitic differentiates (terminology after Kanayama et al. 2012, 2013; and Pearce and Reagan 2019), occurring as lava flows and hyaloclastites, capped with a sequence of late-stage high-Si boninite (HSB) hyaloclastites and lava flows, which are mineralogically and chemically similar to those found on Chichijima and other IBM sites. In contrast, Site U1439 (Holes U1439A and U1439C) reflects greater lithologic diversity, with diabasic rocks that appear to represent...
boninite feeder dikes overlain by LSB and differentiates, which are themselves separated from
overlying HSB by a layer of what was described as basaltic boninite (Reagan et al. 2015, Figure
2). Also evident in the U1439C cores are what were described as "magma mingling" textures,
interpreted as intercalated evolved and primitive boninitic melts (Reagan et al. 2015), pointing to
complexities in the generation and evolution of the Expedition 352 boninitic magmas.

SAMPLES AND METHODS

The IODP Expedition 352 boninite sequences were initially targeted for examination as
part of a multi-year, course-based undergraduate research experience (CURE) for University of
South Florida Geology undergraduates, overseen by co-author Ryan as part of an ongoing
educational investigation into the use of research microbeam instrumentation in geoscience
courses (see Ryan 2013). Boninite samples were selected to provide representative coverage of
the different lithologies at each site and were also chosen to be comparatively crystal-rich, to
facilitate petrographic and microprobe examination of the different crystallizing phases
encountered in the samples. Thirty samples from Holes U1442A, U1439A, and U1439C were
obtained from the IODP Core Repository at Kochi, Japan specifically for classroom study, and
an additional fifteen samples came from the samples selected by Ryan for post-cruise
geochemical study. Polished thin-sections were prepared from each of the samples for polarized-
light petrographic analysis. Initial petrographic analyses of the samples were conducted during
the course by participating students, who also helped to identify petrographically interesting
samples for subsequent mineral chemistry studies. Four of the forty five samples (U1439C-
2R3W 2-3, U1439C-15R1W 8-10, U1439C-19R2W 46-48, and U1439C-25R2W 18-19) will be
the primary focus throughout this paper do to the mineral zoning and overgrowth texture they
exhibit.
Micro-imaging and mineral chemistry measurements were conducted using the JEOL 8900R Superprobe EPMA system of the Florida Center for Analytical Electron Microscopy (FCAEM) at Florida International University, and the Cameca SXFive of the Center for Material Characterization at Boise State University. Samples were explored in electron backscatter mode, with quick energy dispersive spectrometer (EDS) measurements to identify major mineral phases. For quantitative WDS mineral analyses, operating conditions were a 15 kV accelerating voltage and a 20 nA beam current, 15 s count time per element, with a spot size of 1-2 µm on the JEOL 8900R Superprobe and 5-10 µm on the Cameca SXfive. The elements Si, Al, Fe, Mg, Ca, Mn, Na, K, Ti, and Cr, were routinely measured on all samples on both instruments. For the JEOL 8900R Superprobe, a selection of mineral standards from SPI, Inc., and Micro-Analysis Consultants, Ltd. were used to calibrate WDS measurements of unknowns (fayalite, olivine, Cr-diopside, An65 plagioclase, kaersutite, augite, enstatite, and chromite). Re-calculation or re-analysis using a smaller set of compositionally matched standards after minerals were identified (e.g., the SPI, Inc. olivine #AS5200-AB standard was used to re-calculate olivine analysis, the SPI, Inc. diopside #AS5130-AB standard was used to re-calculate pyroxene analysis; Online Material Table OM1). For the Cameca SXFive a selection of synthetic mineral standards, as well as natural mineral and glass standards from the Smithsonian Institution, Harvard Mineralogical Museum, and the United States Geological Survey (USGS) were used to calibrate WDS measurements (San Carlos olivine, chromite, sillimanite, diopside, synthetic tephroite, synthetic fayalite, synthetic rutile, and Amelia albite). A similar re-analysis procedure was also used on the Cameca SXfive, for olivine analysis the San Carlos olivine NMNH-111312-44 standard was used and for pyroxene analysis the diopside NMNH-117733 standard was used (Online Material Table OM1). EPMA measurements were used to confirm microscope-based
phase identifications, to identify important minor phases (Cr rich spinels, and rare ilmenites and apatites), and to characterize the mineral zoning and overgrowth textures that were encountered in some of the samples.

Elemental maps were created using the Cameca SXFive at the Center for Material Characterization at Boise State University and the TOFWERK icpTOF 2R at TOFWERK AG in Switzerland. The instrumental setup used for the laser ablation inductively coupled mass spectrometry imaging (LA ICP-MS) experiments consisted of a laser ablation system (excimer ArF 193 nm wavelength, Teledyne CETAC Analyte G2) equipped with an ultra-fast laser ablation chamber (van Malderen et al., 2020) and interfaced with a time-of-flight mass spectrometer (icpTOF 2R). The coupling of the two instruments was carried out via the Aerosol Rapid Introduction System (ARIS), which allowed the acquisition of full pulse signals of less than 3 ms (FW0.1M). The instrumental operating conditions are listed in the supplemental data (Online Material1 Table OM2). The resulting images were generated using the HDIP software (van Malderen, 2017).

RESULTS

Petrography

The common phenocryst assemblage in the boninites examined in this study is low-Ca pyroxene (enstatite and clinoenstatite) + olivine, in a groundmass of later-formed acicular crystals of clinoenstatite, pigeonite, and high-Ca pyroxene in a glassy or crystalline matrix (Table 1, Online Material1 Fig. S1). Some enstatite crystals enclose small olivine grains, indicating that these enstatites formed in part via the peritectic reaction of olivine. Some HSB samples lack olivine, consisting exclusively of low-Ca pyroxenes and groundmass clinopyroxene in a glassy or crystalline matrix. In more differentiated samples (high-Mg andesites and dacites),
The primary crystallizing phases are augitic clinopyroxene and plagioclase, with rare grains of ilmenite and apatite. Olivine grains are typically rounded and embayed, indicating partial resorption associated with the growth of enstatite and clinoenstatite at lower pressures. Olivine xenocrysts were observed in sample U1439C-25R2W18-19; these xenocrysts are much larger (>6 mm) than the primary olivine phenocrysts (≤1.5 mm) observed in this sample and exhibit resorbed textures. Red to purple chromium-rich spinel is a common accessory mineral in boninite, often found enclosed within larger olivine and (rarely) enstatite and clinoenstatite crystals (but never within pigeonite grains), and as free grains within the sample matrices (Figure S.1). Melt inclusions with vapor bubbles and crystals nucleating from the walls of the inclusion have also been observed in some samples (Figure S.2c.-2f.).

Mineral chemistry

Table 2 presents typical major element compositions for the Expedition 352 boninite phenocryst phases. Enstatite and clinoenstatite phenocrysts vary from En$_{80-86}$, with Wo$_{3-5}$ (Fig. 3), broadly similar to those reported from Chichijima by Umino (1986). We did not see enstatite rimming clinoenstatite, as was reported by Dobson et al. (2006), but instead found that most of our low-Ca pyroxene phenocrysts were homogeneous, with optical characteristics suggestive in most cases of enstatite. The more calcic clinopyroxene compositions in our samples are pigeonite (En$_{70±3}$Fs$_{12±0.6}$Wo$_{16±2}$) and augite (En$_{42±9}$Fs$_{14±4}$Wo$_{36±4.5}$). Augite from the most differentiated high-Mg andesite is typically En$_{50±5}$Fs$_{7±0.8}$Wo$_{42±2}$, in association with late-crystallized An$_{81-83}$ plagioclase.

Olivine phenocryst compositions range from Fo$_{86-92}$, similar to those reported at Chichijima by Umino (1986) and Dobson et al. (2006). Olivine xenocrysts in sample U1439C-25R2W18-19 exhibit consistent compositions of Fo$_{88}$ (Table 3), while olivine phenocrysts from
the sample have compositions between Fo$_{89.92}$. Cr-spinel grains contain 8-10 wt% Al$_2$O$_3$, 11-13 wt% MgO, 18-24 wt% FeO, and 56-60 wt% Cr$_2$O$_3$ (Table 2).

**Mineral zoning and overgrowths**

A subset of the samples examined in the study (samples U1439C-2R3W 2-3, U1439C-15R1W 8-10, U1439C-19R2W 46-48, and U1439C-25R2W 18-19) showed prominent mineral zoning/overgrowth textures (these will be referred to as 2R3, 15R1, 19R2, and 25R2 for brevity). These samples were all from volcanic units in Hole U1439C, and encompass both HSB and LSB boninite subtypes (Reagan et al. 2015; 2017). These four samples contain olivine, enstatite, and clinoenstatite as phenocrysts in a groundmass dominated by acicular clinopyroxene (pigeonite to augite) in glass (Figure S.2).

Most of the larger pyroxene phenocrysts show calcic overgrowths (En$_{42±9}$Fs$_{14±4}$Wo$_{36±4.5}$) around enstatite cores (En$_{84±3}$Fs$_{12±0.6}$Wo$_{4±1}$) that are evident both optically and in electron backscatter imaging (Online Material$^1$ Table OM3 and Fig. OM2). Some of the larger enstatite grains and even a few of the large olivines appear to be nucleation sites for clinopyroxene. Large enstatite grains in samples 2R3 and 15R1 exhibit oscillatory zoning that is visible optically as well as via electron backscatter imaging. A subset of the calcic overgrowths exhibit anomalous enrichments in Al$_2$O$_3$ (typical pyroxenes ~4.0 wt%; anomalous overgrowths: up to 13.5 wt%), as well as high TiO$_2$ contents. When plotted on the pyroxene quadrilateral (Figure 3), the cores, standard rims/overgrowths, and aluminous overgrowths from samples 19R2 and 2R3 form three distinct clusters. Samples 15R1 and 25R2 differ from the other samples in this study as pyroxene compositions observed in these samples are more continuous from enstatite to augite (Figure 3, data can be found in Online Material$^1$ Table OM3 and OM4.). EPMA and ICP-TOF analyses revealed multiple zoning patterns. Small groundmass pyroxenes in sample 25R2 exhibit the most...
complex zoning patterns with oscillatory, sector, and patchy zoning patterns appearing in many of these crystals. Groundmass pyroxenes that show oscillatory zoning often contain magnesian cores (i.e., Mg#: 80±5.5, Cr#: 25±4.1, and Wo8±7.3) and calcic rims/overgrowths (i.e., Mg#: 50±10, Cr#: 1±2.8, and Wo26±6.6); however, reverse zoning patterns have also been observed (Figure S.3). Groundmass pyroxenes in samples 2R3, 15R1, and 19R2 exhibit patchy and sector zoning with no evident oscillatory zoning. Some of the larger pyroxene grains in sample 15R1 show oscillatory zoning with minor changes in En and Fs components. Mn appears to be following Fe in these oscillatory zoned pyroxenes. These larger pyroxenes also exhibit sector zoning patterns with enriched Cr, Al, and Ti concentrations in sector zones (Figure 4). Large pyroxene grains in sample 2R3 display oscillatory zoning with minor changes in En and Fs components; however, sector zoning is not observed in this sample.

In sample 25R2, many olivine grains exhibit oscillatory zoning, with Fo92-91 cores and less magnesian Fo90-86 rims (Online Material1 Table OM5 and Fig. OM4). Sample 25R2 also included multiple olivine grains with reverse oscillatory zoning, from Fo88-87 cores to Fo91-90 inner-rims, and then to Fo88-87 outer rims (Online Material1 Fig. OM4). Olivine zoning was not observed in any samples other than 25R2.

DISCUSSION

Mineralogical and Mineral Chemistry Variations

The majority of the Expedition 352 boninite samples examined in this study and recent studies (e.g., Whattam et al. 2020) exhibit phenocryst and matrix mineral compositions consistent with fractional crystallization. The most common phenocryst assemblages encountered are enstatite + olivine, sometimes enclosing Cr-spinel, with groundmass pigeonite and, in some cases, late-forming augitic clinopyroxene. Plagioclase is only encountered as a
matrix phase in the highly differentiated high-Mg andesites/dacites, and always in association
with augite. These assemblages are consistent with the progressive crystallization of magnesian
boninite parental magmas, as has been documented by Umino (1986), Arculus et al. (1992), and
Dobson et al. (2006).

However, a subset (~10%) of our samples, all at different stratigraphic levels, preserve
phenocrysts and groundmass crystals that show complex zoning and overgrowth textures (Figure
S.2). While both Umino (1986) and Dobson et al. (2006) report textural evidence for rapid
crystallization (i.e., skeletal and feathery morphologies in microphenocrysts of clinopyroxene),
neither study reports pyroxene overgrowth textures in their Chichijima boninite suites, or
pyroxene compositions with Al$_2$O$_3$ or TiO$_2$ contents as high as those encountered in the Al-rich
overgrowths in our Expedition 352 samples. The only study to report textures similar to those
observed in this subset of boninite samples from Expedition 352 is Ohnenstetter and Brown
(1992). The rocks examined in that study were recovered from a glassy boninite dike in New
Caledonia and exhibit similar pyroxene zoning, overgrowth textures, and crystal morphologies.
The key differences between the samples from that study and the samples from this study are: (1)
the lack of olivine in the boninite dike, (2) oscillatory zoning in the boninite dike is only
observed in microphenocrysts of orthopyroxene and skeletal clinoenstatite crystals, (3) the
appearance of tschermakitic amphibole overgrowths on the pyroxene grains.

The Formation of Ca-Tschermak Pyroxenes

Late crystallizing clinopyroxene overgrowths are easily distinguished in those samples
that include them by their brighter electron backscatter shading, and by their elevated Al and Ti
contents. The overgrowths are similar compositionally to late crystallizing clinopyroxenes
observed in experimental studies on quartz normative lunar basalts (Grove and Bence 1977) and
studies of natural boninite samples (Ohnenstetter and Brown 1992; Dobson et al. 2006). These
overgrowths are believed to develop due to the lack of Al-rich phases like plagioclase
crystallizing prior to eruption. The melt thus becomes enriched in Al and Ti, which is then
incorporated into the pyroxenes during rapid crystallization at high degrees of undercooling,
similar to the way in which tschermakitic amphiboles are proposed to form in a New Caledonia
boninite dike (i.e., Ohnenstetter and Brown 1992). It should also be noted that these pyroxene
overgrowths often become more Al and Ti-rich towards the rim. This phenomenon is likely due
to the rapid crystallization of pyroxene, depleting the crystal interface of compatible elements,
and enriching it in incompatible and slow-diffusing elements like Al and Ti (Mollo et al. 2010,
2013). During this rapid crystallization process, Al substitutes into the tetrahedral site in place of
Si, while Ti substitutes into the M1 site to charge balance the crystal (Ubide et al. 2019; Masotta
et al. 2020). Whattam et al. (2020) suggests that Expedition 352 boninite melts ascended to the
surface rapidly, as they appear to crystallize at similar temperatures to the fore-arc basalts
recovered during Expedition 352, but at much lower pressures. Thus, the boninite melts ascended
rapidly enough that they experienced little to no heat loss until they were near the surface,
creating perfect conditions for crystallization driven by undercooling that resulted from
decreases in pressure.

The fact that tschermakitic amphibole formed in a boninite dike from New Caledonia, but
not in the Expedition 352 samples, is likely due to differences in the compositions of the dike
and lavas. Sisson and Grove (1993) note that Na$_2$O in the melt must be ~4 wt% to stabilize
amphibole in calc-alkaline andesites, so it is possible that the appearance of amphibole in the
boninite dike may be related to increased Na$_2$O in the dike relative to the boninite lavas from this
study. However; Ohnenstetter and Brown 1992 report Na$_2$O concentrations in glasses within the
boninite dike of 2.09 wt% in the glasses from the boninite dike which is nearly identical to the Na$_2$O concentrations in glasses from the Expedition 352 boninite lavas (Coulthard et al. 2021), so it seems unlikely that Na content is the controlling factor in this case. H$_2$O concentrations in glass from the boninite dike are ~5.6 wt%, while concentrations in boninite glasses from Expedition 352 lavas are ~1.32-3.21 wt% (Coulthard et al. 2021). It may be that these comparatively lower H$_2$O concentrations inhibit amphibole crystallization in the Expedition 352 boninite melts.

**Pyroxene Zoning**

Pyroxenes can exhibit normal, reverse, sector, oscillatory, sector, or patchy zoning depending on the magmatic conditions under which they form (Streck 2008). Normal zoning refers to chemical variation that shifts from primitive to evolved in composition (i.e., Mg-rich to Mg-poor in this study), while reverse zoning refers to the opposite of this pattern (i.e., Mg-poor to Mg-rich). Normal and reverse zoning may alternate within a single crystal, forming bands that are typically >10 µm wide. Oscillatory zoning refers to cases where the normal or reverse zoning patterns repeat in an oscillating pattern. These oscillating zones can range in size, but are typically ~1-3 µm in width, and in the case of this study exhibit abrupt compositional changes. Sector zoning refers to crystals which contain chemical variations that correlate with different crystallographic directions.

Normal zoning in pyroxenes is related to fractional crystallization of the parent melt or high degrees of undercooling during crystallization (Shea and Hammer 2013; Benard et al. 2018), whereas reverse zoning is associated with reversals in magma composition (e.g., magma mixing) or abrupt changes in crystallization conditions (Streck 2008; Saunders et al. 2012; Petrone et al. 2016, 2018; Singer et al. 2016). Previous studies suggest that oscillatory zoning in
Pyroxenes can be driven by rapid crystallization and undercooling (Ohnenstetter and Brown 1992; Benard et al. 2018), based on plagioclase crystallization models (i.e., Ghiorso 1987; L’Heureux and Fowler 1996). In these models, less compatible elements (e.g., Cr, Al, Ti) are enriched near the crystal interface and then incorporated into the crystal as crystallization continues. This process repeats as more compatible elements (e.g., Mg, Ca) slowly diffuse toward the interface, and less compatible elements are incorporated into the crystal, resulting in oscillatory zoning. As well, other studies have contended that oscillatory zoning in pyroxenes may be related to magma mixing events (i.e., Petrone et al. 2016, 2018; Ubide and Kamber 2018; Ubide et al. 2019). In cases where boundary layer processes control oscillatory zoning, the zones are narrower (≈1-3 μm wide) and more numerous than what one would see in such features formed during magma mixing events (e.g., only a few oscillations, each ≈10-50 μm in thickness). Sector zoning in pyroxenes forms in response to modest degrees of undercooling (e.g., Shea and Hammer 2013; Ubide and Kamber 2018; Ubide et al. 2019; Masotta et al. 2020). Patchy zoning (i.e., zones which are not consistent with euhedral crystal growth) in pyroxenes has been related to changes in pressure, temperature, and H₂O content in the melt, as well as dissolution and recrystallization effects (Streck 2008; Crabtree and Lange 2010; Shea and Hammer 2013; Waters and Lange 2017).

Samples from this study contain examples of all of these pyroxene zoning patterns, indicating that they experienced a wide range of crystallization conditions during their formation. The appearance of groundmass pyroxenes with low-Ca cores and calcic overgrowths is likely related to rapid crystallization driven by undercooling upon ascent and eruption. As undercooling can be caused by changes in temperature or pressure, we suggest that the undercooling events that generated the calcic overgrowths were the result of decreases in pressure during ascent that...
likely also changed the H$_2$O composition of the melt (e.g., Shea and Hammer 2013; Waters and Lange 2017). This process would have resulted in the rapid nucleation of pyroxene and the formation of patchy and sector zoning patterns observed in the groundmass pyroxenes studied.

Two of the samples from this study (2R3 and 15R1) contain zoned low-Ca pyroxene phenocrysts. Single-element maps of multiple pyroxene phenocrysts in sample 15R1 reveal complex sector and oscillatory zoning patterns, which vary from element to element. Some divalent cations (e.g., Mg, Fe, Mn) exhibit oscillatory zoning patterns while Al, Cr, and Ti exhibit sector zoning patterns (with some variation in the Cr zoning patterns) (Figures 4 & 6). Sector zoning of Al, Cr, and Ti has been observed in recent studies (i.e., Barnes et al. 2016; Ubide and Kamber 2018; Mao et al. 2019; Ubide et al. 2019; Masotta et al. 2020) and has been attributed the sluggish kinetic effects on pyroxene crystallization during moderate degrees of undercooling (ΔT<32 °C).

Chemical data from the sector zoned pyroxenes in this study revealed a positive correlation between Al, Cr, and Ti in most of the sector zones. Similar relationships are observed in undercooled boninite dikes from New Caledonia (Ohnenstetter and Brown 1992). Thus, it is likely that undercooling drove much of the crystallization in these low Ca pyroxenes, resulting in sector zoning due to the crystal kinetics, substitution, and charge balancing processes discussed in Ubide et al. (2019). However, correlations between the Mg/Fe and Cr/Al ratios in these crystals suggest that these pyroxene grains have experienced a more complex crystallization history than consistent undercooling. Elemental maps reveal that high Mg/Fe and Cr/Al oscillations are also correlated with Cr enriched and Al depleted zones, which cut across the sector zones (Figure 6). These oscillations suggest changes occurred in the magmatic system at multiple points in time, which led to interruptions in the growth of sector zoning, and enriched
the melt at the crystal interfaces with Mg and Cr. Based on observations from several previous 

studies (Petrone et al. 2016, 2018; Singer et al. 2016; Ubide and Kamber 2018; Ubide et al. 

2019; Masotta et al. 2020), magma mixing between primitive and evolved boninite melt 
endmembers could cause an increase in temperature and enrich the melt in Mg and Cr (Figure 7). 

Oscillatory zoning is also observed in some of the groundmass pyroxene grains from 

sample 25R2 (Figure 8). The acicular shape and small size (i.e., 50-100 μm) of these pyroxenes 
indicate that groundmass pyroxenes formed rapidly during an undercooling event. This indicates 
that oscillatory zoning in small pyroxenes may have been driven by rapid crystallization and 
undercooling, as suggested by Ohnenstetter and Brown (1992) and Benard et al. (2018). If this 
process were controlling the oscillatory zoning in sample 25R2, we would expect abundances of 
incompatible elements like Cr and Al to show a positive correlation. However, the opposite is 
observed: Cr follows Mg, and Al follows Fe and Ca (Figure 8). This kind of chemical 
relationship is what one would expect during mixing events, in which the crystals are interacting 
with multiple injections of magmas. Such patterns have been interpreted as mixing effects in 
both experimental and natural studies on pyroxene zoning (Ubide and Kamber 2018; Ubide et al. 
2019; Masotta et al. 2020). So, some combination of undercooling and mixing processes are 
most likely affecting the crystallization of these groundmass pyroxenes.

Olivine Zoning and Xenocrysts

Olivine zoning usually appears as normal or reverse zoning in the Mg-Fe contents.

However, oscillatory zoning can also be observed in minor elements (i.e., P, Al, and Cr) (Costa 
and Chakraborty 2004; Costa and Dungan 2005; Costa et al. 2008; Milman-Barris et al. 2008; 
Kahl et al. 2011, 2013; Shea et al. 2015a., 2015b., 2019). Olivine grains from this study are 
unusual in the way that they exhibit oscillatory zoning in both major (i.e., Mg and Fe) and minor
elements (i.e., Ca, Cr, Mn, and Ni) (Figure 5, S.4, & S.5). Our elemental maps reveal oscillatory zoning patterns with respect to Fo content, which is also evident in the compositional transect collected across this grain (Figure 5, S.4, & S.5).

Oscillatory zoning in olivine with respect to elements such as P, Al, and Cr is thought to be caused by very rapid crystallization, which enriches the boundary layer in minor elements because they are incompatible in olivine and slow diffusing (Milman-Barris et al. 2008; Shea et al. 2015b, 2019). Shea et al. (2015b) suggest that a similar process might also cause oscillations in the Fo content of olivine, which are subsequently lost due to the rapid re-equilibration of Mg and Fe. However, if rapid crystallization was the cause for the Fo oscillations in the olivine examined in this study, then Cr abundance patterns should correlate with those of Fe, Ca, and Mn, instead of with more compatible and fast diffusing elements like Mg and Ni. It should also be noted that Al zoning was not observed in any of the olivine grains from this study, further supporting the hypothesis that this zoning was not caused by rapid crystallization (Figure 5).

Based on our geochemical observations, and other shipboard and post-cruise observations on Expedition 352 samples (Reagan et al. 2015; 2017; see Insights from Petrography, Stratigraphy, and Petrology below), we infer that the olivine zoning in this sample records magma mixing events which episodically enriched the melts in Mg, Ni, and Cr.

The large, xenocrystic olivine observed in sample 25R2 likely came from a cumulate pile within an evolving boninitic magmatic system (Figure S.4, OI 6). That these xenocrysts have a consistent composition of Fo$_{88}$ suggests that they formed in equilibrium with a melt more evolved than their current host. The smaller, zoned olivine in 25R2, with Fo$_{92-91}$ cores and rims at $\approx$ Fo$_{88}$, were likely carried into the magma chamber in a more primitive boninite melt. Zoning developed in these grains as a byproduct of this mixing event, resulting in rims that approach the
compositions of the xenocrysts. A similar process can also account for the reversely zoned olivine, which were likely growing suspended in the magma chamber or the cumulate pile, as reflected in their Fo$_{88-87}$ cores. The rims of these olivines approach but never reach compositions as magnesian as olivine cores from the primitive boninite melt, due most likely to the hybridized composition of the mixed magma that they interacted with.

**Magma Mixing**

Mineral chemistry and mineral zoning patterns observed in this study indicate that boninite crystallization occurred in a dynamic and continuously evolving magmatic system. In this magmatic system, crystallization likely occurred as the magma ascended, and as the pressure and temperature decreased, leading to undercooling-driven crystallization. This process caused sector and patchy zoning in the groundmass pyroxenes, as well as the sector zoning patterns in the large low-Ca pyroxenes from 15R1. However, episodically this system experienced mafic (i.e., primitive boninite magma) recharge events, resulting in mixing between primitive and evolved magmas. These recharge events increased the temperature of the magma (i.e., decreasing the amount of undercooling) and enriched the evolving magma in key elements (e.g., Mg, Ni, Cr). These events led to the oscillatory zoning patterns observed in the large low-Ca pyroxenes from samples 15R1 and 2R3. Recharge events also caused normal, reverse, and oscillatory zoning in olivines, and resorption textures on the rims of olivine xenocrysts.

Zoning patterns created by mixing events are often used to determine the time between mixing events and eruptions. Mg-Fe diffusion across pyroxene and olivine zoning profiles has been used in other studies to place constraints on the time between mixing events and eruptions (Costa and Dungan 2005; Costa et al. 2008; Kahl et al. 2011, 2013; Saunders et al. 2012; Shea et al. 2015a., 2015b.; Petrone et al. 2016, 2018; Singer et al. 2016). Data from the transects
conducted in this study are not detailed enough to calculate reliable times; however, some
inferences can be made based on the elements which show zoning in the olivines. Mg and Fe
diffuse relatively fast in olivine (Costa and Chakraborty 2004; Costa et al. 2008; Shea et al.
2015a., 2015b) and are rapidly redistributed through crystals during solid-state re-equilibration
with the evolving host magma. This high diffusivity is likely why the olivine xenocrysts do not
exhibit zoning, as these crystals appear to have resided in a magma chamber for an extended
period, and have thus re-equilibrated with the host magma. Thus, the presence of complex Mg-
Fe oscillatory, normal, and reverse zoning in olivine phenocrysts, as we have found in this study,
indicates that the events which produced them occurred shortly before eruption, before these
crystals had time to re-equilibrate with the melt. Based on calculations of olivine residence time
from previous studies, in which less complex zoning was observed in the olivine grains (i.e.,
Costa and Dungan 2005; Kahl et al. 2011, 2013; Shea et al. 2015a., 2015b), we suggest that the
mixing events which led to these zoning features occurred within a couple of months to a couple
of years before the eruption. While this hypothesis will require more detailed analyses of olivines
to confirm, the likely short duration between mixing and eruption provides evidence that mafic
recharge events may have driven the eruption of lavas through this section of the U1439C core.

Insights from Petrography, Stratigraphy, and Petrology

Shipboard portable X-ray fluorescence (PXRF) chemostratigraphic data (Ryan et al.
2017) document high chemical variability in specific horizons of the U1439C core that are
suggestive of mingled or mixed melts; these trends are confirmed by shore-based XRF and
ICPMS data (Shervais et al., 2021). These "mixing" horizons in the core show a reasonable
alignment with the stratigraphic positions of the samples exhibiting anomalous mineral zoning
(Figure S.6). Complex interactions among rising boninitic melts are also suggested by some of
the macro-scale fabrics found in the Hole U1439C and U1442A cores. Both cores preserve long
(10 cm – 1 m scale) sections that demonstrate magma mingling fabrics, in which two different
boninite melts are vertically intertwined, with visual evidence for interaction along with their
margins (Reagan et al. 2015, 2017; Figure S.7; Shervais et al. 2021). As well, at the scale of
standard thin sections, we see evidence for interaction, and incomplete mixing between more and
less phenocryst-rich boninitic melts (e.g., Reagan et al. 2015, Figure S.8).

These observations, combined with the data from this study, indicate that magma mixing
plays a significant role in the evolution of boninite magmas. The high chemical variability of
some core sections observed in the chemostratigraphic data suggests that magmas at significantly
different points in the fractionation process were present in the magma chamber and erupted
together. Petrologic and chemical evidence from olivine and pyroxene indicate that mixing
events occur within boninite magma bodies and, in some cases, may occur multiple times. The
observation of macro- and microscale magma mingling interfaces, as well as preserved Fe-Mg
oscillations in olivine grains, show that mixing events occurred shortly before or during eruptions.
Barometry from Whattam et al. (2020) indicates that crystallization in the Expedition 352
boninite melts occurred at pressures of ~0.2-0.4 kbar (i.e., 0.7-1.3 km).

We believe that this evidence shows that boninite magma bodies were located at shallow
depths in the middle to the upper crust. Chemical zoning within these bodies, along with mixing
events, could account for the chemical variability observed in the chemostratigraphy. These
bodies include crystal cumulate piles that are overturned during mixing events, resulting in
xenocryst crystal contamination (Figure 9).

**IMPLICATIONS**
Mineral zoning can be related to a variety of processes during crystal formation in magma chambers, and zoning patterns vary between minerals. However, a detailed analysis of mineral zoning patterns can be a powerful tool for understanding pre-eruptive magmatic processes. This study highlights the importance of multi-element chemical maps and chemical transects in studies of zoned minerals in igneous systems. This study and others cited here (e.g., Ubide et al. 2019), emphasize the usefulness of combining laser ablation techniques with traditional EPMA methods to allow us to interpret complex zoning patterns, which can vary between minerals and among elements. Observations from previous investigations indicate that the elemental patterns observed in this study were affected by a combination of undercooling and magma mixing processes. The use of edge-to-edge chemical transects alone, as is standard in many such studies, would have led to an oversimplified interpretation of the pre-eruptive history of the Expedition 352 boninite lavas.

This study also emphasizes the need to improve our understanding of elemental substitution into crystal lattices during different magmatic processes. Our work and that of previous zoning studies (see Pyroxene Zoning, and Olivine Zoning and Xenocrysts sections above for cited references) reveal that elemental substitutions are dependent on the conditions of the magmatic system, as well as the minerals into which the elements are substituting. This observation raises concerns as regards studies that attribute zoning to a specific process, solely based on observations in other mineral systems. Further experimental examinations, using elemental mapping methods, on various mineral systems at variable pressures, temperatures, and melt conditions are required to improve our understanding of elemental zoning. Such studies could further clarify the assignment of particular magmatic signatures to specific zoning patterns,
and increase the number of elements that may be used to interpret the pre-eruptive history of magmas.

A further implication of this study lies in the scientific benefits of conducting ostensibly education-focused investigations on scientifically significant suites of rock samples. The foundational petrographic and microprobe data for this investigation were collected over two years through the efforts of forty-nine University of South Florida undergraduate Geology majors, including three of this paper’s authors, as part of an ongoing, multi-year course-based undergraduate research experience in co-author Ryan’s junior-level GLY 3311C Mineralogy/Petrology/Geochemistry course. In these course-based activities, each student was tasked with completing a basic petrographic description (primary and secondary mineralogy, and textures) of one thin section and handsample from the Expedition 352 boninite suite, working largely in class during twice-weekly laboratory sessions. The course’s laboratory fees pay for an hour of EPMA time per student, and ultimately the students, working in groups based on the depth horizons of their samples in the Site U1439 cores, selected those samples to be examined via microprobe based on their petrographic findings. EPMA measurements were largely conducted in the classroom by students under co-author Ryan’s supervision, taking advantage of the remote operation capabilities of the Florida Center for Analytical Electron Microscopy EPMA system.

Having a large number of students spend an extended period of time microscopically examining Site U1439 boninite samples led to the recognition (by authors Scholpp, Hill, and Mack) of the small subset of samples that preserved anomalous mineral zoning and overgrowth features, features which have largely not been reported or highlighted in past studies of IBM boninites, including the recent study by Whattam et al. (2020) on these same cores. While
course-based undergraduate research experiences are predominantly touted for their educational benefits (see PCAST 2012; NAS 2015, 2017), there is also a real scientific value in bringing many sets of unbiased eyes to bear on complex igneous and metamorphic sample suites, such as may be recovered during IODP Expeditions.

**Acknowledgments**

Thanks go to Tom Beasley and postdoctoral fellows Sven Holbik and Chris Vidito for invaluable logistical support on the FCAEM EPMA and SEM systems, both for Ryan and all of the GLY 3311C students across several years. Thanks also go to Nick Bulloss for his assistance with the EPMA system at Boise State University. We also thank IODP for supporting an extended education-focused project with recovered Expedition 352 samples, and to the staff at the Kochi Core Repository for their creative aid in identifying suitable boninite samples for classroom petrographic and EPMA analysis. This project was supported by NSF grants OCE-1558855 and DUE-1323275 to Jeff Ryan and OCE-1558689 to Shervais.

**References**


Engage to Excel: Producing One Million Additional College Graduates with Degrees in Science, Technology, Engineering and Mathematics. 103 p.


List of Figure Captions

Figure 1
Drillsite map and theoretical crosssection of the IBM forearc. (a) Location of drill-sites U1439, U1440, U1441, U1442 in relation to the Bonin Islands (e.g., Chichijima) on the Ogasawara Plateau. (b) Theoretical cross section of the forearc, showing the location of the drill sites for IODP Expedition 352 (modified from Reagan et al. 2015).

Figure 2
Core summary from hole U1439C and U1442A based on Reagan et al. (2015). Red Arrows to the left of the U1439C stratigraphic section, point to the core section which samples U1439C-2R3W 2-3, U1439C-15R1W 8-10, U1439C-19R2W 46-48, and U1439C-25R2W 18-19 came from. Zones indicating mixed magmas on the stratigraphic sections were identified by the shipboard crew.

Figure 3
Pyroxene Quadrilateral with pyroxenes from samples samples U1439C-2R3W 2-3 (2R3), U1439C-15R1W 8-10 (15R1), U1439C-19R2W 46-48 (19R2), and U1439C-25R2W 18-19 (25R2) plotted. Enstatite (En), Wollastonite (Wo), Ferrosilite (Fs), and Ca-Tschermak (CaTs).
Pyroxenes that have anomalous Al concentration show a trend towards ferrosilite and can be seen in the brown dashed circle. Data can be found in Online Material\(^1\) Table OM3 and OM4.

Figure 4

Elemental maps of low-Ca pyroxene phenocrysts from sample 15R1. Red arrows in elemental maps point to zones enriched in Mg & Cr and depleted in Fe, Al, Mn, and Ti. Labels (Px 1) and (Px 2) in map (a) refer to the label used in (Online Material\(^1\) Table OM3.) and (Figs. 6 and Online Material\(^1\) Table OM3) to identify the individual pyroxene grains. Label (UPx) in map (a) refers to the label used in (Fig. 6) as an across grain chemical transect was not made for this pyroxene grain. Unanalyzed Pyroxene (UPx). Elemental maps were produced using LA-ICP-TOF.

Figure 5

Elemental maps of zoned olivine phenocrysts from sample 25R1. Red arrows in elemental maps point to zones enriched in Mg, Cr, and Ni and depleted in Fe, Mn, and Ca. White arrows on maps (b), (e), and (g.) points at a zone between the core and rim of this grain, which is more depleted in Mg, Ni, and Cr than the rim of the grain. Label (Ol 1) in the bottom left-hand corner of map (a) refers to the label used in (Online Material\(^1\) Table OM5) and (Online Material\(^1\) Fig. OM4) to identify the individual olivine grains. Elemental maps (a), (b), (c), and (d) were produced using EPMA. Elemental maps (e), (f.), (g.), and (h.) were generated using LA-ICP-TOF.

Figure 6

Drawn models of the zoning patterns observed in low-Ca pyroxene phenocrysts from sample 15R1 (shown in Fig. 4). Drawings in the first column highlight the oscillatory zoning patterns observed in Mg and Cr. Drawings in the second column highlight the sector zoning pattern observed in Cr, Al, and Ti. Drawings in the last column combine the zoning profiles so they can

...
be compared with each other. Labels (Px 1) and (Px 2) refer to the labels used in Online Material^1 Table OM3, Figure 4, and Figure OM3 to identify the individual pyroxene grains. Label (UPx) refers to the label used in Figure 4 as an across grain chemical transect was not made for this pyroxene grain. Unanalyzed Pyroxene (UPx).

Figure 7

Idealized crystallization model for the development of complex pyroxene zoning patterns observed in this study. (a) Idealized pyroxene crystallization history showing the development of the sector and oscillatory zoning profiles as the crystal grows in an open igneous system. Progression from core to rim is indicated above the models. Crystal shape and sector zones based on the 2D model in (b) (b) Hypothetical 2D model of the crystal of a pyroxene crystal (cutting through the center of the crystal) revealing the sector zoning pattern along the a- and c- axis (the {-111} and {100} prism forms). Modified from Ubide et al. (2019). Note this model is not meant to show the exact zoning profiles observed in pyroxenes from sample 15R1 (Fig. 4) as we do not know the exact angle in which those crystals were cut and polished during sample preparation. This model is only meant to show what the zoning profile would look like in a perfectly cut crystal, based on the hypothesized open-system processes from this paper.

Figure 8

BSE image and elemental maps of zoned groundmass clinopyroxene from sample 25R1. The red box in the BSE image (a) shows the area which was analyzed in elemental maps (b), (c), (d), (e), and (f). Red Arrows in the elemental maps point to Mg & Cr enriched zones in the pyroxene. Blue arrows in the elemental maps point to Mg, Fe, and Cr rich core of the grain, which is depleted in Ca and Al. Green arrow in elemental map (c) points to Fe enrichment around the edge of the grain. Label (Px 14) in the top right-hand corner of map (a) refers to the label used in
Figure 9

Boninite magma chamber and mixing model. Primitive boninite melts pond beneath the fore-arc crust before ascending through a crystal mush zone (a) Primitive melts begin to crystallize as they migrate through the crystal mush, ascending towards a fractionating magma chamber with a cumulate pile (b). Primitive melts enter the chamber and dislodging cumulate material (c). Primitive plume ascends into the evolved magma chamber resulting in magma mixing, along with reverse and normal zoning patterns (c).

Tables

Table 1. Typical Magma End-member Assembleges.

<table>
<thead>
<tr>
<th>End member</th>
<th>Phenocrysts</th>
<th>Minor minerals</th>
<th>Matrix</th>
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<td>HSB</td>
<td>Orthopyroxene ± Olivine</td>
<td>Cr-spinel</td>
<td>Clinopyroxene</td>
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<tr>
<td>LSB</td>
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<td>Cr-spinel</td>
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<td>HMA</td>
<td>Plagioclase + Clinopyroxene</td>
<td>Magnetite + Ilmenite</td>
<td>Clinopyroxene + Plagioclase</td>
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</table>

*End-members: High-Si Boninite (HSB), Low-Si Boninite (LSB), High-Mg Andesite (HMA)*

Table 2. Normal Mineral Composition Observed in Magma Endmembers (Non-Mixing Samples).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>SiO2 (wt%)</th>
<th>TiO2 (wt%)</th>
<th>Al2O3 (wt%)</th>
<th>Cr2O3 (wt%)</th>
<th>FeO (wt%)</th>
<th>MgO (wt%)</th>
<th>MnO (wt%)</th>
<th>NiO (wt%)</th>
<th>CaO (wt%)</th>
<th>Na2O (wt%)</th>
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Minerals: Olivine (Ol), Cr-Spinel (Cr-SP), Enstatite (En), Clinoenstatite (CLEN), Pigeonite (PIG), Augite (AUG), Plagioclase (PLAG).

Mineral end-member components: Enstatite (En), Wollastonite (Wo), Ferrosilite (Fs), Forsterite (Fo), Anorthite (An)

Mg#=100*(Mg/(Mg+Fe)), Cr#= 100*(Cr/(Cr+Al))
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<th>Sample</th>
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<th>Pheno OL</th>
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<td>0.016</td>
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a Mineral: Olivine Xenocryst (Ol Xeno), Olivine Phenocryst (Ol Pheno).
b Samples: U1439C-25R-2-W 18-19 (25R2), U1439C-15R-1-W 8-10 (15R1), U1439C-19R-2-W 46-48 (19R2), U1439C-2R-3-19 (2R3).
c Olivine End-member Components: Forsterite (Fo), Fayalite (Fa).
Table 1.  
Typical Magma End-member Assembleges.

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<th>Minor minerals</th>
<th>Matrix</th>
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<td>Cr-spinel</td>
<td>Clinopyroxene</td>
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<tr>
<td>LSB</td>
<td>Olivine + Orthopyroxene</td>
<td>Cr-spinel</td>
<td>Clinopyroxene ± Plagioclase</td>
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<tr>
<td>HMA</td>
<td>Plagioclase + Clinopyroxene</td>
<td>Magnetite + Ilmenite</td>
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\*End-members: High-Si Boninite (HSB), Low-Si Boninite (LSB), High-Mg Andesite (HMA)
Table 2.
Normal Mineral Composition Observed in Magma Endmembers (Non-Mixing Samples).

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<th>Sample</th>
<th>Mineral</th>
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<th>TiO$_2$ (wt%)</th>
<th>Al$_2$O$_3$ (wt%)</th>
<th>Cr$_2$O$_3$ (wt%)</th>
<th>FeO (wt%)</th>
<th>MgO (wt%)</th>
<th>MnO (wt%)</th>
<th>NiO (wt%)</th>
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<td>0.19</td>
<td>10.87</td>
<td>22.72</td>
<td>0.11</td>
<td>0.08</td>
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a Minerals: Olivine (Ol), Cr-Spinel (Cr-SP), Enstatite (En), Clinoenstatite (CLEN), Pigeonite (PIG), Augite (AUG), Plag

b Mineral end-member components: Enstatite (En), Wollastonite (Wo), Ferrosilite (Fs), Forsterite (Fo), Anorthite (Fo)

c Mg# = 100*(Mg/(Mg+Fe)), Cr# = 100*(Cr/(Cr+Al))
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.plagioclase (PLAG).

An)
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<th>Sample</th>
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<th>TiO2 (wt%)</th>
<th>Al2O3 (wt%)</th>
<th>Cr2O3 (wt%)</th>
<th>FeO (wt%)</th>
<th>MgO (wt%)</th>
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<th>CaO (wt%)</th>
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a Mineral: Olivine Xenocryst (Ol Xeno), Olivine Phenocryst (Ol Pheno).
c Olivine End-member Components: Forsterite (Fo), Fayalite (Fa).
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U1439C-2R-3-W 2-3 (2R3).
Figure 1

- Figure 1a: Map of Chichijima with coordinates and sample locations labeled.
- Figure 1b: Cross-sectional diagram showing layers labeled as Boninite Forearc Basalt, Gabbro, Forearc Basalt, Dolerite, and Depleted Peridotite. Scale is 2 km.
Figure 3

a. 

b.
Figure 4
Figure 5
<table>
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Figure 6
Cr and Al rich sectors form.

Mg and Si rich sectors form.

Cr and Al rich sectors form.

Mg and Cr enriched and Al, Ti, and Mn depleted oscillation to form.

Magmatic recharge causes Mg and Cr enriched and Al, Ti, and Mn depleted oscillation to form.

System reaches near equilibrium conditions again and sector zoning continues.

Process occurs multiple times before eruption resulting in multiple oscillations which cut across sectors.

Figure 7
Primitive Boninite Melts
Evolving Boninite Chamber
Crystal Mush
Solidified Intrusive Rock
Depleted Peridotite

Figure 9

Legend:
- Solidified Intrusive Rock
- Crystal Mush
- Primitive Boninite Melts
- Evolving Boninite Chamber
- Depleted Peridotite
- Cumulate Material