A Geochemical Investigation of Oxygen Fugacity in the Marianas Subduction Factory

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A GEOCHEMICAL INVESTIGATION OF OXYGEN FUGACITY IN THE MARIANAS SUBDUCTION FACTORY

BY

MARYJO N. BROUNCE

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN OCEANOGRAPHY

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OF

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ABSTRACT

Oxygen fugacity is a fundamental thermodynamic property that describes reduction-oxidation (redox) equilibria in the solid Earth. It controls material transfer from the interior to the exterior of the planet by dictating the speciation of multi-valent elements (e.g., Fe, V, S). Oceanic crust ages and oxidizes as it moves from spreading centers to subduction zones, where it returns to the mantle in modified form. Subducting slabs release H$_2$O-rich fluids and SiO$_2$-rich melts to the mantle wedge in subduction zones, contributing significantly to the isotopic and major, trace, and volatile element composition of arc and back-arc magmas, however the effect that the oxidized nature of subducting slabs on arc basalts remains unclear. Arc basalts have a higher proportion of oxidized (Fe$^{3+}$) relative to reduced (Fe$^{2+}$) iron, expressed as the Fe$^{3+}$/ΣFe ratio, than do mid-ocean ridge basalts (MORB) but there is disagreement as to whether this arises due to shallow level differentiation processes (e.g., crystal fractionation, crustal assimilation, degassing) in the arc crust or to differences in the fO$_2$ of the mantle source. This thesis addresses this problem by examining the oxidation state of Fe and other transition element proxies for fO$_2$ in (1) altered oceanic crust prior to subduction, (2) modern eruptive products from the active Mariana arc and back-arc, and (3) eruptive products representative of subduction initiation and margin evolution in the Marianas.

Melt inclusions and submarine glasses record variable magmatic compositions that have the potential to record changes in magma chemistry during crystal fractionation and volcanic degassing. Recent innovations in synchrotron technologies have made studies of Fe redox possible in situ, on small scales (>10 microns),
allowing direct observation of changes in Fe redox during shallow level differentiation processes in arc and back-arc magmas. This study reports observations of Fe redox variation from several Mariana arc volcanic centers as well as from the Mariana trough, demonstrating that shallow level differentiation processes are not responsible for generating the oxidized nature of arc basalts. Constraints for mantle source $f$/$O_2$ show that the mantle wedge is more oxidized than MORB source mantle and link this oxidation to influence from recycling slab fluids. Additionally, we explore other transition row element proxies for $f$/$O_2$ and show that these proxies need not preclude oxidized mantle wedge conditions in the Marianas. We examine changes in Fe redox in samples that record subduction initiation and margin evolution, demonstrating that in zones of melt generation within the mantle wedge, oxidation occurs immediately upon subduction initiation and that the mantle wedge remains oxidized for the majority of a subduction zone’s lifetime. We further constrain the fluxes of Fe$^{3+}$ in to and out of the Mariana convergent margin, demonstrating that the Pacific plate is very oxidized prior to subduction and that 50-70% of this oxidized signature survives the recycling process to be subducted into the deep upper mantle.
ACKNOWLEDGEMENTS

There are many people who have guided me to completing this dissertation, all of whom deserve my deepest and sincere thanks. I acknowledge them here for their dedication, patience, and support.

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I have the honor of being recognized several times for my work during my graduate career. I received honorable mention in the 2010 and 2011 National Science Foundation Graduate Fellowship program. I am the proud recipient of the Watkins Award and Robert L. McMaster Scholarship in Marine Geology, for distinction in graduate studies at the University of Rhode Island Graduate School of Oceanography. I was also awarded the GeoPRISM Student prize for best oral presentation as well as the AGU Outstanding Student Paper Award in Tectonophysics at the 2012 Fall AGU Meeting. Each of these awards came with encouragement when it was needed most, as well as monetary support. The research presented here was supported through the National Science Foundation, MARGINS, and Smithsonian Scholarly Studies. I received additional stipend support from the Deep Carbon Observatory. Access to the National Synchrotron Light Source at Brookhaven National Laboratory was supported by the US Department of Energy, Office of Basic Energy Sciences.

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PREFACE

This dissertation consists of geochemical analyses from natural rock samples from the Mariana volcanic arc, back-arc, and materials from the Pacific plate at ODP Site 801. The dissertation is written in manuscript format and consists of four manuscripts presented in separate chapters.

The first manuscript, “Variations in Fe\(^{3+}/\Sigma\)Fe of Mariana arc basalts and mantle wedge f\(_O\)\(_2\)” presents an investigation of Fe redox in subduction related basaltic glasses, provides constraints for mantle wedge f\(_O\)\(_2\) along the Mariana arc and back-arc, and links the oxidized nature of arc and back-arc basalts to the influence of recycling slab fluids. This work was presented at the 2010 and 2012 Fall Meetings of the American Geophysical Union, winning honorable mention in the GeoPRISMS student paper presentation competition in 2010, first prize in the GeoPRISMS student paper presentation as well as the Tectonophysics section award for Outstanding Student Paper presentation in 2012. This was the subject of two invited talks at Brown University and Boston University in 2011 and 2012, respectively. It has been submitted for publication to the Journal of Petrology.

The second manuscript, “Temporal evolution of mantle wedge oxygen fugacity during subduction initiation” constrains the temporal evolution of f\(_O\)\(_2\) in the Mariana mantle wedge at the onset of subduction initiation, showing that oxidation upon subduction initiation and maturation occurs rapidly. This research was presented at the 2013 Fall meeting of the American Geophysical Union. A manuscript is currently being prepared for submission to Nature.
The third manuscript, “An evaluation of transition row element proxies for mantle source oxygen fugacity”, tests several proxies for mantle source $f$O$_2$ on the same mid-ocean ridge, back-arc, and arc basalts to investigate the origins of disagreement between them and the Fe-based proxy. We demonstrate that the full range of predicted mantle source $f$O$_2$ reported by each proxy does not preclude oxidized mantle wedge conditions in the Marianas. This research was presented at the 2013 Goldschmidt meeting in Florence, Italy. A manuscript is currently being prepared for submission to Earth and Planetary Science Letters.

The fourth and final manuscript, “The redox budget of the Mariana subduction system”, presents the Fe$^{3+}$/ΣFe ratios of sediments and altered oceanic crust recovered from ODP Site 801 in order to constrain the input flux of Fe$^{3+}$ to the Mariana subduction system. Using constraints from chapters 1, 2, and 3 to constrain output fluxes from the Mariana subduction system, we show that greater than 50% of the oxidized signature that the slab acquires as the result of alteration on the seafloor survives the subduction system and is subducted into the deep mantle. A manuscript is currently being prepared for submission to an AGU journal.
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MANUSCRIPT 1: VARIATIONS IN $\text{Fe}^{3+}/\Sigma\text{Fe}$ OF MARIANA ARC BASALTS AND MANTLE WEDGE $fO_2$

In review at Journal of Petrology

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ABSTRACT

Arc basalts are more oxidized than mid-ocean ridge basalts, but it is unclear whether this difference is due to differentiation processes in the Earth’s crust or to a fundamental difference in the oxygen fugacity of their mantle sources. Distinguishing between these two hypotheses is important for understanding redox-sensitive processes related to arc magmatism, and thus more broadly how Earth materials cycle globally. We present major, volatile, and trace element concentrations in combination with Fe$^{3+}/\Sigma$Fe ratios determined in olivine-hosted glass inclusions and submarine glasses from five Mariana arc volcanoes and two regions of the Mariana trough. For individual eruptions, Fe$^{3+}/\Sigma$Fe ratios vary along liquid lines of descent that are either slightly oxidizing (olivine + clinopyroxene + plagioclase fractionation, CO$_2$ ± H$_2$O degassing) or reducing (olivine + clinopyroxene + plagioclase ± magnetite fractionation, CO$_2$ + H$_2$O + S degassing). Mariana samples are consistent with a global relationship between calc-alkaline affinity and both magmatic H$_2$O and magmatic oxygen fugacity, where wetter, higher oxygen fugacity magmas display greater affinity for calc-alkaline differentiation. We find, however, that low-pressure differentiation cannot explain the majority of variations observed in Fe$^{3+}/\Sigma$Fe ratios for Mariana arc basalts, requiring primary differences in magmatic oxygen fugacity. Calculated oxygen fugacities of primary mantle melts at the pressures and temperatures of melt segregation are significantly oxidized over mid-ocean ridge basalts (~QFM), ranging from QFM+1.0 – QFM+1.6 for Mariana arc basalts, while back-arc related samples record primary oxygen fugacities that range from QFM+0.1 – QFM+0.5. This Mariana arc sample suite comprises a diversity of subduction
influences, from lesser influence of a homogeneous H$_2$O-rich component in the back-arc, to sediment melt- and fluid-dominated influences along the arc. Primary melt oxygen fugacity does not correlate significantly with sediment melt contributions (e.g., Th/La), nor can it be attributed to previous melt extraction in the back-arc. Primary melt oxygen fugacity correlates strongly with indices of slab fluids (e.g., Ba/La) from the Mariana trough through the Mariana arc, increasing by 1.5 orders of magnitude as Ba/La increases by a factor of 10 over mid-ocean ridge basalts. These results suggest that contributions from the slab to the mantle wedge may be responsible for the elevated oxygen fugacity recorded by Mariana arc basalts and that slab fluids are potentially very oxidized.

Key words: differentiation; Mariana arc; melt inclusions; oxygen fugacity; redox; subduction

INTRODUCTION

Oxygen fugacity ($f_{O_2}$) is a fundamental thermodynamic property that governs reduction-oxidation (redox) equilibria in solid Earth systems. It controls material transfer from the interior to the exterior of the Earth by setting the speciation of multi-valent elements (e.g., Fe, S, V, C), which in turn controls their crystal/melt partitioning behaviors (e.g., Canil, 2002), their physical state and mobility in the mantle (e.g., Rohrbach & Schmidt, 2011), and their solubility in silicate melts (e.g., Jugo et al., 2010). Despite its power in dictating chemical exchange in the Earth however, the $f_{O_2}$ of the upper mantle and whether it varies through space and geologic
time is widely debated (e.g., Ballhaus, 1993, Bezos & Humler, 2005, Bryndzia & Wood, 1990, Carmichael, 1991, Christie et al., 1986, Cottrell & Kelley, 2011, Cottrell & Kelley, 2013, Kelley & Cottrell, 2009, Kelley & Cottrell, 2012, Lee et al., 2005, Lee et al., 2012, Lee et al., 2010, Parkinson & Arculus, 1999, Rowe et al., 2009, Trail et al., 2011, Wood et al., 1990).

Oceanic crust ages and oxidizes as it moves from spreading centers to subduction zones, where it is recycled into the mantle, and material from the down-going slab contributes chemically to the mantle source of arc magmas (e.g., Alt & Teagle, 2003, Elliott et al., 1997, Lecuyer & Ricard, 1999, Plank & Langmuir, 1993). Arc basalts have a higher proportion of oxidized (Fe$^{3+}$) relative to reduced (Fe$^{2+}$) iron, expressed as the Fe$^{3+}$/ΣFe ratio (i.e., Fe$^{3+}$/[Fe$^{2+}$+Fe$^{3+}$]), than do MORB (Carmichael, 1991). There is disagreement as to whether this arises due to differentiation processes (e.g., crystal fractionation, crustal assimilation, degassing) in the arc crust or to differences in the $f$O$_2$ of the mantle source. Experimentally calibrated trace element proxies for mantle $f$O$_2$, which are potentially more immune to differentiation processes in the arc crust, suggest that the $f$O$_2$ of arc mantle is similar to the MORB primary magmas (Lee et al., 2005, Lee et al., 2012, Lee et al., 2010). Magmatic oxidation may perhaps be influenced by later stage crustal processes, such as the extensive fractionation of Fe$^{2+}$-bearing minerals (e.g., olivine) or by the assimilation of oxidized crustal material, although such relationships have not yet been observed or quantitatively modeled.

Yet, a global study of basaltic glasses shows that those magmas most heavily influenced by subduction have higher Fe$^{3+}$/ΣFe ratios than MORB (Kelley & Cottrell,
Moreover, olivine-hosted melt inclusions from a single eruptive event from Agrigan volcano in the Marianas show that the least differentiated melts have the highest Fe$^{3+}$/ΣFe ratios, and the Fe$^{3+}$/ΣFe ratios of reconstructed primary melts correspond to a source mantle that is oxidized 1 – 1.6 orders of magnitude over the MORB source (Kelley & Cottrell, 2012). In addition, a paired study of whole rock Fe$^{3+}$/ΣFe ratios determined by wet chemical methods and $f$O$_2$ calculated from magnetite-ilmenite mineral pairs demonstrates that andesites from the Mexican volcanic belt experienced no net change in bulk Fe$^{3+}$/ΣFe ratios despite significant changes in volatile content and extent of crystal fractionation (Crabtree & Lange, 2011). These observations suggest that low-pressure crystallization and degassing do not significantly oxidize arc magmas and instead indicate that high Fe$^{3+}$/ΣFe ratios recorded by arc magmas reflect a mantle source that has higher $f$O$_2$ than MORB source mantle.

Outside of mid-ocean ridge settings, Fe redox studies that specifically address the effects of differentiation on Fe speciation have thus far been limited. For example, elevated magmatic water contents, derived from the subducting plate, may suppress plagioclase saturation and decrease the temperature difference between the appearance of silicates and magnetite on the liquidus (Sisson & Grove, 1993), potentially influencing whether a basaltic magma follows a calc-alkaline (Fe-depleted) or tholeiitic (Fe-enriched) differentiation path (e.g., Zimmer et al., 2010). Yet, magmatic H$_2$O and Fe$^{3+}$/ΣFe ratios are strongly correlated (Kelley & Cottrell, 2009), and high magmatic $f$O$_2$ also enhances the appearance of oxides relative to silicates on the basalt liquidus (Botcharnikov et al., 2008, Osborn, 1959). The effects of $f$O$_2$ and H$_2$O on
magmatic differentiation may thus be difficult to segregate. Magnetite fractionation in a system closed to oxygen is also expected to reduce magmatic Fe$^{3+}/${\Sigma}Fe ratios, but this phenomenon has not been observed directly in the natural rock record. If source mantle $fO_2$ at convergent margins is elevated over MORB, the cause of this oxidation and the extent to which it varies are central to developing models for the structure and growth of arc crust, and of the oxygen evolution of Earth through time. Does primary $fO_2$ change as subduction influence varies or diminishes? What effect do variable extents of fluid or sediment melt infiltration have on primary $fO_2$?

To answer these questions, we examine the relationships between crystal fractionation, degassing, mantle source composition, subduction influence, and magmatic or mantle $fO_2$ along the entire Mariana subduction zone. With this work, we investigate a variety of crystal fractionation and degassing processes recorded by arc and back-arc basaltic glasses and examine the relationships between these processes and magmatic Fe redox. We present new major, trace, and volatile element concentrations as well as Fe$^{3+}/${\Sigma}Fe ratios in olivine-hosted melt inclusions from single eruptive events at five sub-aerial volcanic centers along the Mariana arc (Sarigan, Guguan, Alamagan, Pagan, and Agrigan), in addition to submarine glasses from NW Rota-1 and Pagan volcanoes (Tamura et al., 2013, Tamura et al., 2011) and the Mariana trough back arc spreading center (Fig. 1). After assessing the effects of differentiation on magmatic redox, we use major element trends defined by the data to reconstruct primary melt compositions and mantle source $fO_2$ conditions. We then pair these with key trace element ratios (Ba/La, Th/La, and Zr/Y) to assess the extent to which different slab derived materials may influence the $fO_2$ of the mantle wedge.
GEOLOGIC SETTING

The Mariana subduction system is a well-studied ocean-ocean convergent margin with an active sub-aerial and submarine arc made up of ~40 volcanic centers and the Mariana trough, an actively extending back-arc basin (Fig. 1; Bloomer et al., 1989, Fryer, 1996, Hickey-Vargas & Reagan, 1987, Stern, 1979, Tollstrup & Gill, 2005, Woodhead, 1989). The arc is split into three distinct segments, the Northern Seamount Province, the Central Island Province, and the Southern Seamount Province. The Central Island and Southern Seamount Provinces are both built on oceanic lithosphere previously rifted by the opening of the Mariana trough and the Parece-Vela basin (Fryer, 1996). The composition of erupted products along these arc volcanic centers are well studied and are primarily basaltic in composition (Bloomer et al., 1989, Kelley et al., 2010, Martindale et al., 2013, Meijer & Reagan, 1981, Pearce et al., 2005, Shaw et al., 2008, Wade et al., 2005). The northern to central Mariana trough, here termed collectively the northern Mariana trough, is opening asymmetrically in an east-west direction and generally mimics the arcuate shape of the volcanic front (Fryer, 1996). The volcanic arc follows the strike of the Mariana trench north of ~13ºN. South of this latitude, the trench curves sharply to an east-west orientation. In this area, both arc and back-arc volcanism approach the trench and the subducting Pacific plate is shallower beneath this magmatically active area (Ribeiro et al., 2013, Syracuse & Abers, 2006). Taken together, the oceanic upper plate, mafic magmatism, and the presence of a mature back-arc spreading center make the Mariana
arc an ideal setting for studying the competing effects of source $fO_2$ and shallow crustal processes on the Fe$^{3+}/\Sigma$Fe ratios of arc and back-arc basalts.

**SAMPLES AND METHODS**

**Mariana arc tephra samples**

Olivine hosted melt inclusions were targeted for this study for several reasons. First, suites of melt inclusions from a single eruptive event at a volcano potentially display a range of variable, pre-eruptive magmatic compositions that correspond to the changing compositions of a differentiating magma. Olivine is an early fractionating phase in the evolution of basaltic magma, such that melt inclusions hosted in olivine often record early stages of differentiation compared to plagioclase- or clinopyroxene-hosted inclusions, and so their compositions may be closer to the composition of parental magmas than the final erupted lavas. Finally, melt inclusions have also been shown to preserve less degassed volatile concentrations than erupted lavas, allowing the study of the effects of volcanic degassing along with crystal fractionation on Fe redox in subduction zone magmas.

The glass inclusions analyzed in this study were picked from nine Mariana arc tephra samples originating from five volcanoes from the Central Island province of the Mariana arc (numbers indicate disparate eruptions): Sarigan (Sari15-04), Guguan (Gug11 and Gug23-02), Alamagan (Ala02 and Ala03; Shaw *et al.*, 2008), Pagan (Paga8), and Agrigan (Agri07, Agri05 and Agri04, Fig. 1). These samples were collected by a MARGINS-NSF field expedition to the Mariana arc in 2004 and donated to this study by T. Plank (http://sio.ucsd.edu/marianas; Figure 1). Each tephra
sample was washed in de-ionized water and sieved, taking care to avoid any samples with clasts larger than two centimeters to ensure that all material had a short cooling history upon eruption (e.g., Lloyd et al., 2012). Olivine crystals were either hand-picked from sieved size fractions or separated using lithium poly-tungstate heavy liquid separation, using modified techniques from Luhr (2001). Large (0.5-1 mm), euhedral olivines or olivine fragments were immersed in mineral oil to identify glass inclusions, which were selected for analysis if they were >50 µm in diameter, completely glassy, without daughter or co-entrapped minerals, fully contained by the host olivine, and contained no more than one vapor bubble. Representative photomicrographs are shown in Figure 2. Photomicrographs of every inclusion are shown in electronic appendix K.

Submarine glass samples

Glassy pillow lavas from the southernmost Mariana trough (Malaguana-Gadao ridge) were dredged from the seafloor between 12.5° - 13.2°N, during expedition TN273 of the R.V Thomas G. Thompson in 2011-2012 (Southern Mariana trough, Fig. 1). Glassy pillow lavas from submarine volcanic exposures at Pagan and NW Rota-1 volcanoes were provided by Yoshi Tamura (Tamura et al., 2013, Tamura et al., 2011). Glass chips were chiseled and hand picked from the freshest pillow lavas in each dredge and washed in de-ionized water prior to preparation for analysis. We also incorporate previously published data for submarine glass samples from the northern Mariana trough (18.1° - 20.9°N; Kelley & Cottrell, 2009, Newman et al., 2000, Pearce et al., 2005, Stolper & Newman, 1994; Fig. 1).

Analytical methods
Submarine glass chips and glass inclusions were exposed on a single side and polished for electron microprobe analyzer (EMPA) analysis on a JEOL-8900 spectrometer microprobe at the Smithsonian Institution. During major element analysis, the beam was operated at 10nA, an accelerating voltage of 15 kV and 10 µm beam diameter. Sodium and potassium were measured first with 20 second peak count times to minimize alkali loss. Subsequently, Si, Ti, Al, Fe*, Mn, Ca and P were measured with 30-40 second peak count times. All data were subject to ZAF correction procedures. Primary calibration standards include VG-2 glass, Kakanui hornblende, anorthite, microcline, ilmenite, and apatite (Jarosewich et al., 1980). The VG-2 and VG-A99 glasses were monitored as secondary standards during each run (Jarosewich et al., 1980). Sulfur and chlorine were measured separately using a beam operated at 80 nA, an accelerating voltage of 15 kV and 10 µm beam diameter. Scapolite was used as the primary calibration standard (0.529 wt% S, 1.49 wt% Cl). The VG-2 (1320 ppm S, 300 ppm Cl) and NIST 620 (1121 ppm S) glasses were used as secondary standards in each run (Jarosewich et al., 1980, Carroll & Rutherford, 1988, Wallace & Carmichael, 1991).

The major element compositions of the olivine hosts were measured adjacent to the glass inclusions as well as at the rims of the olivines to eliminate zoned hosts that reflect potentially complex magmatic histories. A focused electron beam was operated at 10 nA and an accelerating voltage of 15 kV. San Carlos olivine and fayalite were used as primary calibration standards, San Carlos olivine and Springwater olivine were used as secondary standards during each run (Jarosewich et
al., 1980). Significant olivine zoning was not observed for any samples in this study and the olivine compositions reported in electronic appendix E are average values of all three to six analysis spots on each olivine.

**FTIR Analysis**

After EMPA analysis of melt inclusions, all sample pits were polished away, being careful to account for possible electronic damage within the activation volume of each EMPA spot. Melt inclusions were then polished from the opposite side until doubly exposed, and submarine glasses were wafered to a nominal thickness of 80 µm (though some were as thin as 20 µm) to create wafers with analyzable pools of optically clear glass. All wafered samples were washed gently with acetone to remove all epoxy residues. Dissolved H₂O and CO₂ concentrations in glasses and glass inclusions were analyzed by Fourier-transform infrared (FTIR) spectroscopy at the Smithsonian Institution. All samples were analyzed using either a Bio-Rad MA-500 microscope attached to a Bio-Rad Excalibur FTS 3000 FTIR spectrometer or a Continuum microscope coupled with a Thermo-Nicolet 6700 FTIR spectrometer. Spectra for all samples were collected between 1000-6000 cm⁻¹ using a tungsten-halogen source, KBr beamsplitter and a liquid-nitrogen cooled MCT-A detector. The bench, microscope, and samples were continuously purged by air free of water and carbon dioxide using a Whatman purge-gas generator. Aperture dimensions were selected for each sample depending on the geometry of free glass pathways, ranging in size from 12 µm x 12 µm to as large as 60 µm x 60 µm. Dissolved total H₂O concentrations were determined using the 3530 cm⁻¹ band where possible, although the elevated H₂O concentrations typical of arc glass inclusions frequently result in
saturation at 3530 cm\(^{-1}\). In these cases, the OH absorption (4500 cm\(^{-1}\)) and molecular H\(_2\)O absorption (1630, 5200 cm\(^{-1}\)) bands were summed to calculate total H\(_2\)O concentrations. In samples where the 3530 cm\(^{-1}\) band was not saturated, total H\(_2\)O concentrations calculated from the 4500 + 1630/5200 cm\(^{-1}\) bands agree within error (<10% relative) with those calculated from the 3530 cm\(^{-1}\) band. Dissolved CO\(_3^{2-}\) concentrations were determined by using the 1515 and 1435 cm\(^{-1}\) absorption bands (Dixon et al., 1995). Thicknesses of each sample were measured using a piezometric digimatic indicator (\(\sigma \pm 1 \mu m\)). Glass densities and absorption coefficients relevant to each absorption band were calculated using methods from Dixon et al. (1995) and Luhr (2001).

**XANES analysis**

All samples were analyzed in situ for Fe\(^{3+}\)/\(\Sigma\)Fe ratios via micro X-ray absorption near edge structure spectroscopy (\(\mu\)-XANES) following the methods and techniques of Cottrell et al. (2009) at beamline X26A, National Synchrotron Light Source, Brookhaven National Laboratory. Spectra were collected in fluorescence mode from 7020 eV and 7220 eV using a Si [311] monochromator and a nominal beam size of 9x5 \(\mu m\). A beryllium window over the detector was used to attenuate high count rates above the main Fe K\(\alpha\) fluorescence peak. Reference glass LW-0 was monitored continuously during each experimental session to correct for instrument drift. Further details related to this correction can be found in Cottrell et al. (2009).

Spectra were scrutinized for any influence from host olivines, phenocrysts, or micro phenocrysts in the glass chips and inclusions. If crystal interference was found, these spectra were eliminated from further study. Examples of the influence of crystal
interference on Fe-XANES spectra are provided in Electronic Appendix A (Fig. A1).

Determination of \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratios in basaltic glasses following the methods of Cottrell et al. (2009) have an associated precision of \( \pm 0.005 \).

**LA-ICP-MS analysis**

Abundances of 33 trace elements (Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th, U) were determined in submarine glasses and glass inclusions by laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) at the Graduate School of Oceanography, University of Rhode Island on a Thermo X-Series II quadrupole ICP-MS coupled with a New Wave UP 213 Nd-YAG laser ablation system following techniques outlined by Kelley et al. (2003) and Lytle et al. (2012), normalizing to \(^{43}\text{Ca}\) as the internal standard. The laser energy was 0.20-0.30 mJ at the sample surface for a reference spot (60 \( \mu \text{m}, 10 \text{ Hz} \)) on NIST 612 glass and the repeat rate was decreased to 5 Hz in melt inclusions and thin glass wafers, to achieve a slow drilling rate of \( \sim 1 \mu\text{m/s} \) through thin samples. Spot sizes ranged from 20-80 \( \mu\text{m} \).

United States Geological Survey glass standards BCR-2g, BHVO-2g, BIR-1g, and Max Planck Institute glass standards GOR-132-G, StHls-G, T1-G, ML3B-G and KL2-G were used to create linear calibration curves (\( R^2 > 0.990 \)) for each analytical session (Jochum et al., 2006, Kelley et al., 2003). Melt inclusions were analyzed in single spot analyses. Counting statistics were examined carefully for each element and those elements that did not return strong signals for the entire length of the laser ablation period were discarded. Submarine glasses were analyzed in triplicate and concentrations were reproducible to within 4% rsd for all elements.
RESULTS

In total, 113 olivine-hosted glass inclusions were prepared for analysis. Thirty-four of these inclusions were lost during various stages of preparation or did not return glassy XANES spectra, suggesting that they had an unfavorable geometry for XANES analysis or were otherwise devitrified. The remaining 79 inclusions were subject to data filtering procedures outlined below.

Inclusion/olivine equilibrium and post-entrapment crystallization

Melt inclusions are trapped in olivine phenocrysts at high temperatures. As inclusion and olivine cool during magmatic ascent and eruption, olivine may precipitate along the wall of the inclusion during post-entrapment crystallization (PEC). To screen for the effects of PEC, the predicted equilibrium olivine composition was calculated for each melt inclusion using $\frac{\text{Fe}^{2+}/\text{Mg}}{K_{D}^{\text{Olv/lique}}} = 0.3$ (Roeder & Emslie, 1970), and compared to the measured host forsterite contents ($\text{Fo}; \frac{\text{Mg}/([\text{Fe}^{2+} + \text{Mg}])}{\text{Mg}}$) of the olivine host of each inclusion. If the predicted equilibrium $\text{Fo}_{\text{inclusion}}$ matched the measured $\text{Fo}_{\text{host}}$, equilibrium between inclusion and host was assumed and no action was taken. If the inclusion composition has been modified by PEC, the predicted equilibrium $\text{Fo}_{\text{inclusion}}$ should be lower than the measured $\text{Fo}_{\text{host}}$ (e.g., Anderson, 1973). In these cases, calculated equilibrium olivine was added to the inclusion in 0.1% increments until the inclusion and host reached equilibrium. If the predicted equilibrium $\text{Fo}_{\text{inclusion}}$ was higher than the $\text{Fo}_{\text{host}}$ (indicative of Fe loss, e.g., Danyushevsky et al., 2000) no action was taken. Those inclusions that required >2% PEC correction or whose $\text{Fo}_{\text{host}}$-$\text{Fo}_{\text{inclusion}}$ disagreed by more than 2% were excluded from further consideration or modeling, although their compositions are reported in
Furthermore, for each melt inclusion suite, the inclusion compositions were compared to published whole-rock and melt inclusion data for each volcano, with particular attention to variation in FeO* vs MgO (Electronic Appendix A; Danyushevsky et al., 2000). Inclusion compositions that fell outside of the data field defined by the published whole-rock data were excluded. This rigorous data filtering is meant to avoid melt inclusion compositions with complicated magmatic histories that may cloud the discussion of magmatic redox variations and source fO₂. The remaining discussion considers only the 48 melt inclusions that satisfy the requirements outlined here.

**Compositions of Mariana arc and back-arc melt inclusions and glasses**

In order to constrain the effects of fractional crystallization and volcanic degassing on Fe³⁺/ΣFe ratios in natural basaltic magmas, we first identify the mineral and volatile phases that have fractionated, degassed, or diffused to create the variations in major element and volatile concentrations observed in melt inclusions and submarine glasses from the Mariana arc and trough. Fractional crystallization models that aimed to match the observed major element variations were generated using Petrolog3 (Fig. 3; Danyushevsky & Plechov, 2011) for all sample suites in this study. A single crystallization model was chosen for each geographic location and is compared with published natural sample compositions and data from this study in electronic appendix A. Each model follows the general pattern of olivine ± clinopyroxene ± plagioclase ± magnetite fractionation. Individual model parameters, including mineral-melt models and pressure conditions that were chosen to generate each liquid line of descent (LLD) can be found in electronic appendix A. Volatile
element behavior was investigated for each LLD by examining the behavior of volatile species (e.g., H$_2$O, CO$_2$, S) relative to other volatiles (e.g., CO$_2$ vs H$_2$O). For all samples, we also compare major and volatile element variations to previously published melt inclusion data from the same island (electronic appendix A, Fig. 4). Here, we outline the magmatic processes that are captured by these samples and the magnitude and variations of their Fe$^{3+}/\Sigma$Fe ratios.

**Mariana volcanic arc**

* Agrigan volcano; We include melt inclusions from three eruptive events at Agrigan volcano (tephra layers Agri04, Agri 05, and Agri07). These melt inclusions are basaltic in composition and range in MgO concentration from 3.12 to 5.81 wt% (Fig. 3a-d, A2). The two inclusions with the highest H$_2$O concentrations in this study are from samples Agri07 and Agri04. The inclusion from Agri07 has a low CO$_2$ concentration that is inconsistent with closed system degassing behavior, where high pressure CO$_2$ volatilization and lower pressure H$_2$O volatilization should produce a near vertical relationship between CO$_2$ and H$_2$O on Figure 4a for an ascending, degassing magma (Dixon *et al.*, 1995). There is also no correlation between S and H$_2$O (Figure 4b). Taken together, neither H$_2$O-CO$_2$ nor H$_2$O-S variations are consistent with simple degassing processes, suggesting that the volatile contents of these inclusions represent complex degassing behaviors.

Agrigan melt inclusions have Fe$^{3+}/\Sigma$Fe ratios that range from 0.217 to 0.344. The highest MgO sample in this suite (MgO = 5.82 wt%) has Fe$^{3+}/\Sigma$Fe = 0.242, which is more oxidized than the most oxidized MORB glass at a comparable MgO content (Fe$^{3+}/\Sigma$Fe = 0.178 at 6.18 wt% MgO) from Cottrell and Kelley (2011; Fig. 5). There is
no correlation between H$_2$O concentrations and Fe$^{3+}$/∑Fe ratios among these inclusions, despite >4 wt% difference in the highest and lowest H$_2$O concentrations (Fig. 4c). Specifically, the two inclusions with the highest water contents of all samples in this study are not oxidized or reduced relative to the others in the same suite.

**Pagan volcano:** One glass inclusion and five submarine glasses from Pagan are basaltic in composition and have MgO concentrations ranging from 5.44 – 7.17 wt% (Fig. 3a-d). The single glass inclusion produced interference fringes in the FTIR spectra such that dissolved CO$_2$ was not detectable. Water and S concentrations in the inclusion are among the lowest concentrations observed in all glass inclusions from this study.

The melt inclusion Paga8-2 has an Fe$^{3+}$/∑Fe ratio of 0.222 at MgO = 5.44 wt%. Submarine Pagan glasses have Fe$^{3+}$/∑Fe ratios that range from 0.219 to 0.252 and MgO concentrations similar to those found in MORB glass (~7 wt% MgO). Like Agrigan melt inclusions, these samples are more oxidized than the most oxidized MORB glasses at a comparable MgO content, but their Fe$^{3+}$/∑Fe ratios do not vary systematically with MgO concentrations. It is important to note that the composition and Fe$^{3+}$/∑Fe ratio of the sole melt inclusion from Pagan volcano are consistent with values reported for melt inclusions from other volcanoes studied in this work. Furthermore, it is similar in MgO concentration and Fe$^{3+}$/∑Fe ratio to submarine glasses from Pagan, demonstrating that melt inclusions have the potential to record similar compositional and redox information as submarine glasses (Fig. 5).
Alamagan volcano; Alamagan inclusions come from two separate eruptive events (tephra samples Ala02 and Ala03) that are basaltic in composition and have the widest range in MgO concentrations of any suite in this study (3.87 – 7.40 wt%). Alamagan inclusions have a range in CO₂ and H₂O concentrations that are consistent with CO₂ degassing (Fig. 4a, Dixon et al., 1995). They exhibit a range of sulfur concentrations from 664 - 1544 ppm, which vary with H₂O and are broadly consistent with sulfur degassing (Fig. 4b; e.g., Sisson & Layne, 1993, Wade et al., 2006). Melt inclusions from tephra layer Ala02 from this study overlap with the major element and volatile compositions of melt inclusions from the same tephra layer from Shaw et al. (2008) (Fig. 4a, b, A4).

Alamagan inclusions have Fe³⁺/∑Fe ratios that range from 0.207 – 0.267, with Fe³⁺/∑Fe = 0.244 in the inclusion with the highest MgO concentration (Ala02-15, 7.40 wt% MgO; Fig. 5), significantly more oxidized than MORB glasses with the same MgO concentration (Fe³⁺/∑Fe = 0.16; Cottrell & Kelley, 2011). The Fe³⁺/∑Fe ratios of these inclusions generally decrease with MgO (Fig. 5). There is no systematic variation in Fe³⁺/∑Fe ratios with variable H₂O concentrations (Fig. 4c).

Guguan volcano; Two Guguan glass inclusions are basaltic in composition and have MgO concentrations of 3.96 and 5.70 wt%. It is difficult to assess any compositional trends with only two samples, although both of these samples are consistent with published whole rock and melt inclusion data from Guguan volcano (Electronic Appendix A, Fig. A5). We thus consider their compositional differences within the context of the literature data. One inclusion yielded a resolvable CO₂ concentration, recording a H₂O+CO₂ pressure of entrapment of 4.3 kbar (Fig. 4a;
Newman & Lowenstern, 2002). Sulfur and H₂O concentrations in these inclusions are consistent with sulfur degassing (Fig. 4b). These inclusions have Fe³⁺/∑Fe = 0.257 and 0.263, both more oxidized than the most oxidized MORB glasses, (Fig. 5; Cottrell & Kelley, 2011). Although these melt inclusions are sourced from a different tephra layer, their compositions and oxidation states are consistent with Guguan melt inclusions from Kelley and Cottrell (2009).

**Sarigan volcano:** Sarigan melt inclusions are basaltic and have a narrow range of MgO, from 5.20 - 6.96 wt%. They record pressures of entrapment between 0.87 – 3.4 kbar and demonstrate closed system H₂O-CO₂ degassing behavior (Fig. 4a; Newman & Lowenstern, 2002). They exhibit a range of sulfur concentrations from 1188 to 1614 ppm that suggest minimal sulfur degassing (Fig. 4b).

Sarigan inclusions capture a very narrow range of melt inclusion compositions, but exhibit a large range in Fe³⁺/∑Fe ratios from 0.195 – 0.280, all of which are more oxidized than average MORB glasses with same MgO concentrations (Cottrell & Kelley, 2011). There are no systematic variations in Fe³⁺/∑Fe ratios with indices of crystal fractionation, sulfur or H₂O concentrations (Fig. 5, Fig. 6, Fig. 4c, respectively).

**NW Rota-1 volcano:** Submarine glasses from NW Rota-1 submarine volcano are basaltic and have MgO = 5.15-6.29 wt%. These glasses have Fe³⁺/∑Fe ratios between 0.190 – 0.237, all more oxidized than MORB glasses with the same MgO concentrations (Cottrell & Kelley, 2011). Like the submarine Pagan glasses, Fe³⁺/∑Fe ratios do no vary systematically with MgO concentration.

*Mariana trough*
*Northern Mariana trough:* Submarine Mariana trough glasses are split into two geographical groups, the northern Mariana trough samples and the southern Mariana trough samples. Northern Mariana trough major element and volatile concentrations are taken from Pearce *et al.* (2005), Stolper and Newman (1994), and Newman *et al.* (2000). They are basaltic in composition and range in MgO from 3.87 – 7.72 wt%. Dissolved H₂O and CO₂ concentrations are consistent with the pressure of the water column at an eruption depth of approximately 4 km. Stolper and Newman (1994) and Newman *et al.* (2000) have shown that these glasses are the result of magmas that were variably saturated with a H₂O-CO₂ rich fluid upon eruption. The range in H₂O contents of these samples results from the variable influence of the subducting slab in the genesis of northern Mariana trough magmas (Stolper & Newman, 1994).

Fe³⁺/ΣFe ratios for these glasses are reported by Kelley and Cottrell (2009) and examined here in the context of the Mariana subduction system. Fe³⁺/ΣFe ratios range from 0.150 – 0.182, overlapping the MORB array in samples with <1.0 wt% H₂O, but vertically offset to ~1% higher Fe³⁺/ΣFe ratios for samples with >1.0 wt% H₂O. There is a strong positive correlation between Fe³⁺/ΣFe ratios and H₂O in the northern Mariana trough sample suite (Fig. 4c).

*Southern Mariana trough:* Southern Mariana trough glasses are more evolved than the northern submarine glasses, with SiO₂ ranging from 51.90 to 59.83 wt%, and MgO ranging from 2.15 – 5.87 wt%. Although separated geographically from Northern Mariana trough samples by greater than 700 km, major element variations for southern Mariana trough glasses are similar to those of the northern trough, but extend to more evolved compositions. Importantly, samples below 4 wt% MgO show
evidence for magnetite saturation in both major element variations (Fig. 3e-h) and in select trace element contents (V, Cr; Fig. A9). This is also supported by the modeled LLD (black line, Fig. 3e-h).

Only two of these samples have resolvable CO₂ concentrations, but these yield saturation pressures that are consistent with their depths of collection (Fig. 4a; Newman & Lowenstern, 2002). Sulfur concentrations vary from 157 – 583 ppm, increasing with decreasing H₂O concentrations until H₂O ~ 2 wt%, at which point sulfur concentrations begin to decrease with decreasing H₂O concentrations. Samples from the southern portion of the Mariana trough display a range in Fe³⁺/∑Fe ratios from 0.171 – 0.207, although in contrast to the northern Mariana trough glasses, these ratios do not correlate strongly with MgO, H₂O or S concentrations (Fig. 5a, 4c, 6, respectively).

**DISCUSSION**

**Relationships of Fe³⁺/∑Fe to magmatic differentiation processes**

*Fractional crystallization*

If Fe³⁺ behaves simply as an incompatible element and magmatic fO₂ is not buffered, low pressure fractionation of olivine, clinopyroxene, and plagioclase from basaltic magmas should lead to an increase in the Fe³⁺/∑Fe ratio of the magma. Data for MORBs are consistent with this behavior, showing slight oxidation during fractional crystallization (Cottrell & Kelley, 2011). In such a system that is closed to oxygen exchange with its surroundings, Fe²⁺ partitions into olivine and clinopyroxene, while Fe³⁺ remains in the melt. As fractionation proceeds, the total volume of liquid
decreases, the Fe$^{2+}$ content of the melt decreases, and the Fe$^{3+}$ content of the melt increases, resulting in an increase in magmatic Fe$^{3+}/\Sigma$Fe ratio. Each modeled LLD for the Mariana arc demonstrates these principles of crystal fractionation-induced oxidation (Fig. 5, electronic appendix A).

Major element variations of melt inclusion and submarine glass suites from the Mariana arc are consistent with the general pattern of olivine ± clinopyroxene ± plagioclase fractionation. In all cases, the Fe$^{3+}/\Sigma$Fe ratios in both arc melt inclusions and submarine glasses are more oxidized than the most oxidized MORB glasses from Cottrell and Kelley (2011). Importantly, melt inclusions from Sarigan and Alamagan volcanoes and submarine glasses from Pagan and NW Rota-1 volcanoes are more oxidized than MORB glasses with similar MgO concentrations. This indicates that the composition and Fe$^{3+}/\Sigma$Fe ratios of any arc melt inclusion or submarine glass in this study cannot be recreated simply by extensively fractionating a MOR-type primary melt (Fig. 5). In fact, low-pressure fractionation of olivine, clinopyroxene, and plagioclase in any combination cannot generate the observed variations in Fe$^{3+}/\Sigma$Fe ratios in most of the Mariana arc samples. The exceptions to this are in two inclusions from Agrigan volcano, where an increase in Fe$^{3+}/\Sigma$Fe ratios from 0.225 to 0.283 and 0.343 occurs approximately coincident with the onset of abundant plagioclase fractionation. In our modeling, plagioclase represents ~2% of the total proportion of fractionating phases (olv~64%, cpx~34%) before this increase in magmatic Fe$^{3+}/\Sigma$Fe ratios. At melt MgO = 4.1 wt%, the modal proportion of plagioclase increases to ~10% (olv~55%, cpx~35%), and continues to rise as fractionation continues. At the same time, the modal proportion of olivine decreases. The associated increase in
Fe$^{3+}/\Sigma$Fe ratios is predicted by the fractionation model (Fig. 5a) and arises as a result of the incompatibility of Fe$^{3+}$ during crystallization, as described above. It is important to note that although plagioclase contains no Fe$^{2+}$ or Fe$^{3+}$ in our modeling, the decrease in total liquid volume associated with abundant plagioclase fractionation, combined with a slight decrease in Fe$^{2+}$ in the liquid by continued olivine fractionation can result in a significant increase in magmatic Fe$^{3+}/\Sigma$Fe ratios. Our data are consistent with this model prediction (Fig. 5a) and these two samples suggest that this increase in Fe$^{3+}/\Sigma$Fe ratios may be as great as ~0.1 (absolute).

High-pressure spinel phases may be saturated early in magmas and cease to fractionate prior to olivine fractionation, leaving no physical evidence of its saturation in olivine-hosted melt inclusions. If this has occurred and D$^{Fe^{3+}} > 1$ for the spinel that saturated, in a system closed to oxygen the impact of spinel fractionation from the magma will reduce Fe$^{3+}/\Sigma$Fe ratios in the magma. In this case, the Fe$^{3+}/\Sigma$Fe ratios of the highest MgO melt inclusions in this study are lower than their actual parental or primary values and the estimates presented here are minima. Magnetite (Fe$^{3+}$$_2$Fe$^{2+}$O$_4$) is the next solid phase with D$^{Fe^{3+}} > 1$ to fractionate from basaltic magmas. In a system closed to oxygen exchange with its surroundings, magnetite fractionation is expected to drive magmatic reduction through the preferential removal of Fe$^{3+}$ from the liquid. In the modeled LLD for the Mariana back-arc samples, however, significant magmatic reduction does not occur at the point of magnetite-in (4 wt% MgO; Fig. 5a). Rather, magnetite fractionation in the model appears to combat the oxidizing effects of olivine ± clinopyroxene ± plagioclase such that the net effect is to maintain roughly constant magmatic Fe$^{3+}/\Sigma$Fe ratios after magnetite-in (Fig. 5; electronic appendix A). The
Fe\(^{3+}/\sum\)Fe ratios of Mariana back-arc samples are consistent with the predicted magmatic oxidation from the modeled LLD until \(\sim 5.5\) wt\% MgO (Fig. 5a), although at lower MgO concentrations, the Fe\(^{3+}/\sum\)Fe ratios of Mariana trough samples are remarkably constant. It is possible that this reflects the combined effects of olivine + clinopyroxene + plagioclase + magnetite fractionation, as demonstrated by the modeled LLD (Fig. 5a), but geochemical evidence for magnetite saturation does not appear until \(\sim 4\) wt\% MgO, much lower MgO than the point where the natural data fall away from the modeled LLD (Fig. 3e-h, A9). Other processes, such as sulfide fractionation or sulfur degassing, may influence magmatic redox conditions for these samples.

Sulfide fractionation may impact magmatic Fe\(^{3+}/\sum\)Fe ratios via the Fe-S redox couple:

\[
8Fe^{2+} + S^{6+} \leftrightarrow 8Fe^{3+} + S^{2-} \quad \text{EQ 1}
\]

For example, EQ 1 has been invoked to explain the stabilization of solid sulfide phases in oxidized, magnetite saturated magmas with relatively low S contents from the Pual Ridge in the Manus Basin (Jenner et al., 2010). The saturation of magnetite from a basaltic melt will remove a greater proportion of Fe\(^{3+}\) than Fe\(^{2+}\) from a melt, provided the magnetite has a higher Fe\(^{3+}/\sum\)Fe ratio than the melt. If the concentrations of both Fe\(^{2+}\) and Fe\(^{3+}\) are controlled only by crystal fractionation, when magnetite begins fractionating, EQ 1 will shift to the right to maintain the equilibrium constant, \(K_{eq}\). This will reduce S\(^{6+}\), producing S\(^{2-}\) and potentially promoting the saturation of a solid sulfide phase at relatively low dissolved sulfur concentrations. Importantly, this shift in equilibrium to the right of EQ 1 will also produce a new equilibrium proportion of
Fe$^{3+}$. If EQ 1 is important in Fe and S bearing basaltic magmas, then S and Fe species cannot be treated as conservative during any volcanic process that may disturb the equilibrium.

Sulfur concentrations in Mariana trough glasses begin to decrease below 5 wt% MgO (not shown) and 2 wt% H$_2$O (Fig. 4b). Experimentally constrained estimates for the sulfur content at sulfide saturation (SCSS) for relevant pressures, temperatures, compositions, and fO$_2$ range from 950 ppm to >2000 ppm for all Mariana trough glasses (Jenner et al., 2010, Jugo et al., 2010, Liu et al., 2007). The maximum sulfur content observed in these samples is only 553 ppm, suggesting that the Mariana trough magmas are not sulfide saturated. Instead, sulfur may have partitioned into a vapor phase, a process that has been shown to reduce magmas if the vapor phase is SO$_2$ (Fig. 4b; Kelley & Cottrell, 2012), although H$_2$S degassing could also oxidize magmas under the right conditions (Métrich et al., 2009). It is difficult to assess the independent importance of sulfur degassing on the Fe$^{3+}$/∑Fe ratios of these samples because of the evidence for simultaneous magnetite fractionation. The relative constancy of Fe$^{3+}$/∑Fe ratios in Mariana trough samples with MgO < 5.5 wt% suggests that the redox equilibria illustrated by EQ 1 may have played an important role in controlling Fe$^{3+}$/∑Fe ratios in these samples, particularly if both magnetite fractionation and S degassing reduce magmas. Further work in quantifying the relative reduction potentials of Fe and S in basaltic magmas will aid in understanding the evolution of Fe$^{3+}$/∑Fe ratios during magmatic processes.

*The effect of fO$_2$ on tholeiitic index*
Magmatic differentiation may influence the $\text{Fe}^{3+}/\sum\text{Fe}$ ratio, as discussed above, but magmatic $f_O^2$ also plays an important role in determining the differentiation path of basaltic magmas, which may follow variably tholeiitic or calc-alkaline trends, depending on the extent of FeO* enrichment or depletion that occurs in the early stages of crystallization (Irvine & Baragar, 1971, Miyashiro, 1974, Zimmer et al., 2010). Predominant models for generating these trends involve the interplay of plagioclase and magnetite fractionation and the petrological factors that control these phases. The generation of calc-alkaline magmas (i.e., FeO* depleted) in subduction settings may be related to the high pre-eruptive water contents of arc magmas, which suppress plagioclase, but not magnetite, crystallization (Botcharnikov et al., 2008, Sisson & Grove, 1993, Spulber & Rutherford, 1983). The tholeiitic index (THI) was introduced as a way to quantify the behavior of Fe during early magmatic differentiation, defined as the $[\text{FeO*}]$ at MgO = 4.0 ± 1.0 wt% divided by the $[\text{FeO*}]$ at MgO = 8.0 ± 1.0 wt% ($\text{FeO*}_{4.0}/\text{FeO*}_{8.0}$), such that a tholeiitic magma has a THI>1.0, and a calc-alkaline magma has a THI<1.0 (Zimmer et al., 2010). Samples from both the Mariana arc and trough from this study are consistent with observations from Zimmer et al. (2010), where Mariana arc volcanoes display slightly calc-alkaline trends and also have higher pre-eruptive water contents (>1.5 wt%) than the Mariana trough, which falls distinctly in the tholeiitic field (THI>1.2) and has lower pre-eruptive water contents (Fig. 7). Globally, the THI is also well correlated with magmatic $f_O^2$, where arc samples are more oxidized than back-arc and MORB (Fig. 7). This suggests that the oxidized nature of arc basalts may also play an important role in the generation of calc-alkaline differentiation trends by promoting magnetite
saturation over silicates (Osborn, 1959, Sisson & Grove, 1993). If magmatic $fO_2$ and $H_2O$ contents are linked in global subduction settings, then magmas that are more calc-alkaline than Mariana arc basalts may also record higher magmatic $fO_2$s. For example, magmas erupted from Augustine volcano have a THI of 0.65, lower than any of the predicted THI for the Mariana arc volcanoes in this study, and pre-eruptive $H_2O$ contents above 6 wt% (Zimmer et al., 2010). A single inclusion from Augustine volcano (Kelley & Cottrell, 2009) records a magmatic $fO_2$ of $\sim$QFM+2.0 at reasonable conditions for magma storage (0.2 GPa, 1150°C), four times more oxidized than the most oxidized inclusion in this study (Fig. 7). These results are consistent with the hypothesis that, in addition to water, $fO_2$ may play a role in generating calc-alkaline differentiation trends in arc magmas. Additionally, it may be difficult to isolate the specific roles of $H_2O$ and $fO_2$ on the differentiation style of natural arc basalts because they are closely correlated in subduction zones.

*The role of volatiles*

Melt inclusions from Sarigan and Alamagan volcanoes each show evidence for $\sim$2 wt% $H_2O$ degassing, but show no corresponding variations in $Fe^{3+}/\sum Fe$ ratios (Fig 4). This demonstrates that $H_2O$ degassing is not an oxidizing process in basaltic magmas, rather it is redox neutral (Carmichael, 1991, Cottrell & Kelley, 2011, Crabtree & Lange, 2011, Frost & Ballhaus, 1998). Water concentrations correlate strongly with $Fe^{3+}/\sum Fe$ ratios in northern Mariana trough samples, where they range from MORB-like (e.g., dry, reduced) to more oxidized as $H_2O$ contents increase. Modeled mantle source $H_2O$ contents for the northern Mariana trough lavas increase as fluid addition from the subducting slab increases (Newman et al., 2000, Stolper &
Newman, 1994). Using H$_2$O as a proxy for slab-derived influence on the arc and back-arc mantle sources, subduction influence has also been linked to magmatic and mantle source oxidation (e.g., Fig 4d; Kelley & Cottrell, 2009). It is important to note that H$_2$O itself does not drive oxidation of the mantle (Frost & Ballhaus, 1998), rather our observations in the Marianas indicate that slab fluids may be oxidized relative to ambient upper mantle and impart both elevated H$_2$O concentrations as well as their oxidized condition on the mantle source beneath the Mariana arc and trough (see below).

Kelley and Cottrell (2012) suggested that sulfur degassing played a dominant role in controlling Fe$^{3+}/\Sigma$Fe ratios during the eruption recorded by Agrigan tephra 19-02. They outlined a simple model for electronic exchange between Fe and S during S degassing, where six moles of electrons are transferred to Fe*$_{\text{(melt)}}$ for every one mole of S$^{2-}_{\text{(melt)}}$ that is degassed as S$^{4+}_{\text{(vapor)}}$ (black line, Fig. 6) as a possible explanation for magmatic reduction and associated S loss. Figure 6 shows the relationship between sulfur concentrations and Fe$^{3+}/\Sigma$Fe ratios, as observed in melt inclusion suites from Sarigan, Alamagan, Agrigan, and Guguan volcanoes. Sulfur degassing is likely recorded by Alamagan, Agrigan, and Guguan melt inclusions. Agrigan inclusions show a slight reduction in Fe$^{3+}/\Sigma$Fe ratios with decreasing sulfur concentration that is consistent with the melt inclusion suite studied by Kelley and Cottrell (2012). In contrast, the two Guguan inclusions are different in their sulfur concentrations by >1000 ppm but do not vary significantly in their Fe$^{3+}/\Sigma$Fe ratios, and there is no correlation between the sulfur concentrations and Fe$^{3+}/\Sigma$Fe ratios of Alamagan
inclusions, suggesting that reduction of Fe during S degassing is not a universal process for all arc volcanoes.

The effect of post entrapment processes

The large range in Fe$^{3+}$/∑Fe ratios (0.195-0.281, $\bar{x} = 0.243$) captured by melt inclusions from Sarigan volcano does not appear to be controlled by crystal fractionation or volcanic degassing. Here, we consider processes specific to melt inclusions that may impact the Fe$^{3+}$/∑Fe ratios of melt inclusions in this study. The Fe$^{3+}$/∑Fe ratios of hydrous melt inclusions have been postulated to be affected by hydrogen diffusion in to or out of an inclusion after entrapment as the host magma cools and/or degasses (e.g., Danyushevsky et al., 2002). In the case of cooling, the pressure of the inclusion decreases and hydrogen fugacity in the inclusion may be lower than in the surrounding melt. This would result in hydrogen diffusion into the inclusion and potentially, the reduction of iron. Alternatively, in the case of degassing a host magma, hydrogen fugacity in the inclusion may be higher than in the surrounding melt, causing hydrogen to diffuse out of the melt inclusion and potentially oxidizing iron contained in the inclusion (Danyushevsky et al., 2002). Experimental observations by Gaetani et al. (2012), however, have shown that Fe$^{3+}$/∑Fe ratios in melt inclusions that have been dehydrated or hydrated are rapidly re-equilibrated with the Fe$^{3+}$/∑Fe ratios of the external melt. They hypothesize that point defects in host olivines on the metal sites (i.e., Fe$^{2+}$ or Mg$^{2+}$ deficiencies or similarly, O$^{2-}$ excesses) diffuse on the same time scale as hydrogen in olivine and move in the opposite sense as hydrogen. For example, if hydrogen diffuses out of a melt inclusion, point defects in the host olivine diffuse towards the melt inclusion, effectively communicating the
$f_{O_2}$ of the external melt to the melt inclusion. Several lines of evidence suggest that $H^+$ diffusion does not explain the diversity of Fe$^{3+}/\sum$Fe ratios in melt inclusions from this study. First, figure 4 demonstrates coherent trends with respect to $H_2O$ degassing for Sarigan melt inclusions, diminishing the likelihood that this particular melt inclusion suite records massive diffusion. Second, the $H_2O$ contents of inclusions from Pagan, Alamagan, Guguan, and Sarigan in this study are consistent with those of Shaw et al. (2008), who used hydrogen isotopes to conclude that post-entrapment hydrogen loss was not significant for carefully chosen melt inclusions. In the case of Alamagan inclusions, we studied inclusions from the same tephra sample as the inclusions from Shaw et al. (2008), enabling a direct comparison between studies. Additionally, similar heterogeneity in Fe$^{3+}/\sum$Fe ratios that is uncorrelated with MgO is observed for submarine glasses from Pagan and NW Rota-1 volcanoes, suggesting that this heterogeneity is not simply a melt inclusion-related phenomenon (Fig. 5). There is also no relationship between the size of inclusion and major element compositions, measured Fe$^{3+}/\sum$Fe ratios, or apparent disequilibrium between melt inclusion-olivine pairs, which suggests that the large melt inclusions in this study have not been diffusively re-equilibrated (see electronic appendix A, Fig. A11). Finally, the trace element heterogeneity recorded in melt inclusion populations from Sarigan and Alamagan volcanoes show strong evidence of retaining magmatic trace element variability (see electronic appendix A, Fig. A10), supporting the notion that the heterogeneity recorded in melt inclusion suites in this study reflect true magmatic heterogeneity rather than post-entrapment melt inclusion processes.

Why are arc basalts more oxidized than MORB?
Primary melt compositions and fO$_2$

Arc basalts are shown here to be more oxidized than MORB, even at comparable MgO concentrations. Additionally, we show that fractional crystallization and degassing processes are capable of both oxidizing and reducing Fe$^{3+}/\Sigma$Fe ratios in arc basalts, although these effects are minor, and neither can explain the oxidation of Fe in arc basalts over MORB. This suggests a fundamental difference between the Fe$^{3+}/\Sigma$Fe ratios of mantle-derived primary arc magmas and primary MORB magmas.

To test this, primary melt compositions (i.e., in equilibrium with mantle olivine at Fo$_{90}$) were reconstructed using methods modified after Klein and Langmuir (1987), where modeled or data-defined LLDs provide constraints to account for the effects of fractional crystallization on magmatic composition. The fractionation models generated for each geographic location were used to calculate the primary magma composition for each sample with MgO > 5 wt%. Each composition was projected back to MgO = 7.0 wt% using the slope of the fractionation model between 5 and 7 wt% MgO for all major elements (excluding Fe). In some cases, the fractionation model was poorly fit to the most incompatible major elements (e.g., P$_2$O$_5$) and the slope of a line defined by the natural data was used for the calculation instead (Electronic Appendix E). For Fe, FeO$_{\text{actual}}$ and Fe$_2$O$_3$$_{\text{actual}}$ concentrations were plotted versus MgO concentration and projected back along the slopes of lines defined by the natural data for each sample suite. The point of MgO = 7.0 wt% was chosen because data for the arc basaltic glasses above 7 wt% MgO are sparse, and selecting a higher MgO limit would be arbitrary. At or above 7 wt% MgO, both the data-defined and modeled LLDs suggest that olivine or olivine + clinopyroxene are the only phases
on the liquidus, due mostly to the suppression of plagioclase saturation in water rich magmas (Gaetani et al., 1993, Kelley et al., 2010, Parman et al., 2010). Once at MgO = 7 wt%, each composition was subject to addition of equilibrium composition olivine in 0.1% increments until in equilibrium with Fo90 olivine (Electronic Appendices A, E-G). Alternatively, clinopyroxene could be included along with olivine as a liquidus phase to higher MgO concentrations, although it is difficult to know when olivine becomes the only liquidus phase. Because of this uncertainty, we also used PetroLog to add clinopyroxene and olivine simultaneously back until achieving equilibrium with Fo90 olivine. When applied to a suite of 20 melt inclusions from Sarigan volcano, this method returned nearly identical average primary melt Fe$^{3+}$/ΣFe ratios as the olivine only method (0.217 using PetroLog, 0.220 using the olivine only method) and because of differences in major element composition, a primary melt $fO_2$ ~0.28 log units below that of the method described above. This is within the ± 0.5 log unit uncertainty of the Fe$^{3+}$/Fe$^{2+}$ proxy for $fO_2$ (Kress & Carmichael, 1991), so we chose to use the olivine-only addition method described above because it can be applied consistently to all samples discussed below (MORB, BABB, and arc samples). An important conclusion drawn from this test is that the choice of correction method does not significantly impact the reconstructed primary oxygen fugacity. Temperatures and pressures of last equilibration with peridotite for each calculated primary melt composition were determined using the melt thermobarometer of Lee et al. (2009; Tables 1, 2). Primary $fO_2$ was calculated using the algorithm of Kress and Carmichael (1991; Tables 1, 2) relative to the QFM buffer calculated at pressure and temperature according to Frost (1991).
Mid-ocean ridge primary magmas have $fO_2$ similar to that of the QFM buffer (Fig. 8; Cottrell & Kelley, 2011). Northern Mariana trough primary melts overlap with the most oxidized MORB primary melts (~QFM+0.1 to QFM+0.3), but extend to QFM+0.8. Southern Mariana trough primary melts extend to QFM+0.5. Primary melts from the Mariana arc range between QFM+0.2 to QFM+1.8, which is 0.4 to 1.5 orders of magnitude more oxidized than the most oxidized MOR primary melts. After considering the effects of crystallization and degassing on magma composition and redox, it is evident that both Mariana arc and back-arc basalts are more oxidized than MORB due to a fundamental difference in $fO_2$ of the mantle source for these magmas.

The mantle wedge beneath Mariana arc volcanoes generates melts with $fO_2$ of ~QFM+1., the average primary melt $fO_2$ calculated for melt inclusions and submarine glasses from arc volcanoes (including NW Rota-1) in this study. These oxidized magmas migrate into the arc crust and differentiate, possibly experiencing minor modifications to $Fe^{3+}/ΣFe$ ratios due to the effects of crystallization or degassing (<0.05, absolute). Similarly, the mantle wedge under the Mariana trough generates melts with $fO_2$s that range from QFM+0.1 to QFM+0.8 in the north and from QFM+0.3 to QFM+0.5 in the south. These melts move into the crust and experience minor fractional crystallization-related Fe oxidation, or in the case of samples from the southern Mariana trough, maintain constant $Fe^{3+}/ΣFe$ ratios despite evidence for sulfur degassing and magnetite fractionation. Mariana trough basalts erupt with $Fe^{3+}/ΣFe$ ratios that range from MORB-like to significantly more oxidized than MORB.

There are several trace element proxies (e.g., V-based, Cu and Zn/Fe* ratios) for modeling mantle source $fO_2$ from the compositions of erupted basalts that can
provide important additional constraints on the $fO_2$ of the mantle wedge in the Marianas. The application of these models requires knowledge of the composition and mineral mode of the mantle source, the mechanisms for melt generation, and constraints on LLDs on a volcano-to-volcano basis (Lee et al., 2005, Lee et al., 2012, Lee et al., 2010). These parameters are not likely to be uniform from mid-ocean ridge settings to subduction zones, and all are challenging to constrain. A comparison between Fe redox and trace element proxies for mantle source $fO_2$ from this dataset is currently in progress.

**The source of elevated $fO_2$ in the mantle wedge**

*Tracking sediment melt and slab fluid influences;* Trace element and isotopic compositions of subduction related lavas are influenced by contributions from the downgoing slab that may include sediment melts, aqueous fluids, and slab melts. Key trace element ratios (e.g., Th/La, Ba/La) have been shown to record the contributions from these sources in lavas erupted within the arc and back-arc system of a convergent margin (e.g., Elliott et al., 1997, Plank, 2005, Plank & Langmuir, 1993). Thorium is enriched in subducted terrigenous sediment and will become mobile when the sediments cross their solidi and begin to melt. Sediment melts move into the mantle wedge and contribute to the production of arc and back-arc magmas that have elevated Th/La ratios relative to MORBs. Barium, on the other hand, is mobilized preferentially over melt-mobile La via aqueous fluids that escape the subducting slab as it descends into the mantle, generating aqueous slab-derived fluids that are expected to have elevated Ba/La ratios (Johnson & Plank, 1999, Kessel et al., 2005). In the Marianas in particular, the Ba/La ratio of the bulk subducting sediment package is low (Ba/La ~
15, Plank & Langmuir, 1998), and thus sediment melts that move from the slab into the mantle wedge likely also have low Ba/La ratios. The high Ba/La ratios of Mariana arc lavas (commonly >20) require the presence of aqueous fluids to transport Ba preferentially over La into the mantle wedge. The Marianas is a special case among global subduction settings in this respect, because trends between key trace element ratios require that separate sediment melts and aqueous fluids contribute to the composition of arc lavas (Elliott et al, 1997, Plank, 2005, Plank & Langmuir, 1998).

Arc and back-arc samples from the Marianas fall on a mixing line between mantle with Sm/La ~ 1.35 and Th/La ~ 0.02 and the bulk composition of sediments recovered from ODP Site 801, ~1,100 km east of the Mariana Islands (Fig. 9a; Plank, 2005). Some samples from Sarigan, Alamagan and Guguan volcano mix to slightly higher Th/La ratios, which may be more representative of the Th/La ratio of wind-blown sediments derived from the Asian continent that may be presently subducted beneath the Marianas, but not present at Site 801 (orange line, Fig. 9a; Plank et al., 2007). Back arc samples deviate from the MORB array in Figure 9b towards a fluid with high Ba/La ratio, though lower Ba/La ratio than the fluid influencing the arc samples (Pearce et al., 2005, Stolper & Newman, 1994). Mariana arc samples display a large range in Ba/La ratios that reflect significant slab fluid influence that varies in magnitude along the Mariana margin. NW Rota-1 is the least influenced by slab fluids, with Ba/La ratios similar to southern Mariana trough samples. This is an interesting observation considering its position relative to the trench, where it sits approximately 50 kilometers farther from the trench than the main subaerial arc, where the slab depth to slab is 50-100 km deeper (Syracuse & Abers, 2006). NW Rota-1 may thus receive a
different style of slab fluid (or less of it) than the subaerial arc volcanic centers. Sarigan and Alamagan melt inclusions span a large portion of the entire range of Ba/La ratios observed for the arc, suggesting that there is trace element heterogeneity in parental magma compositions at Sarigan and Alamagan volcanoes.

Mantle wedge composition: In addition to containing geochemical signatures of the subducting slab, melts generated in the mantle wedge at the back-arc spreading center and under the volcanic arc may reflect variations in mantle source composition that is inherent to the mantle (Langmuir et al., 2006) or generated by prior melt extraction (e.g., Kincaid, 2003, McCulloch & Gamble, 1991, Woodhead et al., 1993). Here, we use the Zr/Y ratio to characterize mantle source composition. Zirconium and yttrium are not significantly fractionated during low-pressure crystal fractionation and, are expected to be relatively absent from slab-derived materials in the Marianas (Pearce & Parkinson, 1993, Pearce et al., 2005). The Zr/Y ratios of arc and back-arc lavas are thus assumed to reflect the mantle source composition, independent of slab-derived additions to the mantle wedge. The Zr/Y ratio of the mantle source is, however, fractionated as the result of prior melting episodes because Zr is more incompatible than Y during mantle melting. Therefore, melts of fertile mantle will have high Zr/Y ratios, but progressive melting of the same parcel of mantle will generate subsequent melts with lower Zr/Y ratios. Mantle entering the wedge in the Marianas passes through the back-arc melting triangle and experiences melt extraction there before moving under the volcanic arc, such that the mantle under the arc is more depleted in trace elements due to melt extraction at the back-arc (Pearce et al., 2005; Woodhead et al., 1993). The Zr/Y ratios of Mariana trough and arc magmas reflect
this contrast, with high Zr/Y ratios of Mariana trough basalts reflecting a relatively enriched MORB-type mantle (Fig. 9c; Table 1, 2; Langmuir et al., 2006). The Zr/Y ratios of Mariana arc basalts are significantly lower, however, reflecting the more depleted arc mantle source, consistent with the predicted effects of back-arc spreading in mantle circulation and prior geochemical studies of the Mariana arc (Kelley et al., 2010, McCulloch & Gamble, 1991, Pearce et al., 2005). The Zr/Y ratios in the Marianas do not follow the mixing relationships between the estimated source composition and the sediment materials (orange and green lines, Fig. 9c), supportive of the notion that Zr and Y do not travel with slab-derived materials into the mantle source.

Despite observed heterogeneity in trace element compositions discussed here, we emphasize that major element compositions are relatively narrow and uncorrelated with trace element ratios like La/Yb, which is greater than can be expected from simple fractionation of La from Yb during differentiation (Fig. A13). This suggests that while trace elements record the presence and mixing of several different parent magmas, mixing does not control the major element relationships in these magmas and major elements can reasonably be described by simple crystal fractionation (electronic appendix A).

*Variations in fO2 with mantle source-related variables:* To assess the source of elevated fO2 in the mantle wedge, we now examine relationships between tracers of mantle wedge composition (Zr/Y) and subduction influence (Th/La, Ba/La), and primary fO2. There are no systematic relationships between primary fO2 and Zr/Y ratio within the arc or back-arc data (Fig. 10a), beyond a first-order contrast between the arc
(higher $fO_2$, lower Zr/Y) and the back-arc (lower $fO_2$, high Zr/Y). Mariana trough Zr/Y ratios on average are higher than for mid-ocean ridge or arc samples, suggesting (a) that the Mariana trough taps an enriched mantle source (Langmuir et al., 2006), and (b) that sub-arc mantle is more depleted than back-arc mantle by virtue of previous melt extraction in the back-arc melting regime. It is possible that melt extraction varies the activity of Fe$^{3+}$ in mantle spinel phases. If it increases, then melting could contribute to the oxidized nature of arc basalts relative to back-arc primary magmas (i.e., Parkinson & Arculus, 1999). Arc primary melts are offset towards more oxidized $fO_2$s than the Mariana trough, and also record a more depleted mantle source, however there is no relationship within either the Mariana trough or arc samples between extent of depletion and mantle source $fO_2$. Moreover, MORBs encompass the full range in Zr/Y ratios observed at the Mariana arc and back-arc, with no coincident variation in $fO_2$ (Fig. 10a), suggesting that the observed oxidation in the Marianas is not solely a result of variable mantle source composition. We conclude that the mantle composition alone (as recorded by Zr/Y ratio) is not responsible for the elevated $fO_2$ of arc and back-arc basalts.

There is a weak relationship between primary $fO_2$ and Th/La ratio in the northern Mariana trough, but not among Mariana arc samples (Fig. 10b), and the Mariana arc and trough largely overlap in Th/La ratios. It is clear that the oxidized nature of the mantle source under the arc is unrelated to sediment melt influence, as indicated by Th/La ratio, because all of the arc samples have higher $fO_2$ than the northern Mariana trough samples within the same range of Th/La ratios (Fig. 10b). These observations indicate that melts of the sediments at this arc either (a) are not
significantly oxidized relative to MOR source mantle, and/or (b) make up too small a proportion of total primary melt to impact mantle $fO_2$. The northern Mariana trough samples range from having no detectable subduction component to moderate influence from the subducting slab. Those samples from the northern Mariana trough with higher Th/La ratios also have higher Ba/La ratios, which is in contrast to the arc, where high Th/La ratios correlate with low Ba/La ratios. The composition of the subduction component reaching the northern Mariana trough is likely to be significantly different than the compositions of the subduction components that reach the volcanic arc and may be neither a “sediment melt” or an “aqueous fluid”. This may give rise to the observed strong correlation between Th/La ratios and increasing source $fO_2$ for these samples, but no correlation within the arc samples, where sediment melts and slab fluids are clearly segregated by systematic co-variation of Ba/La and Th/La ratios.

There is a strong correlation between primary $fO_2$ and the extent of slab fluid influence, as recorded by the Ba/La ratio, within the MORB-Mariana back-arc-Mariana arc system (Fig. 10c, $R^2=0.86$, $P=0.01$). Samples within the MORB field are an exception, where lavas with elevated Ba/La ratios are relatively reduced, although the systematics within MORB are not attributed to modern subduction (Cottrell & Kelley, 2013). The northern Mariana trough has primary $fO_2$ that ranges from that of primary MORB mantle (QFM) where slab fluid influences are minor (Ba/La ~ 5), increasing as slab fluid influence increases, up to QFM+0.50 (Ba/La ~13). The southern Mariana trough has primary $fO_2$ that is slightly more oxidized than the northern Mariana trough (QFM+0.5), with evidence for greater slab fluid influence
Primary melts from NW Rota-1 have \( f_{O_2} \approx \text{QFM}+0.6 \), which is only slightly elevated over the southern Mariana trough primary \( f_{O_2} \). Northwest Rota-1 also sits farther from the trench and the slab surface than the rest of the Mariana arc, and records a smaller slab fluid influence (Ba/La ~ 17). Within the arc, increasing Ba/La ratio correlates with increasing average primary \( f_{O_2} \) from NW Rota-1 to Guguan (Ba/La ~ 48, QFM+1.6). A positive relationship between Ba/La ratio and \( f_{O_2} \) is also observed within individual calculated primary melts at Pagan volcano (\( R^2 = 0.77 \)), although their \( f_{O_2} \)s overlap within uncertainty. These observations link oxidation to subduction influence, specifically with Ba-enriched fluids derived from the subducted slab. Small additions of slab fluids (or possibly different fluids) in the back-arc increase primary \( f_{O_2} \) in the mantle wedge up to 5 times that of MOR primary \( f_{O_2} \). Elevated slab fluid additions under the volcanic arc increase primary \( f_{O_2} \) up to \(~\text{QFM}+1.6\). These conclusions have several important implications for potential buffering assemblages in the mantle wedge and the \( f_{O_2} \) of slab fluids.

Taken together, these results suggest that slab-derived, Ba-rich fluids are significantly more oxidized than the upper mantle. There is strong evidence that the slab lithosphere is highly serpenitized prior to subduction (Ivandic et al., 2008, Ranero et al., 2003, Savage, 2012, Van Avendonk et al., 2011) and deserpentinization reactions (dehydrating serpentinite assemblages) in the subducting slab may contribute a significant proportion of the fluids that lead to the formation of arc magmas (Hacker, 2008, Schmidt & Poli, 1998, van Keken et al., 2011). Serpentinization reactions that occur on the seafloor prior to subduction involve the infiltration of fluids (e.g., seawater) into peridotite. Iron is oxidized, transforming Fe\(^{2+}\) contained in olivine into
Fe$^{3+}$ to form magnetite at the expense of oxygen contained in H$_2$O molecules. This reaction generates magnetite, brucite, and serpentine coexisting with reduced aqueous fluids (Frost, 1985) that are ultimately lost from the system, resulting in a net oxidation of the rock. When the slab travels along a prograde P-T path during subduction, serpentinite minerals become unstable at ~600$^\circ$ C and release aqueous fluids (e.g., Ulmer & Trommsdorff, 1995, Spandler et al., 2014), which happens at 150-180 km depth for the southern Mariana subducting slab geotherm (van Keken et al., 2011). The deserpentinization reactions over the P-T path of subducting slabs are complicated, but these may potentially consume magnetite and serpentine minerals to form olivine, which would reduce Fe and create oxidized fluids (e.g., Nozaka, 2005) or fluids carrying oxidized species (e.g., sulfate or SO$_2$; Alt et al., 2013). These oxidized fluids must percolate through the subducting slab, where they may scavenge Ba from the altered oceanic crust and overlying sediment package, before ultimately entering the the mantle wedge where they lower the peridotite solidus and generate oxidized hydrous melts with high Ba/La ratios under the volcanic arc. Additionally, there is a distinct contrast with the $f$O$_2$ of primary melts under the back-arc, where subduction influence is lower than the arc and the fluid composition is fundamentally different. This may be because 1) the influence from oxidized slab fluids is less and thus the oxidizing power of the slab fluids is diminished beneath the back-arc, and/or 2) the fluids that are generated by the dehydrating slab that reach the back-arc have different sources from those fluids that contribute to arc volcanism and perhaps are not as oxidized. It is unlikely that fluids percolate through the entire volume of the mantle wedge. Rather, they may concentrate in rising diapirs or along interconnected
networks (e.g., Hall & Kincaid, 2001, Marchall & Schumacher, 2012). This limits the proportion of mantle wedge that interacts with slab fluids significantly, and may make it possible for slab fluids to create oxidized primary melts that relate linearly to the extent of slab fluid influence. Fingerprinting the source of fluids from within the slab is a major challenge in subduction zone studies, and requires further investigation to test explicitly.

It is also possible that the mantle wedge contains important buffering assemblages that control the mantle source $f_O$ for arc basalts, although the relationship between slab fluid influence (Ba/La) and primary $f_O$ in Figure 10c indicates that there are no buffering species present in the mantle wedge in this range of $f_O$. Sulfur speciation is shown to be highly sensitive to changes in $f_O$ between QFM and QFM+2.0 (Jugo, 2009, Jugo et al., 2010). If a solid sulfide phase exists in the mantle wedge and is not exhausted during melting under the volcanic arc, the solid sulfide-sulfate phase boundary may serve to buffer the mantle wedge during melting, such that increasing the influence of oxidized slab fluids cannot increase primary $f_O$ until either the sulfur phase is exhausted or another, more oxidized phase is added (e.g., Fe$_2$O$_3$; Mungall, 2002). The complete conversion of $S^{2-}$ to $S^{6+}$ does not occur until QFM+2 (Jugo et al., 2010), about 5 times more oxidized than the most oxidized primary melts calculated in this work. In subduction zones where slab fluid influence is greater, slab fluids may be capable of oxidizing the mantle wedge up to the point of sulfide destabilization, at which point the $f_O$ of the mantle wedge may be buffered until all sulfide is transformed to sulfate.
CONCLUSIONS

This combined study of submarine basaltic glasses and olivine hosted melt inclusions from six Mariana arc volcanoes and the Mariana trough examines the variations in Fe$^{3+}/\Sigma$Fe ratios along several liquid lines of descent and across tectonic setting and slab contributions. Mariana arc glasses and melt inclusions preserve liquid lines of descent that take the general form of olivine ± clinopyroxene ± plagioclase crystallization with simultaneous CO$_2$ ± H$_2$O ± S degassing. In all cases, arc melt inclusions and submarine glasses are more oxidized than MORB glasses with similar MgO contents. The composition and Fe$^{3+}/\Sigma$Fe ratios of arc melt inclusions and submarine glasses cannot be recreated by simple fractional crystallization of a MOR-like primary melt. Sulfur degassing, where evidenced in this study, may play a role in reducing arc magmas during differentiation in the arc crust at Agrigan and Alamagan volcanoes, but not necessarily at other Mariana arc volcanoes. Submarine glasses from the Mariana trough preserve a liquid line of descent that takes the form of olivine ± plagioclase ± clinopyroxene ± magnetite crystallization with simultaneous CO$_2$ + H$_2$O ± S degassing. Mariana trough glasses are slightly more oxidized than MORB with similar MgO contents, but are not as oxidized as arc samples. The calc-alkaline affinity and magmatic $f$O$_2$s correlate between MORB, Mariana trough, and arc samples, suggesting that $f$O$_2$, as well as water, plays a role in influencing the differentiation style of basalts. Reconstructed primary melts for arc and back-arc basalts reveal that the mantle source $f$O$_2$ at both back-arc and arc volcanoes are elevated over MORB mantle source. The mantle source for arc volcanoes is on average, about one order of magnitude more oxidized than the mantle source for the
back-arc, and about 1.3 orders of magnitude more oxidized than the mantle source for MORBs. Primary $f/O_2$ correlates with slab fluid indices (Ba/La) from the back-arc to the arc, as well as between arc volcanic centers and among discrete samples from Pagan volcano, linking the oxidized nature of back-arc and arc basalts to slab fluid influence. The arc source may be more oxidized than the back-arc source due to a greater role for subduction influence, and/or to variable fluid composition. It is possible that slab fluids are oxidized as a result of deserpentinization reactions in the subducting slab, although further data is necessary to test this hypothesis.

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Figure 1.1 Location map for samples used in this study. All colored symbols for Agrigan, Alamagan, Guguan, and Sarigan volcanoes, as well as the solid blue square for Pagan volcano represent olivine hosted melt inclusions. Checkered square for Pagan volcano, cross for NW Rota-1 volcano, and light grey inverted triangles along the Mariana trough represent submarine glasses. Dark grey triangles in the northern Mariana trough are seafloor glasses from Kelley and Cottrell (2009) and Newman et al. (2000). The basemap was created using GeoMapApp (http://www.geomapapp.org; Ryan et al., 2009).
Figure 1.2 Representative photomicrographs of melt inclusions in this study. (a) Melt inclusion Gug23-02-01 is doubly polished and the photomicrograph is taken in cross polarized light. (b) Sari15-04-25, (c) Ala03-01, and (d) Agri07-06 are doubly exposed melt inclusions and photomicrographs are taken in transmitted light.
Figure 1.3 Major element variations for Mariana arc melt inclusions and submarine glasses (a-d) and back-arc submarine glasses (e-h). All symbols are as in Figure 1. Black line in panels e – h show the trajectory of olv±plag±cpx±mgt fractionation, generated using Petrolog3 (Danyushevsky & Plechov, 2011) fractionating the composition of 80-1-3 (VG10498) at 1.5 kbar, using mineral melt models of Roeder and Emslie (1970), Danyushevsky (2001), and Ariskin and Barmina (1999) in a system closed to oxygen. FeO* is total Fe expressed as FeO. Error bars are shown in the lower left hand corner of each plot, in panels (a) through (d).
Figure 1.4 Volatile element variations for Mariana arc melt inclusions and back-arc submarine glasses. Textured regions in panels (a), (b) are melt inclusion data from (Shaw et al., 2008) and Kelley et al. (2010), shown for comparison. (a) Plot of H$_2$O vs. CO$_2$ variation. Isobars and open system degassing curve were calculated for a basalt at 1200°C using VolatileCalc (Newman & Lowenstern, 2002). Error associated with H$_2$O concentrations are ~0.25 wt% and ~75 ppm for CO$_2$ concentrations.
Figure 1.4 con’t (b) Plot of S vs. H₂O concentrations. Model curve for concomitant S and H₂O degassing are semi-empirical and taken from Wade et al. (2006, small cross) and Sisson and Layne (1993, black square). Dashed line represents the extension of the degassing trajectory to high sulfur concentrations. Black star represents an approximately degassed magma. (c) Fe³⁺/ΣFe ratios vs. H₂O concentrations for Mariana arc melt inclusions from this study as well as from Kelley and Cottrell (2012, light grey diamonds), and back-arc submarine glasses. Grey MORB field are data taken from Cottrell and Kelley (2011). Additional melt inclusions in this panel are from Kelley and Cottrell (2009), shown for comparison. Error bars are shown in the upper left hand corner of each plot.
Figure 1.5 (a) Fe\(^{3+}\)/\(\Sigma\)Fe ratios vs. MgO concentrations for samples from this study and Kelley and Cottrell (2012, light grey diamonds). Grey field represents global MORB glass data from Cottrell and Kelley (2011). Black line is the trajectory of olv±plag±cpx±mgt fractionation, as in Figure 2. Dashed purple line is the trajectory of olv±cpx±plag fractionation from a starting composition similar to the composition of melt inclusion Agri04-05, generated using Petrolog3 (Danyushevsky & Plechov, 2011) at 1 kb, using mineral-melt models of Roeder and Emslie (1970) and Danyushevsky (2001) in a system closed to oxygen. (b) Magmatic \(f_2O\), plotted relative to the QFM buffer vs. MgO for the same samples. The \(f_2O\)'s and position of the QFM buffer (Frost, 1991) are calculated at the pressures and temperatures of melt inclusion entrapment using the algorithm of Kress and Carmichael (1991). Pressures for each melt inclusion suite are taken as the average pressure of entrapment recorded by CO\(_2\)-H\(_2\)O contents of the inclusions in the suite (Newman & Lowenstern, 2002). Temperatures for each melt inclusion suite are taken as the average olivine-liquid temperature of the inclusions in the suite (Putirka et al., 2007). The dashed black line marks the position of QFM. Error bars are shown in the lower left hand corner of each plot.
Figure 1.6 Fe$^{3+}$/ΣFe ratios vs. S concentrations for melt inclusions from Agrigan, Pagan, Guguan, Sarigan, and Alamagan volcanoes, as well as melt inclusions from Agrigan volcano from Kelley and Cottrell (2012, light grey diamonds). The black line with tick marks is a model for S degassing and associated Fe reduction, taken from Kelley and Cottrell (2012). Error bars are shown in the upper left hand corner.
Figure 1.7 Tholeiitic index (THI) versus (a) pre-eruptive H$_2$O content and (b) magmatic fO$_2$ relative to the QFM buffer. THI calculations, small circles in panel (a) and the black line are from Zimmer et al. (2010). The grey line marks the boundary between tholeiitic and calc-alkaline differentiation trends, as defined by Zimmer et al. (2010). Magmatic fO$_2$s are calculated as in figure 5. Brown square represents the average of MORB data from Cottrell and Kelley (2011). Grey triangle represents both northern and southern Mariana trough samples from this study. Error bars for H$_2$O and magmatic fO$_2$ represent the standard deviation of the sample population from the average. Error bars for THI represent the minimum and maximum estimates of THI, based on the available data for each location.
Figure 1.8 Histogram showing calculated primary $f_O^2$ ($\Delta$QFM) for several tectonic regimes. MORB data are calculating by adding equilibrium olivine compositions in 0.1% increments to the compositions of MORB glasses with MgO > 7 wt%, data taken from Cottrell and Kelley (2011). Pressures and temperatures of melt generation were calculated using the Si-thermobarometer of Lee et al. (2009). Oxygen fugacities were calculated from Fe$^{3+}$/ΣFe ratios after Kress and Carmichael (1991). Gray bars with dashes represent primary $f_O^2$s for Agrigan volcano, calculated by Kelley and Cottrell (2012). The dashed line marks the position of QFM, which is equal to the approximate primary $f_O^2$ for MORB source mantle (Cottrell & Kelley, 2011).
Figure 1.9 (a) Th/La, (b) Ba/La, and (c) Zr/Y vs. Sm/La for samples in this study. The grey field is Pacific MORB data from Niu and Batiza (1997), shown for comparison. Data for discrete materials from the Pacific plate taken from ODP sites 800 and 801 are shown as small black and white stars, respectively, and their calculated bulk compositions are shown as large black and white stars (Plank & Langmuir, 1998). Orange and green dashed lines show approximate mixing lines between the suggested arc mantle source composition (black circle; Plank, 2005) and various discrete components of the sediments at ODP Sites 800 and 801. The solid black line is an approximate mixing line between the suggested back-arc mantle source composition (grey circle; Stolper & Newman, 1994) and the bulk composition of sediments at ODP Site 801. Dashed black lines in panel (b) show approximate mixing trajectories to fluids of unconstrained composition.
Figure 1.10 Primary $f_O^2$ (ΔQFM) vs. (a) Zr/Y, (b) Th/La, and (c) Ba/La for samples in this study. MORB data are from Cottrell and Kelley (2013). In (c), large symbols represent the average calculated primary $f_O^2$ and measured Ba/La ratio for each volcano. The error bars on these symbols represent the standard deviation of the population from the average value. The bold dashed line marks the position of QFM, which is equal to the approximate primary $f_O^2$ for MORB source mantle (Cottrell & Kelley, 2011). Individual primary melt compositions for each location are shown as small symbols. The short-dashed, thin black line is a standard linear regression through the average $f_O^2$ and Ba/La ratio for the MORB, all of the northern Mariana trough data, and the average $f_O^2$ and Ba/La ratio for the southern Mariana trough and each of the volcanic centers.
Table 1.1: Maximum Fe\(^{3+}/\Sigma\)Fe ratios and average calculated primary melt compositions and fO\(_2\) for the Mariana arc and southern Mariana trough

| Volcano  | Agrigan | Pagan | Alamagan | Guguan | Sarigan | NW Rota | S. Mariana trough |
|----------|---------|-------|----------|--------|---------|---------|------------------|
| MgO\(_{\text{max}}\)\(^1\) | 5.66 | 7.17 | 7.40 | 5.70 | 7.23 | 6.33 | 5.93 |
| Fe\(^{3+}/\Sigma\)Fe | 0.254 | 0.219 | 0.244 | 0.263 | 0.240 | 0.211 | 0.185 |
| (MgO\(_{\text{max}}\))^2 | 0.2 | 0.3 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 |
| Pressure\(^3\) | 1164 | 1100\(^{12}\) | 1196 | 1100 | 1203 | 1100\(^{12}\) | 1200\(^{12}\) |
| Temp\(^4\) | 29 | nd | 30 | nd | 9 | nd | nd |
| 1σ | 1.44 | 1.23 | 1.30 | 1.50 | 1.30 | 1.02 | 0.51 |
| Magmatic log (fO\(_2\))^5 | 0.36 | 0.15 | 0.22 | 0.03 | 0.27 | 0.22 | 0.30 |
| Pre-eruptive H\(_2\)O (wt%)^6 | 3.78 | 1.81 | 3.70 | 4.05 | 3.96 | nd | 0.50 |
| THI\(^7\) | 0.950 | 0.933 | 1.108 | 1.058 | 0.824 | nd | 1.276 |
| Fe\(^{3+}/\Sigma\)Fe\(_{\text{prim}}\)\(^8\) | 0.182 | 0.192 | 0.219 | 0.242 | 0.216 | 0.163 | 0.167 |
| 1σ | 0.01 | 0.01 | 0.02 | 0.00 | 0.02 | 0.01 | 0.01 |
| Pressure\(^9\) | 1.8 | 1.5 | 1.3 | 1.1 | 1.1 | 0.8 | 0.64 |
| 1σ | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 0.08 |
| Temp\(^10\) | 1384 | 1403 | 1256 | 1234 | 1256 | 1303 | 1263 |
| 1σ | 46 | 22 | 26 | 6 | 13 | 30 | 21 |
| Primary log(fO\(_2\))\(^11\) | 1.18 | 1.09 | 1.34 | 1.56 | 1.29 | 0.59 | 0.48 |
| 1σ | 0.1 | 0.2 | 0.2 | 0.1 | 0.2 | 0.2 | 0.01 |
| Ba/La | 19.5 | 40.8 | 34.9 | 48.0 | 46.4 | 17.3 | 15.9 |
| 1σ | 0.91 | 8.0 | 11 | - | 6.5 | 0.93 | 1.10 |
| Th/La | 0.101 | 0.086 | 0.095 | 0.108 | 0.107 | 0.104 | 0.072 |
| 1σ | 0.01 | 0.01 | 0.02 | - | 0.02 | 0.01 | 0.02 |
| Zr/Y | 2.24 | 2.03 | 2.53 | 1.26 | 2.41 | 2.60 | 3.27 |
| 1σ | 0.05 | 0.37 | 0.52 | - | 0.39 | 0.29 | 0.74 |

A "-" for 1σ fields indicates that trace element concentrations were measured on a single sample.
Footnotes to Table 1.1 continued…

1σ values represent the standard deviation of the sample population from the average values reported.

"nd" indicates that insufficient data were available to perform the calculation

1Highest MgO concentration measured for a melt inclusion or submarine glass sample at a given geographic location.

2Fe\(^{3+}/\Sigma\)Fe ratio of the sample with the highest MgO concentration.

3Pressure (GPa) from PetroLog fractionation model.

4Average magmatic temperature (°C) recorded by melt inclusion/olivine thermobarometry, calculated after Putirka et. al., 2007.

5Average magmatic log(\(f_O^2\)) relative to the quartz-fayalite magnetite oxygen buffer (ΔQFM) at the pressures and temperatures recorded by melt inclusions. Calculated using the algorithm of Kress and Carmichael (1991).

6Pre-eruptive water content determined by averaging the H\(_2\)O contents of inclusions that form vertical paths on a CO\(_2\)-H\(_2\)O diagram (Fig. 4b). For Guguan, this is the H\(_2\)O concentration of the single inclusion for which we have data. The uncertainty in these values is +/- 0.5-1.0 wt%.

7calculated after Zimmer et. al., 2010.

8Average Fe\(^{3+}/\Sigma\)Fe ratio calculated for a primary magma at a given geographic location.

9Pressure of melt generation (GPa), calculated using the Si-thermobarometer of Lee et. al. (2009)

10Temperature of melt generation (°C), calculated using the Si-thermobarometer of Lee et. al. (2009)

11log(\(f_O^2\)) relative to the quartz-fayalite-magnetite oxygen buffer (ΔQFM) at pressure and temperature of melt generation. Calculated using the algorithm of Kress and Carmichael (1991).

12Estimated from melt inclusion data from other suites in this study.
Table 1.2: Primary melt Fe\textsuperscript{3+}/ΣFe, fO\textsubscript{2} and trace element compositions for Northern Mariana Trough lavas

| Sample  | Fe\textsuperscript{3+}/ΣFe\textsubscript{prim} | Pressure\textsuperscript{2} | Temp\textsuperscript{3} | log fO\textsubscript{2}\textsuperscript{4} | Ba/La | Th/La | Zr/Y |
|---------|---------------------------------|------------------|------------------|-----------------|--------|--------|------|
| 73-2-1  | 0.151                           | 0.9              | 1262             | 0.25            | 6.97   | 0.083  | 3.76 |
| 71-1-14 | 0.173                           | 0.8              | 1232             | 0.52            | 9.91   | 0.123  | 3.79 |
| 82-1-1  | 0.164                           | 0.8              | 1249             | 0.45            | 7.34   | 0.080  | 3.19 |
| 76-1-1  | 0.133                           | 1.3              | 1356             | 0.08            | 5.04   | 0.066  | 3.26 |
| 75-1-2  | 0.145                           | 1.1              | 1301             | 0.18            | 5.87   | 0.077  | 3.91 |
| 80-1-3  | 0.139                           | 1.3              | 1322             | 0.17            | 8.31   | 0.073  | 2.21 |
| 46-1-6  | 0.151                           | 0.9              | 1267             | 0.26            | 11.27  | 0.081  | 2.86 |
| 74-1-1  | 0.165                           | 0.8              | 1241             | 0.40            | 7.11   | 0.101  | 3.52 |
| 47-1-5  | 0.160                           | 0.8              | 1246             | 0.34            | 12.66  | 0.107  | 2.64 |

\textsuperscript{1}Calculated primary Fe\textsuperscript{3+}/ΣFe ratio.

\textsuperscript{2}Pressure of melt generation (GPa), calculated using the Si-thermobarometer of Lee et. al. (2009).

\textsuperscript{3}Temperature of melt generation (°C), calculated using the Si-thermobarometer of Lee et. al. (2009).

\textsuperscript{4}log(fO\textsubscript{2}) relative to the quartz-fayalite-magnetite oxygen buffer (ΔQFM) at pressure and temperature of melt generation.
Electronic Appendix A: Supplementary material to accompany the manuscript, “Fe$^{3+}$/∑Fe in Mariana Arc basalts and primary $fO_2$”

Screening for olivine interference in Fe-$\mu$-XANES spectra

When collecting Fe-$\mu$-XANES spectra on olivine-hosted melt inclusions, it is important to avoid hitting the olivine crystal with the beam during analysis. Olivine contains several weight percent of Fe$^{2+}$ and even a very small amount of olivine interference will “contaminate” the pre-edge structure of Fe-$\mu$-XANES spectra collected for melt inclusions and bias the result towards more reduced values. The region of XANES spectra at higher energies than the Fe-K$\alpha$ absorption edge contains information related to Fe-coordination and can be used to distinguish glass structure (random and on average, uncoordinated) from olivine signal (strong coordination, Fig. A1). All melt inclusion and seafloor glass spectra were visually inspected and compared to spectra taken on San Carlos olivine and standard glasses from Cottrell et al. (2009) in order to screen for crystal contamination. Any spectra demonstrating signs of spectral features similar to those observed in San Carlos olivine were not considered in this study and additional spectra were collected to accommodate for this elimination.

Model liquid lines of descent

To constrain the effects of fractional crystallization on magmatic Fe$^{3+}$/∑Fe ratios, model liquid lines of descent that match the observed major element variations were generated using PetroLog3 (Danyushevsky & Plechov, 2011). The mineral-melt
models that most closely replicate the natural data were chosen for each location, resulting in some variation in the models used from volcano to volcano. Individual model parameters chosen to generate each LLD are provided in the figure captions to Fig A2-A6. If crystal fractionation is the main control on magmatic Fe redox, each model is meant to assess the extent to which Fe redox ratios may vary as a result of the relative incompatibility of Fe$^{3+}$ in each fractionating phase. Implicit in this assessment is the assumption that fractional crystallization proceeds in a system closed to oxygen. Evidence from a global study of MORB glass suggests that closed system fractionation of olivine ± plagioclase ± clinopyroxene explains variations in Fe$^{3+}/\sum$Fe ratios (Cottrell & Kelley, 2011). In our present study, each modeled LLD assumes a $D_{Fe^{3+}} = 0$ and a $D_{Fe^{2+}}$ that varies according to the mineral-melt models chosen, for olivine ± clinopyroxene ± plagioclase fractionation. Magnetite mineral-melt models use a non-zero $D_{Fe^{3+}}$ that depend upon the composition of the melt. Each model was generated using a starting composition from a measured sample in this study.

_Agrigan_

Agrigan tephra samples Agri7, Agri04, and Agri05 all contain crystals of olivine, plagioclase, clinopyroxene, and magnetite. The clasts are red-brown, rounded and slightly weathered. In tephra sample Agri04, there are occasional clay fragments present. In tephra sample Agri05, there are occasional clasts of country rock that are red in color. The largest size fraction observed in these tephra samples is ~0.5 cm in diameter.

The modeled LLD begins with sample Agri-04-05 as the parental composition. The model crystallizes olivine isobarically at 1 kbar, then saturates clinopyroxene at
4.3 wt% MgO and then saturates plagioclase at 4.2 wt% MgO (Fig. 3a-d, A2). The whole rock and melt inclusion data for Agrigan from the literature and this study are broadly consistent with this model and in the case of all major elements except for FeO$_{\text{actual}}$ and Fe$_2$O$_3$$_{\text{actual}}$, the fractionation slope defined by the modeled LLD between 5-7 wt% MgO was used to correct for the effects of fractional crystallization (Electronic Appendix E). For FeO$_{\text{actual}}$ and Fe$_2$O$_3$$_{\text{actual}}$, an empirical fractionation slope constrained by the trend in the melt inclusion data from this study was used (Electronic Appendix E).

**Pagan**

Tephra sample Paga8 is black in color and fresh. The largest size fraction observed in this tephra sample is ~1 cm in diameter. This tephra sample contains plagioclase, olivine, and clinopyroxene. Submarine pillow basalts are vesicular and have a glassy pillow rind. Pillow interiors contain plagioclase, clinopyroxene, and olivine.

The modeled LLD begins with sample HDP1147-R06 as the parental composition. Starting at 2.5 kbar and decompressing at a constant rate of 5 bar per 1°C, the model crystallizes olivine and clinopyroxene, and then saturates plagioclase at 7.0 wt% MgO, and then magnetite at 6.5 wt% MgO (Fig. 3a-d, A3). The whole rock and melt inclusion data for Pagan from the literature and this study are broadly consistent with this model, except for TiO$_2$ and SiO$_2$ (Fig. A3). This may result from magnetite saturation too early or in too great abundance in the modeled LLD. It is also important to note that whole rock data may contain accumulated crystals that pull the whole rock compositions away from the true liquid compositions. Systematic offsets
between melt inclusions and whole rock compositions in Al$_2$O$_3$ or CaO/Al$_2$O$_3$
variations with MgO are evidence for this phenomenon. In the case of all major
elements except for TiO$_2$, SiO$_2$, FeO$^\text{actual}$ and Fe$_2$O$_3$$^\text{actual}$, the fractionation slope
defined by the modeled LLD between 5-7 wt% MgO was used to correct for the
effects of fractional crystallization (Electronic Appendix E). For TiO$_2$, SiO$_2$, FeO$^\text{actual}$
and Fe$_2$O$_3$$^\text{actual}$, an empirical fractionation slope constrained by the trend in the melt
inclusion and submarine glass data from this study was used (blue line on TiO$_2$ panel,
Fig. A3; Electronic Appendix E).

*Alamagan*

Tephra samples Ala02 and Ala03 both contain olivine, plagioclase,
clinopyroxene, and magnetite. Both tephra samples have vesiculated tephra fragments.
The largest size fraction in Ala03 is ~2 cm in diameter, and ~1 cm in diameter in
Ala02. Tephra sample Ala03 is altered, brown-red in color. Tephra sample Ala02 is
black-brown in color.

The modeled LLD begins with sample Ala02-01 as the parental composition.
Starting at 2 kbar and decompressing at a constant rate of 15 bar/°C, this model
crystallizes olivine, then saturates clinopyroxene at 4.6 wt% MgO and then saturates
plagioclase at 4.5 wt% MgO (Fig. 3a-d, A4). The whole rock and melt inclusion data
for Alamagan from the literature and this study are broadly consistent with this model
and in the case of all major elements except for FeO$^\text{actual}$ and Fe$_2$O$_3$$^\text{actual}$, the
fractionation slope defined by the modeled LLD between 5-7 wt% MgO was used to
correct for the effects of fractional crystallization (Electronic Appendix E). For
FeO\text{actual} and Fe_2O_3\text{actual}, an empirical fractionation slope constrained by the trend in the melt inclusion data from this study was used (Electronic Appendix E).

**Guguan**

Tephra samples Gug11 and Gug23-02 are black in color and are fresh. The largest size fraction in both tephras is ~0.5 cm in diameter. Both tephra samples contain crystals of olivine, plagioclase, and clinopyroxene.

The modeled LLD begins with sample SD46-1-1 as the parental composition (Stern et al., 2006). Starting at 2 kbar and decompressing at a constant rate of 5 bar/°C, this model crystallizes olivine, then saturates clinopyroxene at 6.3 wt% MgO, then saturates plagioclase at 5.3 wt% MgO, and magnetite at 4.4 wt% MgO (Fig. 3a-d, A5). The whole rock and melt inclusion data for Guguan from the literature and this study are broadly consistent with this model. Some melt inclusions from this study and those from previous work have higher FeO* concentrations than do whole rock samples from Guguan, suggesting that melt inclusions from Guguan tephras frequently gain Fe. The careful screening procedures in this study eliminate any melt inclusion compositions that deviate significantly from the whole rock compositions, in order to avoid interpreting melt inclusion compositions that have experienced complicated magmatic histories in this work. Another important observation is that the model LLD does not fit the absolute variation between TiO_2 and MgO because the starting composition, chosen as such because of its elevated MgO content, happens to have higher TiO_2 than other whole rock samples from Guguan volcano. Though the line is offset from the data array, the slope of the line however is a good match. In the case of all major elements except for FeO\text{actual} and Fe_2O_3\text{actual}, the fractionation slope defined
by the modeled LLD between 5-7 wt% MgO was used to correct for the effects of fractional crystallization (Electronic Appendix E). For FeO$_{\text{actual}}$ and Fe$_2$O$_3$$_{\text{actual}}$, an empirical fractionation slope constrained by the trend in the melt inclusion data from this study was used (Electronic Appendix E).

*Sarigan*

Tephra sample Sari15-04 is brown in color and show signs of slight alteration. The largest size fraction observed in this tephra sample is ~0.25 cm in diameter. This tephra sample contains crystals of olivine, clinopyroxene, plagioclase, and magnetite.

The modeled LLD begins with sample Sari15-04-27 as the parental composition. Starting at 1.8 kbar and decompressing at a constant rate of 0.9 bar/°C, this model crystallizes olivine, then saturates clinopyroxene at 7.1 wt% MgO, then saturates magnetite at 6.8 wt% MgO, and then saturates plagioclase at 4.1 wt% MgO (Fig. 3a-d, A6). The whole rock and melt inclusion data for Sarigan from the literature and this study are broadly consistent with this model, with a few exceptions. While the model LLD is a good match for the variation in FeO* and TiO$_2$ with decreasing MgO in the compositional range of the melt inclusions in this study, whole rock compositions that extend to lower MgO concentrations are not well fit by the model. This may be because magnetite does not saturate in this model and the fractionation of plagioclase drives FeO* and TiO$_2$ contents to increasingly higher values, opposite to the trends observed in the natural whole rock data. If magnetite is allowed to saturate in the model, it saturates too early and the LLD is inconsistent with the natural data in the compositional range of melt inclusions in this study. Because none of our Sarigan melt inclusions have MgO < 5.0 wt%, we chose the model that better describes the
compositional range of samples at higher MgO concentrations. For melt inclusion compositions in this study, in the case of all major elements except for FeO$_{\text{actual}}$ and Fe$_2$O$_3^{\text{actual}}$, the fractionation slope defined by the modeled LLD between 5-7 wt% MgO was used to correct for the affects of fractional crystallization (Electronic Appendix E). For FeO$_{\text{actual}}$ and Fe$_2$O$_3^{\text{actual}}$, an empirical fractionation slope constrained by the trend in the melt inclusion data from this study was used (Electronic Appendix E).

**NW Rota-1**

Submarine pillows from NW Rota-1 are vesicular and have glassy pillow rinds. The pillow interiors have crystals of plagioclase, clinopyroxene, and olivine.

The modeled LLD begins with sample HD488-R11 as the parental composition. This model crystallizes olivine isobarically at 0.1 kbar, then saturates plagioclase at 7.2 wt% MgO, and then saturates clinopyroxene at 6.1 wt% MgO (Fig. 3a-d, A7). Though there is a paucity of data for NW Rota-1, the submarine glass data from this study are broadly consistent with this model and in the case of all major elements except for FeO$_{\text{actual}}$ and Fe$_2$O$_3^{\text{actual}}$, the fractionation slope defined by the modeled LLD between 5-7 wt% MgO was used to correct for the effects of fractional crystallization (Electronic Appendix E). For FeO$_{\text{actual}}$ and Fe$_2$O$_3^{\text{actual}}$, an empirical fractionation slope constrained by the trend in the submarine glass data from this study was used (Electronic Appendix E).

**Northern and Southern Mariana Trough**

Northern Mariana trough glasses discussed here were provided only as chipped glass fragments. These glass fragments are fresh and some are vesicular. Southern
Mariana trough pillow basalts are vesicular and have glassy pillow rinds. The interior of some vesicle walls are lined with small sulfide crystals. The pillow interiors have olivine ± plagioclase ± clinopyroxene.

Northern Mariana trough samples range in H$_2$O contents, from 0.5 to 2.5 wt% (Fig. 4d). Water effects magmatic differentiation by suppressing the saturation of plagioclase and clinopyroxene and parental magmas with the same major element composition but different H$_2$O concentrations may have different model LLDs (e.g., Lytle et al., 2013). However, the major element variations in the Mariana trough samples are similar and so will be described by a single LLD. The modeled LLD begins with sample 80-1-3 from Stolper and Newman (1994) as the parental composition. This model crystallizes olivine isobarically at 1.5 kbar, then saturates plagioclase at 8.5 wt% MgO, then saturates clinopyroxene at approximately 6.1 wt% MgO, then saturates magnetite at 3.9 wt% MgO (Fig. 3e-h). The submarine glass data from this study are broadly consistent with this model and in the case of all major elements except for FeO$^{\text{actual}}$ and Fe$_2$O$_3$$^{\text{actual}}$, the fractionation slope defined by the modeled LLD between 5-7 wt% MgO was used to correct for the effects of fractional crystallization (Electronic Appendix E). For FeO$^{\text{actual}}$ and Fe$_2$O$_3$$^{\text{actual}}$, an empirical fractionation slope constrained by the trend in the submarine glass data from this study was used (Electronic Appendix E).

**Diffusive re-equilibration of melt inclusions**

To assess whether melt inclusion suites in this study are significantly changed by diffusive re-equilibration, we compare the trace element variability recorded in
suites of melt inclusions from Sarigan, Agrigan, and Alamagan volcanoes to submarine glasses from the southern Mariana trough (Fig. A10; i.e., Cottrell et al., 2002, Kent, 2008). There is a simple relationship between the variability in trace element compositions within a population of basaltic glasses and the bulk partition coefficient of the element (peridotite/melt), where more incompatible elements yield glasses with greater population variability. The same correlations should be recorded in suites of melt inclusions if diffusive re-equilibration has not significantly modified the trace element composition of the inclusion. To apply this principle to subduction related magmas, we look only at elements that are not recycled from the subducting slab in the Marianas (Fig. A10, Pearce et al., 2005) because addition of an element to the mantle wedge by an aqueous fluid, for example, will mask relationships between the element’s abundance and variability and the partitioning behavior of the element during simple mantle melting. As expected, there is a correlation between bulk partition coefficient and the percent standard deviation of incompatible trace elements in southern Mariana trough glasses. Melt inclusion suites from Sarigan and Alamagan also show this correlation, suggesting that these melt inclusions are not significantly affected by diffusive re-equilibration on the timescales relevant to trace element diffusion in olivine. Melt inclusions from Agrigan volcano, however, do not show this correlation and may thus have experienced some amount of diffusive equilibration.

We also examine the relationship between the sizes of melt inclusion and their major element composition and Fe redox, to test whether smaller diameter melt inclusions have been re-equilibrated and larger diameter melt inclusions have not. There is no relationship between the size of melt inclusion and the major element
composition, measured $\text{Fe}^{3+}/\sum \text{Fe}$ ratios in the inclusions, or the amount of
disequilibrium between melt inclusion and olivine host (Fig. A11). The exception to
this is the apparent disequilibrium between four Agrigan melt inclusions and their
olivine hosts, where the smallest diameter melt inclusions appear to have undergone
more post-entrapment crystallization than larger inclusions. These melt inclusions
require more than 2% post-entrapment crystallization correction to reach equilibrium
with its olivine host and are not considered in this study. These results suggest either
that diffusive re-equilibration (a) has not occurred in melt inclusions used in this
study, or (b) has gone to completion such that even slow diffusing elements in olivine
(e.g., Ca) have completely re-equilibrated in melt inclusions with 50-300 µm diameter.

**Trace element heterogeneity and magma mixing**

Melt inclusions and submarine glasses from a single arc volcano
commonly record significant heterogeneity in trace element compositions that
potentially reflect contributions and mixing between several parental magmas (e.g.,
Figure 9 in the main text, Fig. A13). If the parent magmas are also heterogeneous in
the major element compositions there is some concern that the major element
relationships reflect magma mixing rather than crystal fractionation. This potentially
introduces error in the calculations described above, of the compositions and $fO_2$ of
primary magmas in the Marianas. Figure A13 shows the La/Yb ratios of melt
inclusions and submarine glasses versus the Fo# of olivine host (for melt inclusions),
$\text{SiO}_2$ content, measured $\text{Fe}^{3+}/\sum \text{Fe}$ ratios, $\text{Na}_2\text{O}$ content, $\text{TiO}_2$ content, and $\text{K}_2\text{O}$
content. The variation in La/Yb ratio versus the Fo# of the olivine host demonstrates
the heterogeneity in trace element composition of melt inclusions in this study (vertical dashed line), which is greater than can be expected by simple fractionation of La from Yb during differentiation. Neither La nor Yb are thought to be a significant component slab fluids or sediment melts in the Marianas, and the variation observed here likely reflects heterogeneity in the mantle source and/or variations in the extent of melting at each location. Despite this variation in trace element composition, the parental melts generated under the arc are still basalt to basaltic andesite in composition. The wide variation in La/Yb ratios (1 to >4) observed within a single suite of melt inclusions occurs in a relatively narrow range of SiO₂ concentrations (44-49 wt%). There is no correlation between SiO₂, Na₂O, and TiO₂ concentrations, or Fe redox ratios and La/Yb ratios, suggesting that any magma mixing the produces a range of trace element heterogeneity is not reflected in the major element compositions of the melt inclusions. The exception to this are K₂O concentrations in melt inclusions from Sarigan volcano, in which four melt inclusions with high K₂O concentrations (>0.30) also have La/Yb ratios that are a factor of two higher than the main melt inclusion population (>2.0). However, the high K₂O concentrations of these samples did not influence the choice of the fractionation model used for calculating primary melt compositions, instead these inclusions were corrected back to MgO = 7.0 wt% along a shallow slope that fit the main melt inclusion population best, creating a range in primary melt compositions used to calculate primary fO₂. We note that these inclusions can not be readily distinguished from the main melt inclusion population in other major elements, and that changing the K₂O concentrations of primary melts by a factor of two does not impact calculated fO₂. Additionally, the same trace element
heterogeneity recorded by melt inclusion populations is also recorded in submarine
glasses from the Mariana trough, Pagan volcano, and NW Rota-1 volcanoes,
suggesting that this observation is not simply a melt inclusion phenomenon. We
conclude that the major element relationships observed in Figure 3 in the main text, as
well as in Figures A2-A7 in the electronic appendix can be reasonably described by
simple crystal fractionation.

Sensitivity test of primary melt model results

The method used to calculate primary melt compositions and $fO_2$ has many
sources of error, uncertainty in the inputs, and calculation constraints. Here, we
present the results of sensitivity tests of the model results for a subset of samples.

The calculations in the main text reference all primary melt compositions to a
mantle olivine at Fo90. If the mantle is more depleted by melt extraction, as might be
the case under the volcanic arc, or more fertile, the final endpoint of the calculation
may reasonably be Fo91 or Fo89, respectively. Figure A12, panel a, demonstrates the
sensitivity of the final calculation to mantle olivine Fo#. The difference between
primary $fO_2$ calculated for arc and back-arc primary melts in equilibrium with Fo89
and Fo90 olivine, or Fo90 and Fo91 olivine, is equal to ~0.07 log units relative to the
QFM oxygen buffer. This is much smaller than the observed offset between MORB,
Mariana trough, and Mariana arc magmas.

The calculations in the main text correct the major element compositions of
samples with MgO between 5 and 7 wt% to a reference MgO = 7.0 wt%, after which
the calculation assumes that olivine is the only liquidus phase back to a melt
composition in equilibrium with Fo90 olivine. For the arc samples, it is possible that clinopyroxene remains a liquidus phase to higher MgO concentrations. Figure A12, panel b shows the sensitivity of the final calculation to (1) the choice of MgO reference value (blue stars use a reference MgO = 8.0 wt%) and (2) the inclusion of clinopyroxene as a liquidus phase back to equilibrium with Fo90 olivine (pink stars include olivine and clinopyroxene as liquidus phases back to equilibrium with Fo90 olivine). Increasing the MgO reference value to 8.0 wt% increases the primary melt $fO_2$ by 0.17 log units. If clinopyroxene is included along with olivine as a liquidus phase, primary melt $fO_2$ is reduced by 0.23-0.42 log units. Each of these outcomes is less than the difference of primary melt $fO_2$ between MORB, the Mariana trough, and the Mariana arc.

Finally, there are several model inputs that have some uncertainty associated with them. To assess the total impact of these uncertainties, we have performed a Monte Carlo error analysis. The error analysis uses an uncertainty of 0.5%, 1%, 3%, 2%, and 5% on the raw concentrations of Al$_2$O$_3$, FeO$, CaO$, Na$_2$O, K$_2$O in the glasses associated with electron probe micro analysis and an uncertainty of 3% on the determination of Fe$^{3+}/\Sigma$Fe ratios. It uses a 10% uncertainty in the slope of the lines used to calculate the reference compositions for these same elements to MgO7.0. We assign a 20% uncertainty to the constraints on primary melt T and P and a 15% uncertainty in the raw concentrations of Ba and La measured in the glasses by LA-ICPMS. The error simulation for calculating primary melt $fO_2$ was run through 100 iterations, allowing each variable to vary randomly within the limits of uncertainty described here. The 95 intermediate solutions are shown as error ellipses around the
model calculations presented in the main text and shown in Figure A12, panel c. The error ellipses are much smaller than the variation between MORB, Mariana trough and Mariana arc constraints in either Ba/La ratio or primary melt $f_{O_2}$, indicating that the model results for each point are distinct.

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Figure 1.1A Example Fe-μ-XANES spectra for San Carlos olivine (green line), standard glass LW+1.0 (brown line; Cottrell et al., 2009), melt inclusion sample Ala03-01 with olivine interference (solid black line) and melt inclusion sample Ala03-01 without olivine interference (dashed black line). Inset shows the pre-edge feature for all spectra in greater detail. All spectra are normalized to an arbitrary absorption intensity of 1.0 for the region between 7205 and 7210 eV.
Figure 1.2A Major element variations (FeO*, CaO/Al₂O₃, Al₂O₃, and TiO₂) vs. MgO for Agrigan melt inclusions from tephras Agri04, Agri05, and Agri07, compared to the available literature data for Agrigan melt inclusions and lavas. Large diamonds are melt inclusions used in this study. Small diamonds are olivine hosted melt inclusions that have been eliminated from this study due to Fo₁₋₂₃ Fo₃₃ melt inclusion disequilibrium. The light gray diamonds, dotted diamonds, and open diamonds are olivine hosted melt inclusions from Kelley and Cottrell (2012), Kelley et al., (2010), and Shaw et al. (2008), respectively. The white circles are whole rock data for tephras collected at Agrigan volcano (Plank, unpublished data). Black circles are whole rock data for lavas collected at Agrigan volcano, compiled using GeoROC (Electronic appendix J). The black line is the Petrolog3 fractionation model, using a starting composition equal to Agri04-05 and fractionating olivine, clinopyroxene, and plagioclase at 1 kbar, using mineral melt models of Roeder and Emslie (1970) and Danyushevsky (2001), treating Fe²⁺/Fe³⁺ as a closed system (Danyushevsky & Plechov, 2011).
Figure 1.3A Major element variations (FeO*, CaO/Al₂O₃, Al₂O₃, and TiO₂) vs. MgO for Pagan melt inclusions from tephra Paga8 and submarine glasses, compared to the available literature data for Pagan melt inclusions and lavas. Large squares are a melt inclusion (solid blue) and submarine glasses (checkered) used in this study. The dotted squares and open squares are olivine hosted melt inclusions from Kelley et al. (2010) Shaw et al. (2008), respectively. Black circles are whole rock data for lavas collected at Pagan volcano, compiled using GeoROC (Electronic appendix J). The black line is the Petrolog3 fractionation model, using a starting composition equal to HDP1147-R06 and fractionating olivine, plagioclase, clinopyroxene, and magnetite at 3 kbar and decompressing at a rate of 5 bar/°C. Mineral melt models of Roeder and Emshie (1970), Danyushevsky (2001), and Ariskin and Barmina (1999) were used, treating Fe²⁺/Fe³⁺ as a closed system (Danyushevsky & Plechov, 2011).
Figure 1.4A Major element variations (FeO*, CaO/Al$_2$O$_3$, Al$_2$O$_3$, and TiO$_2$) vs. MgO for Alamagan melt inclusions from tephras Ala02 and Ala03, compared to the available literature data for Alamagan melt inclusions and lavas. Large circles are melt inclusions used in this study. Small circles are olivine hosted melt inclusions that have been eliminated from this study due to Fo$_{\text{host}}$-Fo$_{\text{melt inclusion}}$ disequilibrium (light green) and to elevated FeO* relative to the literature data (dark green). The open, thick lined circles are olivine hosted melt inclusions from Shaw et al. (2008). The open, thin lined circles are whole rock data for tephras collected at Alamagan volcano (Plank, unpublished data). Black circles are whole rock data for lavas collected at Alamagan volcano, compiled using GeoROC (Electronic appendix J). The black line is the Petrolog3 fractionation model, using a starting composition equal to Ala02-01 and fractionating olivine, plagioclase, and clinopyroxene at 2 kbar and decompressing at a rate of 15 bar/°C. Mineral melt models of Roeder and Emslie (1970) and Danyushevsky (2001) were used, treating Fe$^{2+}$/Fe$^{3+}$ as a closed system (Danyushevsky & Plechov, 2011).
**Figure 1.5A** Major element variations (FeO*, CaO/Al$_2$O$_3$, Al$_2$O$_3$, and TiO$_2$) vs. MgO for Guguan melt inclusions from tephras Gug11 and Gug23-02, compared to the available literature data for Guguan melt inclusions and lavas. Large hexagons are melt inclusions used in this study. Small hexagons are olivine hosted melt inclusions that have been eliminated from this study due to Fo$_\text{host}$-Fo$_\text{MI}$ disequilibrium (solid and checkered light yellow). The dotted hexagons, slashed hexagons, and open hexagons are olivine hosted melt inclusions from Kelley et al. (2010), Kelley and Cottrell (2009), and Shaw et al. (2008), respectively. The white circles are whole rock data for tephras collected at Guguan volcano (Plank, unpublished data). Black circles are whole rock data for lavas collected at Guguan volcano, compiled using GeoROC (Electronic appendix J). The black line is the Petrolog3 fractionation model, using a starting composition equal to SD46-1-1 and fractionating olivine, plagioclase, clinopyroxene, and magnetite at 2 kbar and decompressing at a rate of 5 bar/°C. Mineral melt models of Roeder and Emslie (1970), Danyushevsky (2001), and Ariskin and Barmina (1999) were used, treating Fe$^{2+}$/Fe$^{3+}$ as a closed system (Danyushevsky & Plechov, 2011).
Figure 1.6A Major element variations (FeO*, CaO/Al2O3, Al2O3, and TiO2) vs. MgO for Sarigan melt inclusions from tephra Sari15-04, compared to the available literature data for Sarigan melt inclusions and lavas. Large stars are melt inclusions used in this study. Small stars are olivine hosted melt inclusions that have been eliminated from this study due to Fohost-FoMelt inclusion disequilibrium (light orange) and to elevated FeO* relative to the literature data (dark orange). The dotted stars and open stars are olivine hosted melt inclusions from Kelley et al. (2010) and Shaw et al. (2008), respectively. The white circles are whole rock data for tephras collected at Alamagan volcano (Plank, unpublished data). Black circles are whole rock data for lavas collected at Sarigan volcano, compiled using GeoROC (Electronic appendix J). The black line is the Petrolog3 fractionation model, using a starting composition equal to Sari15-04-27 and fractionating olivine, plagioclase, and clinopyroxene at 1.8 kbar and decompressing at a rate of 9 bar/°C. Mineral melt models of Roeder and Emslie (1970), Danyushevsky (2001), and (Nielsen, 1988) were used, treating Fe2+/Fe3+ as a closed system (Danyushevsky & Plechov, 2011).
Figure 1.7A Major element variations (FeO*, CaO/Al$_2$O$_3$, Al$_2$O$_3$, and TiO$_2$) vs. MgO for NW Rota-1 submarine glasses. The black line is the Petrolog3 fractionation model, using a starting composition equal to HD288-R11 and fractionating olivine, plagioclase, and clinopyroxene at 0.1 kbar. Mineral melt models of Roeder and Emslie (1970), and Danyushevsky (2001) were used, treating Fe$^{2+}$/Fe$^{3+}$ as a closed system (Danyushevsky & Plechov, 2011).
Figure 1.8A Calculated Fo# of an equilibrium olivine host for each melt inclusion included in this study, using an FeO/MgO $K_D = 0.3$ (Roeder & Emslie, 1970) vs. the measured Fo# of the olivine host. Solid black line is a 1:1 relationship. Dashed black lines represent the error envelope of the equilibrium Fo# calculation. This error envelope is calculated by propagating average analytical error for FeO* and MgO through the equations for calculating equilibrium Fo#. Any melt inclusion that falls below the 1:1 line is subject to the PEC correction described in the main text, until the melt inclusion composition is in equilibrium with the composition of its olivine host. Any melt inclusion composition that falls above the 1:1 line, but lies within the error envelope, is left uncorrected.
Figure 1.9A Plot of V vs. MgO variation for Mariana trough samples (southern Mariana trough, this study; white circles are Mariana trough data from Pearce et al., 2005). The arrow shows the general expectation of the effect of magnetite fractionation on V concentrations in a magma.
Figure 1.10A A plot of percent standard deviation of select trace element concentrations within a population of samples versus bulk $D_{\text{perid/melt}}$ for melt inclusions from Sarigan, Agrigan, and Alamagan volcanoes, as well as submarine glasses from the southern Mariana trough. Bulk $D_{\text{perid/melt}}$ are from Cottrell et al., (2002).
Figure 1.11A Plots of the size of melt inclusions versus CaO, Fe\(^{3+}/\Sigma\) Fe ratios, and the apparent disequilibrium between melt inclusion and olivine host pairs. Melt inclusion shapes vary between circular and oblate. In the cases where the melt inclusions are oblate, the left hand panels use the short axis and the right hand panels use the long axis of the inclusions. In the bottom panels, the gray dashed line marks the position of Fo\(_{EQ}\)-Fo\(_{host}\) equal to 0, or apparent equilibrium between melt inclusion and olivine host. Any melt inclusion within the gray box are those that are used in this study.
Figure 1.12A Plots demonstrating the results of sensitivity tests for the calculations in this study (panels a and b) and a Monte Carlo error simulation demonstrating the effects of accumulated errors on the final calculation (panel c).
Figure 1.13A Plots of La/Yb ratios in melt inclusions and submarine glasses versus (a) Fo# of the olivine host, (b) SiO$_2$, (c) Fe$^{3+}/\sum$Fe ratios, (d) Na$_2$O, (e) TiO$_2$, and (f) K$_2$O. The vertical dashed line emphasizes the heterogeneity in La/Yb ratio at fixed values for Fo#, SiO$_2$, or Fe$^{3+}/\sum$Fe ratio that is unrelated to crystal fractionation. The solid line illustrates the direction that crystal fractionation drives the variables.
Table 1.1A (Electronic Appendix B) Major element and volatile compositions and Fe$^{3+}$/ΣFe ratios for melt inclusions and host olivines from Mariana Arc volcanoes

| Volcano | Sample | Inclusion # | IGSN designation |
|---------|--------|-------------|------------------|
| Sarigan | Sari15-04 | 1 | MNB000001 |
| | | 3 | MNB000002 |
| | | 4 | MNB000003 |
| | | 7 | MNB000004 |
| | | 10 | MNB000005 |
| | | 11 | MNB000006 |
| | | 13 | MNB000007 |
| | | 15 | MNB000008 |

**Glass inclusion**

| Element | Inclusion #1 | Inclusion #3 | Inclusion #4 | Inclusion #7 | Inclusion #10 | Inclusion #11 | Inclusion #13 | Inclusion #15 |
|---------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| SiO$_2$ | 45.70        | 47.46        | 49.19        | 46.98        | 47.71        | 48.13        | 46.98        | 47.38        |
| TiO$_2$ | 1.17         | 0.63         | 0.72         | 0.62         | 0.67         | 0.67         | 0.65         | 0.74         |
| Al$_2$O$_3$ | 17.27 | 15.56 | 17.07 | 14.75 | 16.31 | 15.63 | 16.35 | 15.53 |
| FeO* | 11.15 | 9.13 | 8.95 | 8.95 | 9.58 | 8.99 | 9.46 | 9.17 |
| FeO | 8.74 | 6.63 | 6.82 | 6.69 | 6.97 | 6.76 | 7.07 | 7.03 |
| Fe$_2$O$_3$ | 2.68 | 2.78 | 2.37 | 2.51 | 2.63 | 2.48 | 2.66 | 2.38 |
| MnO | 0.25 | 0.22 | 0.19 | 0.17 | 0.22 | 0.19 | 0.21 | 0.17 |
| MgO | 5.95 | 6.96 | 5.20 | 6.76 | 6.63 | 6.46 | 6.31 | 6.29 |
| CaO | 10.72 | 13.73 | 14.18 | 13.99 | 13.34 | 13.06 | 13.02 | 13.32 |
| Na$_2$O | 2.62 | 1.56 | 1.90 | 1.51 | 1.62 | 1.66 | 1.66 | 1.66 |
| K$_2$O | 0.51 | 0.22 | 0.31 | 0.23 | 0.23 | 0.42 | 0.28 | 0.36 |
| P$_2$O$_5$ | 0.20 | 0.06 | 0.07 | 0.05 | 0.05 | 0.12 | 0.06 | 0.08 |
| Total | 95.53 | 95.53 | 97.78 | 94.01 | 96.36 | 95.33 | 94.97 | 94.70 |
| H$_2$O | 3.48 | 2.82 | 1.48 | 4.8 | 3.68 | 3.9 | 3.8 | 3.35 |
| CO$_2$ | n.d. | 230 | n.d. | 961 | 284 | 551 | 368 | 498 |
| S | 1593 | 1306 | 1214 | 1370 | 1246 | 1410 | 1314 | 1350 |
| Cl | 1327 | 740 | 790 | 730 | 620 | 870 | 690 | 687 |
| Fe$^{3+}$/ΣFe | 0.216 | 0.274 | 0.238 | 0.252 | 0.247 | 0.248 | 0.253 | 0.233 |
| Equilibrium Fo$^\#^2$ | 0.802 | 0.862 | 0.819 | 0.857 | 0.845 | 0.850 | 0.841 | 0.842 |
### Electronic Appendix B con’t...

| Inclusion # | MNB000001 | MNB000002 | MNB000003 | MNB000004 | MNB000005 | MNB000006 | MNB000007 | MNB000008 |
|-------------|------------|------------|------------|------------|------------|------------|------------|------------|
| IGSN designation |            |            |            |            |            |            |            |            |
| Volcano Sample | Sarigan Sari15-04 |            |            |            |            |            |            |            |

| Olivine Host | SiO₂ | FeO | MnO | MgO | NiO | Total | Fo# |
|--------------|------|-----|-----|-----|-----|-------|-----|
|              | 39.16 | 17.31 | n.d. | 43.24 | 0.06 | 99.76 | 0.817 |
|              | 39.46 | 13.69 | 0.24 | 45.45 | 0.11 | 98.94 | 0.855 |
|              | 39.94 | 13.32 | 0.25 | 46.01 | 0.11 | 99.62 | 0.860 |
|              | 39.30 | 13.19 | 0.20 | 45.59 | 0.12 | 98.40 | 0.860 |
|              | 39.16 | 14.63 | 0.25 | 45.38 | 0.09 | 99.51 | 0.847 |
|              | 39.85 | 14.67 | 0.26 | 44.74 | 0.10 | 99.62 | 0.845 |
|              | 39.23 | 15.27 | 0.24 | 44.53 | 0.08 | 99.35 | 0.839 |
|              | 39.40 | 15.66 | n.d. | 44.42 | 0.10 | 99.58 | 0.835 |
| Volcano | Sarigan Sample |
|---------|----------------|
| Inclusion # | 1 | 3 | 4 | 7 | 10 | 11 | 13 | 15 |
| IGSN designation | MNB000001 | MNB000002 | MNB000003 | MNB000004 | MNB000005 | MNB000006 | MNB000007 | MNB000008 |

**Post-entrapment, normalized corrected glass**

| Olivine added (%) | 2.1 | 0.0 | 5.3 | 0.5 | 0.3 | 0.0 | 0.0 | 0.0 |
| SiO₂ | 45.88 | 48.14 | 48.97 | 47.36 | 47.57 | 48.37 | 47.45 | 48.19 |
| TiO₂ | 1.16 | 0.64 | 0.68 | 0.63 | 0.67 | 0.68 | 0.66 | 0.75 |
| Al₂O₃ | 17.03 | 15.78 | 16.30 | 14.81 | 16.22 | 15.71 | 16.51 | 15.80 |
| FeO* | 11.36 | 9.26 | 9.33 | 9.05 | 9.57 | 9.03 | 9.56 | 9.33 |
| FeO | 8.99 | 6.73 | 7.29 | 6.79 | 7.22 | 6.79 | 7.14 | 7.15 |
| Fe₂O₃ | 2.64 | 2.82 | 2.26 | 2.52 | 2.62 | 2.49 | 2.69 | 2.42 |
| MnO | 0.25 | 0.22 | 0.18 | 0.17 | 0.22 | 0.19 | 0.21 | 0.17 |
| MgO | 6.75 | 7.06 | 7.23 | 7.01 | 6.73 | 6.49 | 6.38 | 6.40 |
| CaO | 10.57 | 13.93 | 13.54 | 14.04 | 13.27 | 13.12 | 13.15 | 13.55 |
| Na₂O | 2.58 | 1.58 | 1.82 | 1.51 | 1.61 | 1.67 | 1.67 | 1.69 |
| K₂O | 0.51 | 0.22 | 0.29 | 0.23 | 0.23 | 0.42 | 0.28 | 0.36 |
| P₂O₅ | 0.19 | 0.06 | 0.06 | 0.05 | 0.05 | 0.12 | 0.06 | 0.08 |
| H₂O | 3.43 | 2.86 | 1.41 | 4.82 | 3.66 | 3.92 | 3.84 | 3.41 |
| CO₂ | n.d. | 234 | n.d. | 964 | 283 | 554 | 371 | 506 |
| S | 1571 | 1325 | 1158 | 1375 | 1239 | 1417 | 1327 | 1373 |
| Cl | 1308 | 751 | 754 | 733 | 617 | 874 | 697 | 699 |
| Fe⁷⁺/ΣFe | 0.209 | 0.274 | 0.218 | 0.250 | 0.246 | 0.248 | 0.253 | 0.233 |
| Volcano | Sarigan Sample | Sari15-04 |
|---------|----------------|-----------|
| Inclusion # | 17 | 18 | 19 | 21 | 22 | 23 | 24 | 25 |
| IGSN designation | MNB000009 | MNB000010 | MNB000011 | MNB000012 | MNB000013 | MNB000014 | MNB000015 | MNB000016 |
| Glass inclusion | | | | | | | | |
| SiO$_2$ | 46.99 | 47.83 | 47.26 | 48.05 | 47.48 | 47.46 | 47.22 | 47.01 |
| TiO$_2$ | 0.68 | 0.68 | 0.70 | 0.75 | 0.72 | 0.66 | 0.69 | 0.68 |
| Al$_2$O$_3$ | 16.25 | 14.90 | 15.84 | 15.83 | 15.69 | 15.46 | 16.02 | 16.17 |
| FeO$^*$ | 8.82 | 8.70 | 8.87 | 9.13 | 9.06 | 8.65 | 8.68 | 9.17 |
| FeO | 6.76 | 6.60 | 6.62 | 6.79 | 6.92 | 6.24 | 6.40 | 6.60 |
| Fe$_2$O$_3$ | 2.29 | 2.34 | 2.50 | 2.59 | 2.38 | 2.67 | 2.53 | 2.86 |
| MnO | 0.19 | 0.17 | 0.20 | 0.16 | 0.17 | 0.15 | 0.18 | 0.19 |
| MgO | 6.49 | 6.89 | 6.25 | 6.41 | 6.44 | 6.24 | 6.65 | 6.47 |
| CaO | 13.18 | 13.61 | 13.88 | 13.15 | 13.29 | 13.94 | 13.63 | 13.08 |
| Na$_2$O | 1.61 | 1.55 | 1.55 | 1.57 | 1.59 | 1.31 | 1.64 | 1.54 |
| K$_2$O | 0.26 | 0.26 | 0.27 | 0.35 | 0.36 | 0.23 | 0.27 | 0.28 |
| P$_2$O$_5$ | 0.06 | 0.07 | 0.07 | 0.14 | 0.09 | 0.08 | 0.07 | 0.06 |
| Total | 94.53 | 94.65 | 94.89 | 95.54 | 94.90 | 94.18 | 95.04 | 94.65 |
| H$_2$O | 2.82 | 3.16 | 3.32 | 2.58 | 2.97 | 2.67 | 3.87 | 3.21 |
| CO$_2$ | 65 | 59 | n.d. | 107 | 95 | 108 | 868 | 382 |
| S | 1177 | 1233 | 1193 | 1363 | 1360 | 1260 | 1243 | 1263 |
| Cl | 557 | 590 | 607 | 677 | 683 | 610 | 480 | 577 |
| Fe$^{3+}$/ΣFe | 0.234 | 0.242 | 0.254 | 0.256 | 0.237 | 0.278 | 0.263 | 0.281 |
| Equilibrium Fo$^2$ | 0.851 | 0.861 | 0.849 | 0.849 | 0.847 | 0.856 | 0.861 | 0.854 |
| Volcano | Sarigan | Sample | Sari15-04 | Inclusion # | 18 | 19 | 21 | 22 | 23 | 24 | 25 |
|---------|---------|--------|-----------|-------------|-----|-----|-----|-----|-----|-----|-----|
| IGSN designation | MNB000009 | MNB000010 | MNB000011 | MNB000012 | MNB000013 | MNB000014 | MNB000015 | MNB000016 |
| **Olivine Host** | | | | | | | | |
| SiO$_2$ | 40.08 | 39.99 | 39.98 | 39.72 | 39.72 | 39.99 | 40.20 | 39.61 |
| FeO | 14.30 | 13.07 | 13.39 | 14.43 | 15.01 | 13.35 | 12.90 | 14.09 |
| MnO | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| MgO | 45.67 | 46.47 | 46.40 | 45.28 | 45.01 | 46.19 | 47.04 | 45.48 |
| NiO | 0.10 | 0.12 | 0.12 | 0.11 | 0.10 | 0.11 | 0.12 | 0.11 |
| Total | 100.16 | 99.65 | 99.89 | 99.55 | 99.85 | 99.63 | 100.26 | 99.28 |
| Fo# | 0.851 | 0.864 | 0.861 | 0.848 | 0.842 | 0.860 | 0.867 | 0.852 |
### Electronic Appendix B: con't...

| Volcano     | Sarigan   | Sample  | Sari15-04 |
|-------------|-----------|---------|-----------|
| Inclusion # | 17    | 18      | 19        | 21 | 22 | 23 | 24 | 25 |
| IGSN designation | MNB000009 | MNB000010 | MNB000011 | MNB000012 | MNB000013 | MNB000014 | MNB000015 | MNB000016 |
| Post-entrapment, normalized corrected glass | | | | | | | | |
| Olivine added (%) | 0.0 | 0.5 | 2.0 | 0.0 | 0.0 | 0.7 | 1.1 | 0.0 |
| SiO$_2$ | 48.19 | 48.76 | 47.87 | 48.86 | 48.41 | 48.86 | 47.53 | 47.93 |
| TiO$_2$ | 0.70 | 0.69 | 0.70 | 0.77 | 0.73 | 0.68 | 0.68 | 0.69 |
| Al$_2$O$_3$ | 16.66 | 15.13 | 15.78 | 16.10 | 15.99 | 15.83 | 15.98 | 16.49 |
| FeO* | 9.04 | 8.90 | 9.12 | 9.28 | 9.24 | 8.92 | 8.80 | 9.35 |
| FeO | 6.93 | 6.76 | 6.88 | 6.91 | 7.05 | 6.49 | 6.53 | 6.73 |
| Fe$_2$O$_3$ | 2.35 | 2.38 | 2.49 | 2.64 | 2.43 | 2.74 | 2.52 | 2.91 |
| MnO | 0.19 | 0.17 | 0.19 | 0.16 | 0.18 | 0.15 | 0.18 | 0.19 |
| MgO | 6.65 | 7.23 | 7.13 | 6.52 | 6.56 | 6.71 | 7.14 | 6.60 |
| CaO | 13.51 | 13.82 | 13.83 | 13.38 | 13.55 | 14.27 | 13.60 | 13.34 |
| Na$_2$O | 1.65 | 1.57 | 1.54 | 1.59 | 1.62 | 1.34 | 1.63 | 1.57 |
| K$_2$O | 0.26 | 0.26 | 0.27 | 0.35 | 0.37 | 0.23 | 0.27 | 0.29 |
| P$_2$O$_5$ | 0.07 | 0.08 | 0.07 | 0.14 | 0.10 | 0.08 | 0.07 | 0.06 |
| H$_2$O | 2.89 | 3.21 | 3.31 | 2.62 | 3.03 | 2.73 | 3.86 | 3.27 |
| CO$_2$ | 67 | 60 | n.d. | 109 | 97 | 111 | 866 | 390 |
| S | 1206 | 1252 | 1189 | 1386 | 1387 | 1290 | 1240 | 1288 |
| Cl | 571 | 599 | 604 | 688 | 697 | 624 | 479 | 588 |
| Fe$^{3+}$/$\Sigma$Fe | 0.234 | 0.240 | 0.246 | 0.256 | 0.237 | 0.275 | 0.258 | 0.281 |
## Volcano Appendix B: continued...

| Volcano  | Sarigan   |
|----------|-----------|
| Sample   | Sari15-04 |
| Inclusion # | 27 | 28A | 28B | 29 | 30 | 31A | 32A | 32B |
| IGSN designation | MNB000017 | MNB000018 | MNB000019 | MNB000020 | MNB000021 | MNB000022 | MNB000023 | MNB000024 |
| SiO<sub>2</sub> | 47.09 | 46.34 | 46.79 | 47.48 | 47.22 | 46.68 | 47.73 | 47.89 |
| TiO<sub>2</sub> | 0.61 | 0.63 | 0.66 | 0.59 | 0.59 | 0.64 | 0.63 | 0.65 |
| Al<sub>2</sub>O<sub>3</sub> | 15.48 | 16.32 | 16.12 | 15.12 | 14.80 | 15.90 | 15.74 | 15.86 |
| FeO<sup>1</sup> | 8.90 | 9.64 | 9.63 | 8.72 | 8.91 | 8.86 | 8.67 | 8.67 |
| FeO | 6.90 | 7.39 | 7.41 | 6.55 | 6.85 | 6.63 | 6.55 | 6.59 |
| Fe<sub>2</sub>O<sub>3</sub> | 2.22 | 2.51 | 2.47 | 2.41 | 2.28 | 2.48 | 2.35 | 2.31 |
| MnO | 0.17 | 0.19 | 0.18 | 0.17 | 0.16 | 0.15 | 0.17 | 0.21 |
| MgO | 6.60 | 6.19 | 6.26 | 6.66 | 6.53 | 6.47 | 6.38 | 6.48 |
| CaO | 13.43 | 12.96 | 12.84 | 14.02 | 13.93 | 13.94 | 13.97 | 14.08 |
| Na<sub>2</sub>O | 1.72 | 1.81 | 1.57 | 1.74 | 1.74 | 1.60 | 1.64 | 1.67 |
| K<sub>2</sub>O | 0.26 | 0.27 | 0.26 | 0.26 | 0.24 | 0.28 | 0.26 | 0.24 |
| P<sub>2</sub>O<sub>5</sub> | 0.08 | 0.06 | 0.05 | 0.07 | 0.06 | 0.07 | 0.06 | 0.05 |
| Total | 94.34 | 94.40 | 94.36 | 94.82 | 94.17 | 94.59 | 95.24 | 95.80 |
| H<sub>2</sub>O | 4.08 | n.d. | n.d. | 4.2 | 4.35 | 3.85 | 3.92 | 3.55 |
| CO<sub>2</sub> | 243 | n.d. | n.d. | 731 | 401 | 633 | n.d. | n.d. |
| S | 1500 | 1410 | 1163 | 1487 | 1463 | 1490 | 1430 | 1457 |
| Cl | 663 | 720 | 603 | 843 | 670 | 707 | 640 | 860 |
| Fe<sup>3+</sup>/ΣFe | 0.224 | 0.234 | 0.231 | 0.249 | 0.230 | 0.252 | 0.244 | 0.240 |
| Equilibrium Fo<sup>2</sup> | 0.850 | 0.833 | 0.834 | 0.858 | 0.850 | 0.853 | 0.853 | 0.854 |
| Volcano Sample | Sarigan Sari15-04 |
|----------------|--------------------|
| Inclusion # | 27 28A 28B 29 30 31A 32A 32B |
| IGSN designation | MNB000017 MNB000018 MNB000019 MNB000020 MNB000021 MNB000022 MNB000023 MNB000024 |
| Olivine Host | SiO₂ FeO MnO MgO NiO Total Fo# |
|               | 39.67 39.36 39.36 39.75 39.46 39.91 37.07 37.07 | 13.45 15.25 15.25 13.08 13.23 13.24 13.15 13.15 |
|               | n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. | n.d. n.d. n.d. n.d. n.d. n.d. n.d. n.d. |
|               | 46.81 45.09 45.09 47.03 46.45 46.64 45.88 45.88 | 0.11 0.10 0.10 0.13 0.12 0.11 0.11 0.11 |
|               | 100.03 99.81 99.81 99.98 99.26 99.91 96.21 96.21 | 0.861 0.840 0.840 0.865 0.862 0.863 0.861 0.861 |
### Electronic Appendix B: con't...

| Volcano | Sample | Sarigan | Sari15-04 |
|---------|--------|---------|-----------|
| Inclusion # | 27 | 28A | 28B | 29 | 30 | 31A | 32A | 32B |
| IGSN designation | MNB000017 | MNB000018 | MNB000019 | MNB000020 | MNB000021 | MNB000022 | MNB000023 | MNB000024 |
| Post-entrapment, normalized corrected glass | | | | | | | | |
| Olivine added (%) | | | | | | | | |
| SiO₂ | 47.59 | 48.88 | 49.38 | 47.71 | 47.64 | 47.18 | 47.92 | 47.99 |
| TiO₂ | 0.60 | 0.65 | 0.69 | 0.59 | 0.58 | 0.64 | 0.62 | 0.65 |
| Al₂O₃ | 15.41 | 17.07 | 16.90 | 15.04 | 14.67 | 15.84 | 15.62 | 15.74 |
| FeO* | 9.10 | 10.25 | 10.27 | 8.83 | 9.12 | 9.06 | 8.79 | 8.76 |
| FeO | 7.12 | 7.89 | 7.91 | 6.67 | 7.08 | 6.84 | 6.69 | 6.70 |
| Fe₂O₃ | 2.21 | 2.62 | 2.62 | 2.40 | 2.26 | 2.47 | 2.33 | 2.29 |
| MnO | 0.17 | 0.20 | 0.19 | 0.17 | 0.16 | 0.15 | 0.17 | 0.20 |
| MgO | 7.40 | 6.94 | 6.98 | 7.18 | 7.43 | 7.22 | 6.97 | 6.98 |
| CaO | 13.37 | 13.55 | 13.45 | 13.94 | 13.81 | 13.88 | 13.86 | 13.97 |
| Na₂O | 1.71 | 1.89 | 1.65 | 1.73 | 1.72 | 1.59 | 1.62 | 1.66 |
| K₂O | 0.26 | 0.28 | 0.27 | 0.26 | 0.24 | 0.28 | 0.25 | 0.24 |
| P₂O₅ | 0.08 | 0.06 | 0.06 | 0.07 | 0.06 | 0.07 | 0.06 | 0.05 |
| H₂O | 4.06 | n.d. | n.d. | 4.18 | 4.31 | 3.83 | 3.89 | 3.52 |
| CO₂ | 242 | n.d. | n.d. | 727 | 398 | 630 | n.d. | n.d. |
| S | 1493 | 1475 | 1219 | 1479 | 1451 | 1484 | 1419 | 1445 |
| Cl | 660 | 753 | 632 | 839 | 664 | 704 | 635 | 853 |
| Fe³⁺/ΣFe | 0.218 | 0.230 | 0.230 | 0.244 | 0.223 | 0.245 | 0.239 | 0.235 |
| Volcano | Sarigan | Alamagan |
|---------|---------|----------|
| Sample  | Sari15-04 | Ala02 |
| Inclusion # | 33 | 34 | 35A | 35B | 36 | 1 | 2 | 3 |
| IGSN designation | MNB000025 | MNB000026 | MNB000027 | MNB000028 | MNB000030 | MNB000031 | MNB000032 | MNB000033 |
| Glass inclusion | | | | | | | | |
| SiO$_2$ | 47.53 | 46.12 | 46.82 | 46.65 | 47.63 | 45.90 | 48.99 | 49.60 |
| TiO$_2$ | 0.75 | 0.64 | 0.69 | 0.64 | 0.64 | 0.63 | 0.99 | 0.82 |
| Al$_2$O$_3$ | 16.61 | 15.93 | 15.61 | 15.48 | 16.19 | 17.70 | 15.86 | 17.10 |
| FeO$^{\text{eq}}$ | 9.36 | 8.74 | 9.03 | 8.96 | 9.38 | 8.78 | 10.55 | 8.37 |
| FeO | 7.53 | 6.90 | 7.10 | 6.94 | 7.25 | 6.51 | 8.48 | 6.33 |
| Fe$_2$O$_3$ | 2.03 | 2.05 | 2.15 | 2.24 | 2.37 | 2.51 | 2.31 | 2.26 |
| MnO | 0.18 | 0.15 | 0.17 | 0.14 | 0.17 | 0.16 | 0.16 | 0.20 |
| MgO | 5.87 | 6.58 | 6.53 | 6.48 | 6.28 | 6.91 | 5.00 | 5.60 |
| CaO | 11.49 | 13.88 | 13.68 | 13.96 | 12.53 | 12.82 | 8.51 | 11.08 |
| Na$_2$O | 2.13 | 1.60 | 1.66 | 1.62 | 1.69 | 1.36 | 2.60 | 2.08 |
| K$_2$O | 0.62 | 0.26 | 0.25 | 0.25 | 0.29 | 0.31 | 1.04 | 0.74 |
| P$_2$O$_5$ | 0.17 | 0.07 | 0.14 | 0.07 | 0.07 | 0.10 | 0.20 | 0.16 |
| Total | 94.70 | 93.97 | 94.60 | 94.25 | 94.87 | 94.65 | 93.88 | 95.75 |
| H$_2$O | 4.14 | 3.81 | 3.9 | n.d. | 3.75 | 3.96 | 3.01 | 3.87 |
| CO$_2$ | 1476 | 1104 | n.d. | n.d. | 261 | 207 | 177 | 452 |
| S | 1333 | 1607 | 1397 | 1457 | 1440 | 993 | 560 | 663 |
| Cl | 1187 | 710 | 667 | 663 | 703 | 643 | 890 | 763 |
| Fe$^{3+}$/$\Sigma$Fe | 0.195 | 0.211 | 0.214 | 0.225 | 0.227 | 0.258 | 0.197 | 0.243 |
| Equilibrium Fo$^{\#2}$ | 0.822 | 0.850 | 0.845 | 0.847 | 0.837 | 0.863 | 0.778 | 0.840 |
| Inclusion # | IGSN designation       | Sarigan Sample | Alamagan Sample |
|------------|------------------------|----------------|-----------------|
|            |                        | Sari15-04      | Ala02           |
| 33         | MNB000025              |                |                 |
| 34         | MNB000026              |                |                 |
| 35A        | MNB000027              |                |                 |
| 35B        | MNB000028              |                |                 |
| 36         | MNB000030              |                |                 |
| 1          | MNB000031              |                |                 |
| 2          | MNB000032              |                |                 |
| 3          | MNB000033              |                |                 |

| Olivine Host |                   |                |
|--------------|-------------------|----------------|
| SiO₂         | 39.16             | 39.97          |
|              | 39.03             | 39.03          |
|              | 39.33             | 39.87          |
|              | 39.87             | 38.60          |
|              | 39.77             |                |
| FeO          | 16.96             | 13.57          |
|              | 12.60             | 12.60          |
|              | 15.37             | 14.35          |
|              | 14.35             | 21.68          |
|              | 15.89             |                |
| MnO          | n.d.              | n.d.           |
|              | n.d.              | n.d.           |
|              | n.d.              | n.d.           |
|              | n.d.              | n.d.           |
| MgO          | 43.94             | 46.48          |
|              | 46.30             | 46.30          |
|              | 46.30             | 43.88          |
|              | 45.47             | 39.53          |
|              | 44.71             |                |
| NiO          | 0.09              | 0.10           |
|              | 0.12              | 0.12           |
|              | 0.09              | 0.10           |
|              | 0.10              | 0.06           |
|              | 0.09              |                |
| Total        | 100.15            | 100.13         |
|              | 98.04             | 98.04          |
|              | 98.68             | 99.79          |
|              | 99.87             | 100.45         |
| Fo#          | 0.822             | 0.859          |
|              | 0.868             | 0.868          |
|              | 0.836             | 0.850          |
|              | 0.765             | 0.834          |
### Electronic Appendix B: con’t...

| Volcano | Sample | Sarigan | Alamagan |
|---------|--------|---------|----------|
| Inclusion # | 33 | 34 | 35A | 35B | 36 | 1 | 2 | 3 |
| IGSN designation | MNB000025 | MNB000026 | MNB000027 | MNB000028 | MNB000030 | MNB000031 | MNB000032 | MNB000033 |
| Post-entrapment, normalized corrected glass | | | | | | | | |
| Olivine added (%) | 0.0 | 1.5 | 2.0 | 2.5 | 0.0 | 0.0 | 0.0 | 0.0 |
| SiO₂ | 47.89 | 46.94 | 46.55 | 46.41 | 48.18 | 46.45 | 50.47 | 49.68 |
| TiO₂ | 0.75 | 0.65 | 0.66 | 0.62 | 0.65 | 0.64 | 1.02 | 0.82 |
| Al₂O₃ | 16.74 | 16.00 | 14.98 | 14.91 | 16.37 | 17.92 | 16.34 | 17.13 |
| FeO* | 9.43 | 8.92 | 9.22 | 9.13 | 9.48 | 8.88 | 10.87 | 8.38 |
| FeO | 7.59 | 7.14 | 7.36 | 7.19 | 7.33 | 6.59 | 8.73 | 6.34 |
| Fe₂O₃ | 2.04 | 2.06 | 2.07 | 2.16 | 2.39 | 2.54 | 2.38 | 2.27 |
| MnO | 0.18 | 0.15 | 0.16 | 0.14 | 0.18 | 0.16 | 0.16 | 0.20 |
| MgO | 5.92 | 7.30 | 8.13 | 7.93 | 6.35 | 6.99 | 5.16 | 5.61 |
| CaO | 11.58 | 13.94 | 13.13 | 13.45 | 12.68 | 12.97 | 8.76 | 11.10 |
| Na₂O | 2.14 | 1.61 | 1.59 | 1.56 | 1.71 | 1.38 | 2.67 | 2.09 |
| K₂O | 0.63 | 0.26 | 0.24 | 0.25 | 0.29 | 0.31 | 1.07 | 0.74 |
| P₂O₅ | 0.17 | 0.07 | 0.13 | 0.07 | 0.07 | 0.10 | 0.20 | 0.16 |
| H₂O | 4.17 | 3.83 | 3.74 | n.d. | 3.79 | 4.01 | 3.10 | 3.88 |
| CO₂ | 1487 | 1109 | n.d. | n.d. | 264 | 299 | 182 | 453 |
| S | 1344 | 1614 | 1340 | 1403 | 1457 | 1005 | 577 | 664 |
| Cl | 1196 | 715 | 640 | 639 | 711 | 651 | 917 | 765 |
| Fe³⁺/ΣFe | 0.195 | 0.206 | 0.202 | 0.213 | 0.227 | 0.258 | 0.197 | 0.243 |
| Volcano | Alamagan | Sample  | Ala02 |
|---------|----------|---------|-------|
| Inclusion # | 4 | 5 | 6 | 7 | 8 | 9 | 11 | 12 |
| IGSN designation | MNB000034 | MNB000035 | MNB000036 | MNB000037 | MNB000038 | MNB000039 | MNB000040 | MNB000041 |
| Glass inclusion | | | | | | | | |
| SiO₂ | 48.62 | 45.22 | 47.92 | 47.19 | 45.55 | 45.82 | 45.72 | 45.91 |
| TiO₂ | 0.80 | 0.54 | 0.74 | 0.64 | 0.53 | 0.55 | 0.61 | 0.56 |
| Al₂O₃ | 17.59 | 16.74 | 16.52 | 17.34 | 17.89 | 18.03 | 18.63 | 16.80 |
| FeO*₁ | 8.58 | 8.36 | 11.02 | 8.61 | 8.77 | 9.07 | 8.80 | 8.02 |
| FeO | 6.49 | 6.16 | 8.69 | 6.51 | 6.62 | 6.99 | 6.80 | 6.05 |
| Fe₂O₃ | 2.33 | 2.44 | 2.59 | 2.34 | 2.39 | 2.32 | 2.23 | 2.19 |
| MnO | 0.18 | 0.18 | 0.22 | 0.14 | 0.18 | 0.18 | 0.21 | 0.16 |
| MgO | 6.57 | 6.53 | 5.98 | 6.54 | 6.82 | 6.88 | 5.59 | 6.11 |
| CaO | 11.65 | 14.11 | 9.87 | 11.57 | 12.79 | 12.48 | 13.10 | 14.23 |
| Na₂O | 1.59 | 1.54 | 2.52 | 1.97 | 1.68 | 1.63 | 1.63 | 1.50 |
| K₂O | 0.47 | 0.43 | 0.56 | 0.47 | 0.38 | 0.24 | 0.32 | 0.42 |
| P₂O₅ | 0.11 | 0.11 | 0.13 | 0.11 | 0.09 | 0.06 | 0.09 | 0.12 |
| Total | 96.18 | 93.77 | 95.48 | 94.56 | 94.67 | 94.93 | 94.71 | 93.83 |
| H₂O | 3.91 | 4.11 | n.d. | 3.40 | 3.59 | 3.28 | 3.48 | 4.17 |
| CO₂ | 364 | 793 | n.d. | 334 | 291 | 540 | 988 | 720 |
| S | 1088 | 1367 | 990 | 1147 | 1207 | 927 | 1280 | 1320 |
| Cl | 751 | 817 | 870 | 877 | 750 | 557 | 843 | 833 |
| Fe³⁺/ΣFe | 0.244 | 0.263 | 0.211 | 0.244 | 0.245 | 0.230 | 0.228 | 0.246 |
| Equilibrium Fo#² | 0.858 | 0.863 | 0.804 | 0.856 | 0.860 | 0.854 | 0.830 | 0.857 |
### Electronic Appendix B: con’t...

| Inclusion # | 4     | 5     | 6     | 7     | 8     | 9     | 11    | 12    |
|-------------|-------|-------|-------|-------|-------|-------|-------|-------|
| IGSN designation | MNB000034 | MNB000035 | MNB000036 | MNB000037 | MNB000038 | MNB000039 | MNB000040 | MNB000041 |
| **Volcano** | Alamagan | Alamagan | Alamagan | Alamagan | Alamagan | Alamagan | Alamagan | Alamagan |
| **Sample** | Ala02 | Ala02 | Ala02 | Ala02 | Ala02 | Ala02 | Ala02 | Ala02 |
| **Olivine Host** | | | | | | | | |
| **SiO₂** | 39.83 | 39.66 | 38.35 | 39.33 | 39.57 | 39.65 | 39.61 | 40.05 |
| **FeO** | 14.82 | 12.74 | 21.31 | 15.14 | 14.28 | 15.25 | 15.16 | 12.58 |
| **MnO** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| **MgO** | 45.02 | 47.45 | 40.49 | 45.31 | 45.79 | 45.95 | 45.66 | 47.37 |
| **NiO** | 0.11  | 0.12  | 0.05  | 0.10  | 0.11  | 0.12  | 0.09  | 0.13  |
| **Total** | 99.77 | 99.95 | 100.21 | 99.87 | 99.75 | 100.97 | 100.53 | 100.12 |
| **Fo#** | 0.844 | 0.869 | 0.772 | 0.842 | 0.851 | 0.843 | 0.843 | 0.870 |
### Electronic Appendix B: con’t...

| Volcano Sample | Alamagan Ala02 |
|----------------|----------------|
| Inclusion #    | 4  | 5  | 6  | 7  | 8  | 9  | 11 | 12 |
| IGSN designation | MNB000034 | MNB000035 | MNB000036 | MNB000037 | MNB000038 | MNB000039 | MNB000040 | MNB000041 |
| Post-entrapment, normalized corrected glass | | | | | | | | |
| Olivine added (%) | 0.0 | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1.8 | 2.2 |
| SiO₂ | 48.46 | 45.99 | 50.09 | 48.05 | 46.25 | 46.54 | 46.28 | 46.55 |
| TiO₂ | 0.80 | 0.55 | 0.78 | 0.65 | 0.54 | 0.56 | 0.61 | 0.56 |
| Al₂O₃ | 17.54 | 16.88 | 17.26 | 17.65 | 18.16 | 18.31 | 18.57 | 16.72 |
| FeO* | 8.56 | 8.56 | 11.51 | 8.77 | 8.91 | 9.21 | 9.05 | 8.27 |
| FeO | 6.47 | 6.34 | 9.08 | 6.63 | 6.72 | 7.10 | 7.05 | 6.31 |
| Fe₂O₃ | 2.32 | 2.46 | 2.71 | 2.38 | 2.43 | 2.35 | 2.22 | 2.18 |
| MnO | 0.18 | 0.18 | 0.23 | 0.15 | 0.18 | 0.18 | 0.21 | 0.15 |
| MgO | 6.55 | 7.06 | 6.25 | 6.66 | 6.92 | 6.99 | 6.38 | 7.10 |
| CaO | 11.62 | 14.22 | 10.32 | 11.78 | 12.98 | 12.68 | 13.06 | 14.16 |
| Na₂O | 1.59 | 1.55 | 2.64 | 2.01 | 1.70 | 1.66 | 1.63 | 1.49 |
| K₂O | 0.47 | 0.44 | 0.58 | 0.48 | 0.38 | 0.24 | 0.32 | 0.42 |
| P₂O₅ | 0.11 | 0.11 | 0.14 | 0.11 | 0.09 | 0.06 | 0.09 | 0.12 |
| H₂O | 3.90 | 4.14 | n.d. | 3.46 | 3.64 | 3.33 | 3.47 | 4.15 |
| CO₂ | 363 | 808 | n.d. | 340 | 296 | 549 | 1002 | 732 |
| S | 1005 | 1378 | 1035 | 1168 | 1225 | 941 | 1276 | 1313 |
| Cl | 749 | 823 | 909 | 893 | 761 | 566 | 840 | 829 |
| Fe³⁺/ΣFe | 0.244 | 0.259 | 0.211 | 0.244 | 0.245 | 0.230 | 0.221 | 0.237 |
### Electronic Appendix B: con’t...

| Volcano | Alamagan | Guguan |
|---------|----------|--------|
| Sample  | Ala02    | Gug23-02 |
| Inclusion # | 15  | 16A | 1 | 2 | 8 | 1 | 3 | 4 |
| IGSN designation | MNB000042 | MNB000043 | MNB000044 | MNB000045 | MNB000046 | MNB000047 | MNB000048 | MNB000049 |
| Glass inclusion | | | | | | | | |
| SiO$_2$ | 46.76 | 43.19 | 45.41 | 46.08 | 53.93 | 46.84 | 53.58 | 53.21 |
| TiO$_2$ | 0.62 | 0.68 | 0.66 | 0.68 | 1.08 | 0.80 | 1.12 | 1.09 |
| Al$_2$O$_3$ | 14.07 | 18.75 | 19.58 | 18.85 | 15.36 | 17.57 | 15.84 | 17.94 |
| FeO$^*$ | 8.33 | 9.19 | 7.26 | 7.48 | 10.55 | 10.33 | 8.63 | 8.68 |
| FeO | 6.25 | 7.01 | 5.72 | 5.48 | 8.36 | 7.81 | 5.87 | 6.59 |
| Fe$_2$O$_3$ | 2.31 | 2.43 | 1.71 | 2.22 | 2.43 | 2.81 | 3.07 | 2.31 |
| MnO | 0.17 | 0.21 | 0.17 | 0.17 | 0.21 | 0.18 | 0.21 | 0.19 |
| MgO | 6.68 | 6.64 | 6.49 | 6.97 | 3.96 | 6.32 | 5.38 | 4.28 |
| CaO | 14.39 | 13.04 | 14.58 | 13.97 | 8.67 | 11.56 | 8.72 | 10.52 |
| Na$_2$O | 1.53 | 1.43 | 1.73 | 1.61 | 2.61 | 1.80 | 2.90 | 3.15 |
| K$_2$O | 0.48 | 0.37 | 0.47 | 0.47 | 1.56 | 0.23 | 0.58 | 0.59 |
| P$_2$O$_5$ | 0.12 | 0.11 | 0.11 | 0.11 | 0.25 | 0.07 | 0.10 | 0.16 |
| Total | 93.15 | 93.62 | 96.45 | 96.39 | 98.17 | 95.70 | 97.06 | 99.81 |
| H$_2$O | 4.28 | 4.24 | 2.37 | 3.38 | 3.91 | 3.42 | n.d. | n.d. |
| CO$_2$ | 513 | 981 | 671 | n.d. | n.d. | n.d. | n.d. | n.d. |
| S | 1497 | 1517 | 1133 | 1157 | 120 | 863 | 280 | 220 |
| Cl | 997 | 820 | 793 | 780 | 1370 | 707 | 1203 | 1337 |
| Fe$^{3+}$/ΣFe | 0.249 | 0.238 | 0.212 | 0.267 | 0.208 | 0.245 | 0.320 | 0.240 |
| Equilibrium Fo$^#$ | 0.864 | 0.849 | 0.871 | 0.883 | 0.738 | 0.828 | 0.845 | 0.794 |
### Electronic Appendix B: con’t…

| Volcano | Alamagan | Guguan |
|---------|----------|--------|
| Sample  | Ala02    | Gug23-02 |
| Inclusion # | 15 | 16A | 1 | 2 | 8 | 1 | 3 | 4 |
| IGSN designation | MNB000042 | MNB000043 | MNB000044 | MNB000045 | MNB000046 | MNB000047 | MNB000048 | MNB000049 |
| **Olivine Host** | | | | | | | | |
| **SiO$_2$** | 39.88 | 39.50 | 39.89 | 39.85 | 38.20 | 39.11 | 38.94 | 39.04 |
| **FeO** | 12.47 | 14.69 | 12.44 | 13.06 | 23.90 | 18.51 | 19.83 | 19.62 |
| **MnO** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| **MgO** | 47.57 | 45.49 | 47.00 | 46.96 | 37.57 | 42.47 | 41.34 | 41.64 |
| **NiO** | 0.13 | 0.10 | 0.11 | 0.12 | 0.05 | 0.05 | 0.05 | 0.04 |
| **Total** | 100.06 | 99.78 | 99.44 | 99.99 | 99.72 | 100.14 | 100.17 | 100.34 |
| **Fo#** | 0.872 | 0.847 | 0.871 | 0.865 | 0.737 | 0.804 | 0.788 | 0.791 |
### Electronic Appendix B: con't...

| Volcano | Alamagan | Guguan |
|---------|----------|--------|
| Sample  | Ala02 | Ala03 | Ala02 | Ala03 | Gug23-02 |
| Inclusion # | 15 | 16A | 1 | 2 | 8 |
| IGSN designation | MNB000042 | MNB000043 | MNB000044 | MNB000045 | MNB000046 | MNB000047 | MNB000048 | MNB000049 |
| **Post-entrapment, normalized corrected glass** | | | | | | | | |
| Olivine added (%)<sup>3</sup> | 1.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| SiO<sub>2</sub> | 47.73 | 43.97 | 45.82 | 46.10 | 52.75 | 47.18 | 55.12 | 53.23 |
| TiO<sub>2</sub> | 0.63 | 0.70 | 0.66 | 0.68 | 1.06 | 0.80 | 1.15 | 1.09 |
| Al<sub>2</sub>O<sub>3</sub> | 14.20 | 19.09 | 19.75 | 18.86 | 15.02 | 17.70 | 16.30 | 17.95 |
| FeO* | 8.58 | 9.36 | 7.32 | 7.48 | 10.32 | 10.41 | 8.87 | 8.68 |
| FeO | 6.48 | 7.13 | 5.77 | 5.48 | 8.17 | 7.86 | 6.03 | 6.60 |
| Fe<sub>2</sub>O<sub>3</sub> | 2.33 | 2.47 | 1.72 | 2.22 | 2.38 | 2.83 | 3.16 | 2.32 |
| MnO | 0.17 | 0.22 | 0.18 | 0.17 | 0.21 | 0.18 | 0.22 | 0.19 |
| MgO | 7.40 | 6.76 | 6.55 | 6.98 | 3.87 | 6.37 | 5.54 | 4.28 |
| CaO | 14.51 | 13.28 | 14.71 | 13.98 | 8.48 | 11.65 | 8.97 | 10.52 |
| Na<sub>2</sub>O | 1.54 | 1.46 | 1.74 | 1.61 | 2.55 | 1.81 | 2.99 | 3.15 |
| K<sub>2</sub>O | 0.48 | 0.37 | 0.47 | 0.47 | 1.52 | 0.23 | 0.59 | 0.59 |
| P<sub>2</sub>O<sub>5</sub> | 0.12 | 0.11 | 0.11 | 0.11 | 0.24 | 0.07 | 0.10 | 0.16 |
| H<sub>2</sub>O | 4.32 | 4.32 | 2.39 | 3.38 | 3.82 | 3.44 | n.d. | n.d. |
| CO<sub>2</sub> | 525 | 999 | 677 | n.d. | n.d. | n.d. | n.d. | n.d. |
| S | 1510 | 1544 | 1144 | 1157 | 117 | 870 | 288 | 220 |
| Cl | 1005 | 835 | 801 | 780 | 1340 | 712 | 1238 | 1337 |
| Fe<sup>3+</sup>/ΣFe | 0.244 | 0.238 | 0.212 | 0.267 | 0.208 | 0.245 | 0.320 | 0.240 |
### Volcano Appendix B: con’t...

| Volcano | Guguan | Pagan | Agrigan |
|---------|--------|-------|---------|
| Sample  | Gug11  | Paga8 | Agr07   |
| Inclusion # | 2 | 4 | 5 | 6 | 8 | 2 | 1 | 4 |
| IGSN designation | MNB000050 | MNB000051 | MNB000052 | MNB000053 | MNB000054 | MNB000055 | MNB000056 | MNB000057 |
| Glass inclusion |
| SiO₂ | 48.22 | 50.81 | 49.37 | 51.86 | 52.49 | 50.71 | 48.75 | 45.38 |
| TiO₂ | 0.58 | 0.75 | 0.76 | 0.97 | 0.91 | 0.89 | 0.97 | 0.65 |
| Al₂O₃ | 16.78 | 17.05 | 16.49 | 14.62 | 15.69 | 15.77 | 16.87 | 17.24 |
| FeO*¹ | 8.62 | 8.89 | 11.19 | 12.74 | 9.68 | 11.31 | 8.22 | 10.18 |
| FeO | 6.28 | 6.60 | 8.84 | 9.89 | 7.51 | 8.79 | 6.13 | 7.77 |
| Fe₂O₃ | 2.59 | 2.54 | 2.61 | 3.17 | 2.42 | 2.79 | 2.32 | 2.68 |
| MnO | 0.16 | 0.18 | 0.21 | 0.28 | 0.23 | 0.29 | 0.15 | 0.23 |
| MgO | 5.06 | 3.96 | 4.02 | 4.24 | 4.73 | 5.44 | 3.30 | 5.53 |
| CaO | 13.82 | 9.55 | 11.04 | 8.14 | 7.59 | 10.64 | 11.88 | 12.30 |
| Na₂O | 1.80 | 3.06 | 2.53 | 3.08 | 3.12 | 2.25 | 2.47 | 1.75 |
| K₂O | 0.30 | 1.01 | 0.43 | 0.73 | 0.95 | 0.65 | 0.68 | 0.35 |
| P₂O₅ | 0.07 | 0.21 | 0.10 | 0.18 | 0.19 | 0.14 | 0.48 | 0.10 |
| Total | 95.41 | 95.48 | 96.15 | 96.81 | 95.59 | 98.09 | 93.75 | 93.72 |
| H₂O | 3.93 | 4.23 | n.d. | n.d. | n.d. | 1.81 | n.d. | n.d. |
| CO₂ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 258 |
| S | 2387 | 937 | 1770 | 483 | 615 | 387 | 1116 | 1079 |
| Cl | 1200 | 1200 | 877 | 1220 | 1695 | 497 | n.d. | n.d. |
| Fe³⁺/ΣFe | 0.271 | 0.257 | 0.210 | 0.224 | 0.225 | 0.222 | 0.254 | 0.237 |
| Equilibrium Fo#² | 0.827 | 0.781 | 0.730 | 0.718 | 0.789 | 0.786 | 0.762 | 0.809 |
## Electronic Appendix B: con’t...

| Volcano | Sample | Inclusion # | IGSN designation | SiO$_2$   | FeO     | MnO | MgO   | NiO   | Total   | Fo# |
|---------|--------|-------------|------------------|----------|---------|-----|-------|-------|---------|-----|
|         | Guguan | Gug11       | MNB000050, MNB000051, MNB000052, MNB000053, MNB000054 | 39.59 | 15.34 | n.d. | 45.27 | 0.08 | 100.28 | 0.840 |
|         | Pagan  | Paga8       | MNB000055, MNB000056, MNB000057  | 38.61 | 21.02 | n.d. | 40.58 | 0.03 | 100.25 | 0.775 |
|         | Agrigan| Agr07       |                   | 38.49 | 22.45 | n.d. | 39.56 | 0.05 | 100.55 | 0.759 |
|         |        |             |                   | 37.24 | 28.89 | n.d. | 33.96 | 0.03 | 100.11 | 0.677 |
|         |        |             |                   | 38.10 | 22.38 | n.d. | 39.39 | 0.05 | 99.92  | 0.758 |
|         |        |             |                   | 38.21 | 19.82 | n.d. | 40.69 | 0.08 | 98.79  | 0.785 |
|         |        |             |                   | 39.22 | 17.40 | n.d. | 42.95 | 0.04 | 99.93  | 0.815 |
|         |        |             |                   | 38.93 | 18.65 | n.d. | 42.43 | 0.03 | 100.40 | 0.802 |

**Olivine Host**
**Electronic Appendix B: con't...**

| Volcano | Sample | Guguan | Pagan | Agrigan |
|---------|--------|--------|-------|---------|
| Inclusion # | Gug11 | 2 | 4 | 5 | 6 | 8 | 2 | 1 | 4 |
| IGSN designation | MNB000050 | MNB000051 | MNB000052 | MNB000053 | MNB000054 | MNB000055 | MNB000056 | MNB000057 |
| Post-entrapment, normalized corrected glass | | | | | | | | |
| Olivine added (%) | 1.6 | 0.0 | 2.6 | 0.0 | 0.0 | 0.0 | 0.0 | 4.6 | 0.0 |
| SiO$_2$ | 48.23 | 50.84 | 50.87 | 53.48 | 54.78 | 50.71 | 51.33 | 45.45 |
| TiO$_2$ | 0.58 | 0.75 | 0.77 | 1.00 | 0.95 | 0.89 | 0.98 | 0.65 |
| Al$_2$O$_3$ | 16.57 | 17.07 | 16.66 | 15.07 | 16.37 | 15.77 | 17.13 | 17.27 |
| FeO* | 8.76 | 8.90 | 11.91 | 13.13 | 10.11 | 11.31 | 9.26 | 10.19 |
| FeO | 6.45 | 6.61 | 9.54 | 10.20 | 7.84 | 8.79 | 7.14 | 7.78 |
| Fe$_2$O$_3$ | 2.56 | 2.55 | 2.64 | 3.26 | 2.52 | 2.79 | 2.35 | 2.68 |
| MnO | 0.15 | 0.18 | 0.22 | 0.28 | 0.24 | 0.29 | 0.15 | 0.23 |
| MgO | 5.70 | 3.97 | 5.07 | 4.37 | 4.94 | 5.44 | 5.29 | 5.54 |
| CaO | 13.64 | 9.56 | 11.15 | 8.39 | 7.92 | 10.64 | 12.06 | 12.32 |
| Na$_2$O | 1.77 | 3.07 | 2.56 | 3.17 | 3.26 | 2.25 | 2.51 | 1.75 |
| K$_2$O | 0.30 | 1.01 | 0.43 | 0.75 | 1.00 | 0.65 | 0.69 | 0.35 |
| P$_2$O$_5$ | 0.07 | 0.21 | 0.10 | 0.18 | 0.20 | 0.14 | 0.49 | 0.10 |
| H$_2$O | 3.88 | 4.23 | n.d. | n.d. | n.d. | 1.81 | n.d. | 6.02 |
| CO$_2$ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 189 |
| S | 2356 | 937 | 1788 | 498 | 642 | 387 | 1133 | 1080 |
| Cl | 1185 | 1201 | 885 | 1258 | 1769 | 497 | n.d. | n.d. |
| Fe$^{3+}$/ΣFe | 0.263 | 0.257 | 0.199 | 0.224 | 0.225 | 0.222 | 0.229 | 0.237 |
### Electronic Appendix B: con’t...

| Volcano | Agrigan | Agr07 |
|---------|---------|-------|
| Inclusion # | | |
| IGSN designation | 5 | 6 | 7 | 9 | 10 | 11 | 12A | 12B | 12C |
| MNB000058 | MNB000059 | MNB000060 | MNB000061 | MNB000062 | MNB000063 | MNB000064 | MNB000065 |
| **Glass inclusion** | | | | | | | | | |
| SiO$_2$ | 46.31 | 45.54 | 48.67 | 47.77 | 46.27 | 45.82 | 53.50 | 53.79 |
| TiO$_2$ | 0.70 | 0.67 | 0.89 | 0.76 | 0.69 | 0.69 | 0.76 | 0.82 |
| Al$_2$O$_3$ | 18.94 | 17.95 | 17.88 | 17.14 | 17.53 | 18.67 | 16.55 | 16.63 |
| FeO$^1$ | 9.61 | 9.63 | 7.90 | 9.06 | 9.97 | 8.86 | 6.62 | 6.34 |
| FeO | 7.29 | 7.33 | 5.88 | 6.90 | 7.63 | 6.75 | 5.03 | 4.83 |
| Fe$_2$O$_3$ | 2.58 | 2.55 | 2.25 | 2.40 | 2.60 | 2.35 | 1.77 | 1.69 |
| MnO | 0.23 | 0.21 | 0.17 | 0.18 | 0.20 | 0.18 | 0.18 | 0.15 |
| MgO | 4.38 | 4.80 | 2.66 | 4.77 | 4.27 | 3.54 | 2.89 | 2.95 |
| CaO | 12.06 | 12.46 | 12.40 | 11.97 | 12.44 | 12.95 | 10.31 | 10.13 |
| Na$_2$O | 2.47 | 1.97 | 2.55 | 2.19 | 2.08 | 2.07 | 3.04 | 2.80 |
| K$_2$O | 0.56 | 0.41 | 0.64 | 0.56 | 0.46 | 0.42 | 0.86 | 0.91 |
| P$_2$O$_5$ | 0.13 | 0.12 | 0.18 | 0.13 | 0.12 | 0.14 | 0.23 | 0.20 |
| Total | 95.39 | 93.76 | 93.95 | 94.53 | 94.03 | 93.33 | 94.95 | 94.73 |
| H$_2$O | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| CO$_2$ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| S | 1307 | 1280 | 920 | 823 | 1163 | 1480 | 827 | 907 |
| Cl | 893 | 813 | 1107 | 957 | 883 | 913 | 1560 | 1580 |
| Fe$^{3+}$/ΣFe | 0.242 | 0.239 | 0.256 | 0.238 | 0.235 | 0.239 | 0.241 | 0.239 |
| Equilibrium Fo#2 | 0.781 | 0.795 | 0.729 | 0.804 | 0.769 | 0.757 | 0.774 | 0.784 |
### Electronic Appendix B: con’t...

| Volcano       | Agrigan |
|---------------|---------|
| Sample        | Agr07   |
| Inclusion #   |         |
| IGSN designation |       |
|               | 5       | 6       | 7       | 9       | 10      | 11      | 12A     | 12B     |
|               | MNB000058 | MNB000059 | MNB000060 | MNB000061 | MNB000062 | MNB000063 | MNB000064 | MNB000065 |
| **Olivine Host** |        |
| SiO$_2$       | 38.93   | 39.15   | 39.22   | 38.84   | 38.71   | 39.06   | 39.37   | 39.37   |
| FeO           | 18.15   | 18.94   | 18.46   | 18.59   | 19.26   | 17.29   | 16.79   | 16.79   |
| MnO           | n.d.    | n.d.    | n.d.    | n.d.    | n.d.    | n.d.    | n.d.    | n.d.    |
| MgO           | 42.89   | 42.41   | 42.56   | 42.45   | 42.16   | 43.13   | 44.03   | 44.03   |
| NiO           | 0.04    | 0.03    | 0.03    | 0.03    | 0.03    | 0.04    | 0.03    | 0.03    |
| Total         | 100.27  | 100.79  | 100.54  | 100.19  | 100.42  | 99.80   | 100.46  | 100.46  |
| Fo#           | 0.808   | 0.800   | 0.804   | 0.803   | 0.796   | 0.816   | 0.824   | 0.824   |
**Electronic Appendix B: con’t…**

| Volcano Sample | Agrigan | Agr07 |
|----------------|---------|-------|
| Inclusion #    | 5       | 6     | 7     | 9     | 10    | 11    | 12A   | 12B   |
| IGSN designation | MNB000058 | MNB000059 | MNB000060 | MNB000061 | MNB000062 | MNB000063 | MNB000064 | MNB000065 |

**Post-entrapment, normalized corrected glass**

|                | 5   | 6   | 7   | 9   | 10  | 11  | 12A | 12B |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| SiO₂           | 48.17 | 48.46 | 50.98 | 48.20 | 48.82 | 48.41 | 55.53 | 56.08 |
| TiO₂           | 0.72  | 0.71  | 0.90  | 0.76  | 0.72  | 0.69  | 0.77  | 0.84 |
| Al₂O₃          | 19.25 | 19.10 | 17.94 | 17.29 | 18.09 | 18.83 | 16.71 | 16.96 |
| FeO*           | 10.31 | 10.25 | 9.10  | 9.14  | 10.85 | 10.05 | 7.42  | 7.05 |
| FeO            | 7.95  | 7.80  | 7.07  | 6.96  | 8.44  | 7.92  | 5.81  | 5.50 |
| Fe₂O₃          | 2.62  | 2.72  | 2.25  | 2.42  | 2.68  | 2.37  | 1.79  | 1.72 |
| MnO            | 0.23  | 0.22  | 0.17  | 0.18  | 0.20  | 0.18  | 0.18  | 0.15 |
| MgO            | 5.64  | 5.11  | 4.88  | 4.82  | 5.54  | 5.90  | 4.57  | 4.34 |
| CaO            | 12.25 | 13.26 | 12.44 | 12.08 | 12.83 | 13.06 | 10.41 | 10.33 |
| Na₂O           | 2.51  | 2.10  | 2.56  | 2.21  | 2.14  | 2.09  | 3.07  | 2.85 |
| K₂O            | 0.57  | 0.44  | 0.65  | 0.56  | 0.48  | 0.42  | 0.86  | 0.93 |
| P₂O₅           | 0.14  | 0.12  | 0.18  | 0.13  | 0.12  | 0.14  | 0.23  | 0.20 |
| H₂O            | n.d.  | n.d.  | n.d.  | 4.40  | n.d.  | n.d.  | n.d.  | n.d. |
| CO₂            | n.d.  | n.d.  | n.d.  | 371   | n.d.  | n.d.  | n.d.  | n.d. |
| S               | 1328  | 1362  | 923   | 831   | 1200  | 1492  | 834   | 924  |
| Cl              | 908   | 866   | 1111  | 965   | 911   | 921   | 1574  | 1611 |
| Fe³⁺/ΣFe       | 0.229 | 0.239 | 0.223 | 0.238 | 0.222 | 0.212 | 0.217 | 0.219 |
**Electronic Appendix B: con’t…**

| Volcano Sample | Agrigan | Agr07 | Agr05 | Agr04 |
|----------------|---------|-------|-------|-------|
| Inclusion # | 12C | 13 | 14 | 15A | 15B | 1 | 4 | 3 |
| IGSN designation | MNB000066 | MNB000067 | MNB000068 | MNB000069 | MNB000070 | MNB000071 | MNB000072 | MNB000073 |
| **Glass inclusion** | | | | | | | | |
| SiO₂ | 50.12 | 47.94 | 47.76 | 47.05 | 47.40 | 50.18 | 47.49 | 51.20 |
| TiO₂ | 0.81 | 0.85 | 0.82 | 0.80 | 0.85 | 1.07 | 1.12 | 0.76 |
| Al₂O₃ | 17.82 | 17.32 | 17.01 | 16.49 | 16.63 | 16.98 | 15.31 | 16.34 |
| FeO*¹ | 7.12 | 10.06 | 9.13 | 10.52 | 10.30 | 10.17 | 11.50 | 11.63 |
| FeO | 5.42 | 7.63 | 6.88 | 7.85 | 7.81 | 6.67 | 8.93 | 6.72 |
| Fe₂O₃ | 1.89 | 2.70 | 2.50 | 2.97 | 2.77 | 3.88 | 2.85 | 5.46 |
| MnO | 0.15 | 0.20 | 0.20 | 0.22 | 0.19 | 0.23 | 0.23 | 0.26 |
| MgO | 3.17 | 3.70 | 3.65 | 5.58 | 5.48 | 3.13 | 3.64 | 3.49 |
| CaO | 11.81 | 11.95 | 12.16 | 11.17 | 11.19 | 10.43 | 11.01 | 8.54 |
| Na₂O | 2.31 | 2.54 | 2.31 | 2.27 | 2.32 | 3.19 | 3.22 | 3.35 |
| K₂O | 0.71 | 0.61 | 0.55 | 0.61 | 0.65 | 0.91 | 0.83 | 0.93 |
| P₂O₅ | 0.16 | 0.17 | 0.16 | 0.16 | 0.16 | 0.23 | 0.26 | 0.23 |
| Total | 94.18 | 95.34 | 93.76 | 94.86 | 95.16 | 96.51 | 94.60 | 96.73 |
| H₂O | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| CO₂ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| S | n.d. | 1087 | 977 | 1333 | 1353 | 723 | 1713 | 1030 |
| Cl | n.d. | 1033 | 1007 | 913 | 953 | 1070 | 1157 | 1077 |
| Fe³⁺/ΣFe | 0.238 | 0.242 | 0.246 | 0.254 | 0.242 | 0.344 | 0.223 | 0.422 |
| Equilibrium Fo#² | 0.777 | 0.742 | 0.759 | 0.809 | 0.807 | 0.736 | 0.708 | 0.755 |
Electronic Appendix B: con't...

| Volcano Sample | Agrigan Agr07 | Agr05 | Agr04 |
|----------------|--------------|-------|-------|
| Inclusion #    | 12C          | 13    | 14    | 15A   | 15B   | 1    | 4    | 3    |
| IGSN designation | MNB000066   | MNB000067 | MNB000068 | MNB000069 | MNB000070 | MNB000071 | MNB000072 | MNB000073 |

**Olivine Host**

|                | 12C | 13       | 14       | 15A      | 15B      | 1      | 4       | 3       |
|----------------|-----|----------|----------|----------|----------|-------|---------|---------|
| SiO₂           | 39.37 | 38.92   | 39.02    | 38.95    | 38.95    | 37.98 | 37.88   | 37.87   |
| FeO            | 16.79 | 20.39   | 19.26    | 19.12    | 19.12    | 24.54 | 23.57   | 28.59   |
| MnO            | n.d. | n.d.    | n.d.     | n.d.     | n.d.     | n.d.  | n.d.    | n.d.    |
| MgO            | 44.03 | 41.26   | 42.16    | 42.22    | 42.22    | 38.22 | 39.36   | 35.76   |
| NiO            | 0.03  | 0.03    | 0.03     | 0.03     | 0.03     | 0.03  | 0.03    | 0.03    |
| Total          | 100.46 | 100.88  | 100.75   | 100.58   | 100.58   | 100.77 | 100.84  | 102.24  |
| Fo#            | 0.824 | 0.783   | 0.796    | 0.797    | 0.797    | 0.735 | 0.749   | 0.690   |
### Volcano Agrigan Sample

| Inclusion # | Agrigan 12C | Agrigan 13 | Agrigan 14 | Agrigan 15A | Agrigan 15B | Agrigan 1 | Agrigan 4 | Agrigan 3 |
|-------------|-------------|------------|------------|-------------|-------------|------------|----------|----------|
| IGSN designation | MNB000066 | MNB000067 | MNB000068 | MNB000069 | MNB000070 | MNB000071 | MNB000072 | MNB000073 |

**Post-entrapment, normalized corrected glass**

| Olivine added(%)^3 | 4.0 | 3.6 | 3.2 | 0.0 | 0.0 | 0.0 | 3.4 | 0.0 |
|--------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| SiO₂               | 52.65 | 49.75 | 50.44 | 47.72 | 47.97 | 50.20 | 49.63 | 52.81 |
| TiO₂               | 0.82 | 0.86 | 0.84 | 0.81 | 0.86 | 1.07 | 1.14 | 0.78 |
| Al₂O₃              | 18.15 | 17.46 | 17.50 | 16.73 | 16.83 | 16.98 | 15.57 | 16.86 |
| FeO*               | 8.01 | 10.94 | 10.08 | 10.67 | 10.42 | 10.17 | 12.56 | 12.00 |
| FeO                | 6.28 | 8.49 | 7.77 | 7.96 | 7.90 | 6.67 | 9.94 | 6.93 |
| Fe₂O₃              | 1.92 | 2.73 | 2.57 | 3.01 | 2.80 | 3.88 | 2.90 | 5.63 |
| MnO                | 0.15 | 0.20 | 0.21 | 0.22 | 0.19 | 0.23 | 0.23 | 0.27 |
| MgO                | 4.95 | 5.17 | 5.09 | 5.66 | 5.55 | 3.13 | 4.99 | 3.60 |
| CaO                | 12.03 | 12.05 | 12.52 | 11.33 | 11.33 | 10.44 | 11.20 | 8.81 |
| Na₂O               | 2.35 | 2.56 | 2.38 | 2.31 | 2.35 | 3.19 | 3.28 | 3.46 |
| K₂O                | 0.72 | 0.62 | 0.56 | 0.61 | 0.66 | 0.91 | 0.84 | 0.96 |
| P₂O₅               | 0.16 | 0.17 | 0.17 | 0.16 | 0.16 | 0.23 | 0.26 | 0.24 |
| H₂O                | n.d. | n.d. | n.d. | 3.50 | 3.42 | 3.28 | n.d. | n.d. |
| CO₂                | n.d. | n.d. | n.d. | 449 | 207 | n.d. | n.d. | n.d. |
| S                  | n.d. | 1096 | 1065 | 1352 | 1370 | 724 | 1743 | 1062 |
| Cl                 | n.d. | 1042 | 1036 | 926 | 965 | 1070 | 1177 | 1111 |
| Fe³⁺/ΣFe           | 0.216 | 0.224 | 0.230 | 0.254 | 0.242 | 0.344 | 0.208 | 0.422 |
### Electronic Appendix B: con't...

| Volcano Sample | Agrigan | Agr04 |
|----------------|---------|-------|
| Inclusion #    | 5       | 7     | 11    | 12    | 13    | 14    | 15A   | 15B   |
| IGSN designation | MNB000074 | MNB000075 | MNB000076 | MNB000077 | MNB000078 | MNB000079 | MNB000080 |
| **Glass inclusion** |         |       |       |       |       |       |       |       |
| SiO₂           | 46.34   | 49.18 | 47.32 | 47.86 | 49.88 | 47.41 | 48.14 |
| TiO₂           | 0.60    | 0.78  | 0.83  | 0.77  | 0.79  | 0.77  | 0.74  |
| Al₂O₃          | 17.73   | 17.10 | 18.41 | 16.28 | 16.38 | 18.35 | 17.77 |
| Fe₃O₄          | 9.66    | 9.24  | 9.25  | 10.13 | 8.65  | 8.90  | 8.88  |
| FeO            | 7.40    | 7.09  | 6.59  | 7.82  | 6.77  | 6.67  | 6.57  |
| Fe₂O₃          | 2.51    | 2.39  | 2.97  | 2.57  | 2.09  | 2.48  | 2.57  |
| MnO            | 0.19    | 0.19  | 0.16  | 0.23  | 0.20  | 0.17  | 0.21  |
| MgO            | 5.62    | 4.38  | 4.18  | 5.07  | 4.76  | 4.60  | 3.50  |
| CaO            | 11.82   | 11.69 | 12.30 | 11.00 | 9.95  | 11.89 | 11.79 |
| Na₂O           | 1.96    | 2.21  | 2.07  | 2.18  | 2.68  | 2.05  | 2.32  |
| K₂O            | 0.40    | 0.54  | 0.47  | 0.53  | 0.81  | 0.57  | 0.56  |
| P₂O₅           | 0.10    | 0.16  | 0.30  | 0.13  | 0.19  | 0.15  | 0.16  |
| Total          | 94.40   | 95.48 | 95.27 | 94.17 | 94.27 | 94.87 | 94.07 |
| H₂O            | n.d.    | 6.15  | n.d.  | n.d.  | 3.40  | 1.93  | n.d.  |
| CO₂            | n.d.    | n.d.  | n.d.  | n.d.  | 397   | 140   | n.d.  |
| S              | 1307    | 853   | 1113  | 963   | 957   | 1467  | 1610  |
| Cl             | 773     | 960   | 603   | 937   | 1070  | 843   | 967   |
| Fe³⁺/ΣFe       | 0.233   | 0.232 | 0.288 | 0.228 | 0.217 | 0.251 | 0.260 |
| Equilibrium Fo#² | 0.818   | 0.786 | 0.790 | 0.794 | 0.807 | 0.804 | 0.760 |
| Volcano  | Sample  | Agrigan |
|----------|---------|---------|
| Inclusion # | Agr04  |         |
| IGSN designation | MNB000074 | MNB000075 | MNB000076 | MNB000077 | MNB000078 | MNB000079 | MNB000080 |
| SiO<sub>2</sub> | 39.43 | 39.60 | 39.42 | 39.24 | 39.05 | 39.03 | 39.50 |
| FeO       | 17.50 | 18.52 | 18.48 | 19.84 | 18.90 | 16.96 | 18.07 |
| MnO       | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  | n.d.  |
| MgO       | 43.37 | 41.93 | 41.54 | 40.76 | 41.45 | 43.17 | 42.56 |
| NiO       | 0.04  | 0.04  | 0.04  | 0.03  | 0.02  | 0.05  | 0.03  |
| Total     | 100.34| 100.08| 99.48 | 99.88 | 99.42 | 99.21 | 100.16 |
| Fo#       | 0.815 | 0.801 | 0.800 | 0.786 | 0.796 | 0.819 | 0.808 |
| Volcano  | Agrigan | Agr04 |
|----------|---------|-------|
| Inclusion # | 5 | 7 | 11 | 12 | 13 | 14 | 15A |
| IGSN designation | MNB000074 | MNB000075 | MNB000076 | MNB000077 | MNB000078 | MNB000079 | MNB000080 |
| Post-entrapment, normalized corrected glass | | | | | | | |
| Olivine added (%) | 0.0 | 1.5 | 0.9 | 0.0 | 0.0 | 1.6 | 4.3 |
| SiO$_2$ | 47.96 | 48.17 | 49.48 | 50.72 | 50.94 | 48.70 | 50.51 |
| TiO$_2$ | 0.62 | 0.75 | 0.86 | 0.81 | 0.80 | 0.78 | 0.75 |
| Al$_2$O$_3$ | 18.35 | 16.56 | 19.10 | 17.25 | 16.72 | 18.60 | 18.01 |
| FeO* | 10.00 | 9.22 | 9.78 | 10.74 | 8.83 | 9.31 | 9.87 |
| FeO | 7.66 | 7.15 | 7.02 | 8.29 | 6.91 | 7.05 | 7.53 |
| Fe$_2$O$_3$ | 2.59 | 2.31 | 3.08 | 2.72 | 2.13 | 2.52 | 2.60 |
| MnO | 0.19 | 0.18 | 0.16 | 0.24 | 0.20 | 0.17 | 0.22 |
| MgO | 5.82 | 4.84 | 4.72 | 5.37 | 4.86 | 5.35 | 5.34 |
| CaO | 12.23 | 11.32 | 12.77 | 11.65 | 10.16 | 12.06 | 11.95 |
| Na$_2$O | 2.03 | 2.14 | 2.14 | 2.31 | 2.73 | 2.08 | 2.35 |
| K$_2$O | 0.41 | 0.53 | 0.49 | 0.56 | 0.83 | 0.58 | 0.57 |
| P$_2$O$_5$ | 0.11 | 0.15 | 0.31 | 0.14 | 0.19 | 0.15 | 0.16 |
| H$_2$O | 2.07 | 5.95 | n.d. | n.d. | 3.47 | 1.96 | n.d. |
| CO$_2$ | n.d. | n.d. | n.d. | 405 | 142 | n.d. | n.d. |
| S | 1353 | 826 | 1156 | 1021 | 977 | 1487 | 1632 |
| Cl | 800 | 929 | 626 | 993 | 1093 | 855 | 980 |
| Fe$^{3+}$/ΣFe | 0.242 | 0.225 | 0.283 | 0.228 | 0.217 | 0.243 | 0.237 |

n.d., not determined (no measured data)

1A "**" signifies total Fe (Fe$^{2+}$ + Fe$^{3+}$) expressed as FeO.

2Equilibrium Fo# = X$_{MgO}$/(X$_{MgO}$ + X$_{FeO}$) where FeO = Fe$^{2+}$ (actual) expressed as FeO in an olivine that is in equilibrium with the measured composition, using a K$_D$ = 0.3

3Percentage of equilibrium olivine added into the measured composition to achieve Equilibrium Fo# = Fo# of olivine host.
Table 1.2A (Electronic Appendix C): Major element compositions and Fe$^{3+}$/ΣFe ratios for submarine NW Rota-1 and Pagan glasses

| Volcano Sample | NW Rota-1 | Pagan |
|----------------|-----------|-------|
|                | HD488-R02 | HD488-R06 | HD488-R07 | HD488-R08 | HD488-R09 | HD488-R11 | HD488-R13 | HD488-R15 | HD488-R19 | HD488-R22 | IGSN designation |
|                | MNB000081 | MNB000082 | MNB000083 | MNB000084 | MNB000085 | MNB000086 | MNB000087 | MNB000088 | MNB000089 | MNB000090 | MNB000091 |
| FeO*           | 8.72      | 10.06     | 8.92      | 10.60     | 9.95      | 8.93      | 10.39     | 10.92     | 10.62     | 10.39     | 11.38     |
| FeO            | 7.06      | 7.92      | 6.80      | 8.27      | 7.83      | 7.05      | 8.11      | 8.49      | 8.08      | 7.77      | 8.85      |
| Fe$_2$O$_3$    | 1.85      | 2.37      | 2.35      | 2.59      | 2.36      | 2.09      | 2.53      | 2.70      | 2.83      | 2.91      | 2.81      |
| TiO$_2$        | 1.08      | 1.00      | 0.95      | 1.12      | 1.03      | 1.02      | 0.52      | 0.53      | 0.69      | 0.67      | 1.07      |
| Al$_2$O$_3$    | 15.94     | 15.83     | 16.95     | 15.21     | 15.66     | 15.95     | 16.17     | 16.05     | 15.79     | 15.67     | 15.67     |
| MgO            | 5.73      | 5.57      | 5.19      | 5.15      | 5.38      | 6.30      | 7.19      | 7.08      | 6.65      | 6.65      | 5.90      |
| CaO            | 10.07     | 10.32     | 10.93     | 9.73      | 10.00     | 11.03     | 13.42     | 13.24     | 12.25     | 12.35     | 11.17     |
| Na$_2$O        | 2.59      | 2.20      | 2.26      | 2.26      | 2.22      | 2.42      | 1.72      | 1.75      | 2.05      | 1.99      | 2.44      |
| K$_2$O         | 0.65      | 0.71      | 0.62      | 0.70      | 0.74      | 0.56      | 0.40      | 0.43      | 0.64      | 0.62      | 1.05      |
| P$_2$O$_5$     | 0.19      | 0.19      | 0.17      | 0.22      | 0.19      | 0.16      | 0.07      | 0.07      | 0.12      | 0.11      | 0.23      |
| Total          | 99.27     | 99.47     | 99.46     | 100.54    | 99.54     | 99.28     | 100.24    | 99.37     | 99.75     | 99.51     | 100.10    |
| S              | 63        | 103       | 97        | 97        | 90        | 113       | 117       | 83        | 100       | 73        | 87        |
| Cl             | 1667      | 1828      | 1750      | 1873      | 1850      | 1603      | 1070      | 1113      | 913       | 860       | 687       |
| Fe$^{3+}$/ΣFe  | 0.191     | 0.212     | 0.237     | 0.220     | 0.213     | 0.211     | 0.219     | 0.223     | 0.239     | 0.252     | 0.222     |
Table 1.2A (Electronic Appendix C): con’t...

| Volcano | Sample  | HD488-R02 | HD488-R06 | HD488-R07 | HD488-R08 | HD488-R09 | HD488-R11 | R06 | R12 | R13 | R15 | R19 | R22 |
|---------|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----|-----|-----|-----|-----|-----|
| NW Rota-1 | Pagan |           |           |           |           |           |           |     |     |     |     |     |     |
|          |        |           |           |           |           |           |           |     |     |     |     |     |     |
| IGSN designation |        | MNB000081 | MNB000082 | MNB000083 | MNB000084 | MNB000085 | MNB000086 | MNB000087 | MNB000088 | MNB000089 | MNB000090 | MNB000091 |
| normalized compositions |       |         |           |           |           |           |           |     |     |     |     |     |     |
| SiO2     | 54.43   | 53.58    | 53.48     | 54.90     | 54.32     | 53.02     | 50.06     | 49.38 | 50.86 | 51.10 | 50.93 |
| TiO2     | 1.09    | 1.00     | 0.95      | 1.11      | 1.03      | 1.03      | 0.52      | 0.53  | 0.69  | 0.67  | 1.07  |
| Al2O3    | 16.03   | 15.88    | 17.01     | 15.10     | 15.70     | 16.04     | 16.13     | 16.15 | 15.83 | 15.75 | 15.65 |
| FeO*     | 8.77    | 10.09    | 8.95      | 10.52     | 9.98      | 8.98      | 10.36     | 10.99 | 10.65 | 10.44 | 11.37 |
| FeO      | 7.10    | 7.95     | 6.83      | 8.21      | 7.85      | 7.09      | 8.09      | 8.54  | 8.10  | 7.81  | 8.84  |
| Fe2O3    | 1.86    | 2.38     | 2.36      | 2.57      | 2.37      | 2.10      | 11.52     | 12.21 | 11.83 | 11.61 | 12.63 |
| MnO      | 0.15    | 0.19     | 0.17      | 0.25      | 0.20      | 0.19      | 0.19      | 0.24  | 0.22  | 0.22  | 0.22  |
| MgO      | 5.76    | 5.59     | 5.21      | 5.11      | 5.39      | 6.33      | 7.17      | 7.12  | 6.66  | 6.68  | 5.89  |
| CaO      | 10.13   | 10.36    | 10.97     | 9.65      | 10.02     | 11.09     | 13.39     | 13.33 | 12.29 | 12.41 | 11.16 |
| Na2O     | 2.61    | 2.21     | 2.27      | 2.25      | 2.22      | 2.43      | 1.71      | 1.77  | 2.05  | 2.00  | 2.44  |
| K2O      | 0.66    | 0.71     | 0.62      | 0.70      | 0.74      | 0.56      | 0.40      | 0.43  | 0.64  | 0.62  | 1.04  |
| P2O5     | 0.19    | 0.19     | 0.17      | 0.22      | 0.19      | 0.16      | 0.07      | 0.07  | 0.12  | 0.11  | 0.23  |
| S        | 64      | 103      | 97        | 96        | 90        | 114       | 116       | 84    | 100   | 74    | 87    |
| Cl       | 1676    | 1834     | 1756      | 1860      | 1855      | 1612      | 1066      | 1119  | 915   | 863   | 685   |
| Fe3+/ΣFe| 0.191   | 0.212    | 0.237     | 0.220     | 0.213     | 0.211     | 0.219     | 0.223 | 0.239 | 0.252 | 0.222 |

1normalized to 100 wt%, including S and Cl concentrations
Table 1.3A (Electronic Appendix D): Major element and volatile compositions and Fe\textsuperscript{3+}/ΣFe ratios for submarine Mariana Trough glasses

| Sample       | TN273-02W-01 | TN273-03W-02 | TN273-04W-01 | TN273-05W-01 | TN273-06W-01 | TN273-01D-01-01 | TN273-02D-01-02 | TN273-04D-01-02 |
|--------------|--------------|--------------|--------------|--------------|--------------|----------------|----------------|----------------|
| Latitude (°N)| 13.239       | 13.197       | 13.165       | 13.098       | 13.053       | 13.996         | 13.945         | 13.895         |
| Longitude (°E)| 143.714     | 143.700      | 143.695      | 143.687      | 143.667      | 143.624        | 143.596        | 143.569        |
| Depth (mbsl) | 2971         | 2932         | 2856         | 2905         | 2953         | 2870           | 2894           | 2899           |
| IGSN designation | MNB000092 | MNB000093 | MNB000094 | MNB000095 | MNB000096 | MNB000097 | MNB000098 | MNB000099 |
| SiO\textsubscript{2} | 51.90        | 53.72        | 55.50        | 56.37        | 53.59        | 56.53          | 56.73          | 53.88          |
| TiO\textsubscript{2} | 1.14         | 1.31         | 1.34         | 1.46         | 1.53         | 1.65           | 1.53           | 1.50           |
| Al\textsubscript{2}O\textsubscript{3} | 16.27        | 15.72        | 15.16        | 15.06        | 15.48        | 15.40          | 15.48          | 14.57          |
| FeO\textsuperscript{*} | 8.63         | 9.62         | 10.13        | 9.87         | 10.44        | 9.40           | 9.31           | 10.67          |
| FeO            | 7.03         | 7.81         | 8.22         | 7.95         | 8.58         | 7.79           | 7.39           | 8.62           |
| Fe\textsubscript{2}O\textsubscript{3} | 1.78         | 2.02         | 2.11         | 2.13         | 2.06         | 1.79           | 2.14           | 2.27           |
| MnO            | 0.16         | 0.23         | 0.24         | 0.23         | 0.18         | 0.24           | 0.18           | 0.16           |
| MgO            | 5.88         | 5.24         | 3.92         | 3.82         | 4.33         | 2.93           | 3.42           | 4.31           |
| CaO            | 10.34        | 9.84         | 7.75         | 7.42         | 8.21         | 6.44           | 6.93           | 7.85           |
| Na\textsubscript{2}O | 2.85         | 3.05         | 3.15         | 3.66         | 3.50         | 4.03           | 3.71           | 3.49           |
| K\textsubscript{2}O | 0.18         | 0.21         | 0.37         | 0.28         | 0.23         | 0.37           | 0.38           | 0.24           |
| P\textsubscript{2}O\textsubscript{5} | 0.11         | 0.13         | 0.17         | 0.24         | 0.17         | 0.21           | 0.22           | 0.19           |
| Total          | 97.45        | 99.07        | 97.71        | 98.41        | 97.65        | 97.20          | 97.90          | 96.84          |
| H\textsubscript{2}O | 1.52         | 1.68         | 1.79         | 1.61         | 1.58         | 1.87           | 1.60           | n.d.           |
| CO\textsubscript{2} | n.d.         | n.d.         | n.d.         | n.d.         | n.d.         | 13             | 31             | n.d.           |
| S              | 330          | 317          | 357          | 227          | 527          | 360            | 313            | 423            |
| Cl             | 500          | 677          | 1210         | 1133         | 820          | 1153           | 1330           | 910            |
| Fe\textsuperscript{3+}/ΣFe | 0.185        | 0.189        | 0.188        | 0.194        | 0.178        | 0.171          | 0.207          | 0.192          |
### Table 1.3A (Electronic Appendix D): con’t...

| Sample     | TN273-02W-01 | TN273-03W-02 | TN273-04W-01 | TN273-05W-01 | TN273-06W-01 | TN273-01D-01-01 | TN273-02D-01-02 | TN273-04D-01-02 |
|------------|--------------|--------------|--------------|--------------|--------------|----------------|----------------|----------------|
| Latitude (°N) | 13.239   | 13.197   | 13.165   | 13.098   | 13.053   | 13.996   | 13.945   | 13.895   |
| Longitude (°E) | 143.714 | 143.700 | 143.695 | 143.687 | 143.667 | 143.624 | 143.596 | 143.569 |
| Depth (mbsl) | 2971         | 2932         | 2856         | 2905         | 2953         | 2870         | 2894         | 2899         |
| IGSN designation | MNB000092 | MNB000093 | MNB000094 | MNB000095 | MNB000096 | MNB000097 | MNB000098 | MNB000099 |

**normalized compositions**

|          | MNB000092 | MNB000093 | MNB000094 | MNB000095 | MNB000096 | MNB000097 | MNB000098 | MNB000099 |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| SiO₂     | 52.40     | 53.26     | 55.69     | 56.28     | 53.93     | 56.98     | 56.92     | 55.56     |
| TiO₂     | 1.15      | 1.29      | 1.34      | 1.46      | 1.54      | 1.66      | 1.54      | 1.55      |
| Al₂O₃    | 16.42     | 15.59     | 15.21     | 15.04     | 15.58     | 15.52     | 15.53     | 15.02     |
| FeO*     | 8.71      | 9.54      | 10.16     | 9.85      | 10.50     | 9.47      | 9.35      | 11.00     |
| FeO      | 7.09      | 7.74      | 8.25      | 7.94      | 8.63      | 7.85      | 7.41      | 8.89      |
| Fe₂O₃    | 1.79      | 2.00      | 2.12      | 2.12      | 2.08      | 1.80      | 2.15      | 2.34      |
| MnO      | 0.16      | 0.23      | 0.24      | 0.23      | 0.18      | 0.24      | 0.18      | 0.17      |
| MgO      | 5.93      | 5.19      | 3.93      | 3.81      | 4.36      | 2.96      | 3.43      | 4.45      |
| CaO      | 10.44     | 9.76      | 7.77      | 7.41      | 8.26      | 6.49      | 6.96      | 8.10      |
| Na₂O     | 2.88      | 3.02      | 3.16      | 3.66      | 3.52      | 4.06      | 3.72      | 3.60      |
| K₂O      | 0.18      | 0.21      | 0.37      | 0.28      | 0.23      | 0.38      | 0.38      | 0.24      |
| P₂O₅     | 0.11      | 0.13      | 0.17      | 0.17      | 0.17      | 0.22      | 0.23      | 0.19      |
| H₂O      | 1.53      | 1.67      | 1.80      | 1.61      | 1.59      | 1.88      | 1.61      | n.d.      |
| CO₂      | n.d.      | n.d.      | n.d.      | n.d.      | n.d.      | 13        | 31        | n.d.      |
| S        | 333       | 314       | 358       | 226       | 350       | 363       | 314       | 437       |
| Cl       | 505       | 671       | 1214      | 1132      | 825       | 1162      | 1334      | 938       |
| Fe³⁺/ΣFe | 0.185     | 0.189     | 0.188     | 0.194     | 0.178     | 0.171     | 0.207     | 0.192     |
| Sample          | TN273-05D-01-01 | TN273-06D-01-03 | TN273-06D-02-02 | TN273-06D-03-03 | TN273-07D-01-01 | TN273-08D-01-01 | TN273-09D-01-03 | TN273-12D-01-01 |
|----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|
| Latitude (°N)  | 13.850          | 13.769          | 13.769          | 13.769          | 13.730         | 13.688         | 13.660         | 13.607         |
| Longitude (°E) | 143.520         | 143.488         | 143.488         | 143.488         | 143.437        | 143.384        | 143.355        | 143.219        |
| Depth (mbsl)   | 3006            | 2891            | 2891            | 2891            | 2924           | 2880           | 3050           | 2918           |
| IGSN           | MNB000100       | MNB000101       | MNB000102       | MNB000103       | MNB000104      | MNB000105      | MNB000106      | MNB000107      |
| SiO₂           | 58.23           | 59.82           | 55.71           | 55.43           | 54.96          | 58.26          | 52.99          | 52.80          |
| TiO₂           | 1.56            | 1.35            | 1.72            | 1.79            | 1.51           | 1.69           | 1.64           | 1.67           |
| Al₂O₃          | 16.13           | 16.19           | 14.23           | 14.35           | 15.45          | 14.77          | 16.03          | 15.86          |
| FeO*           | 8.55            | 8.59            | 11.88           | 11.69           | 10.63          | 10.14          | 10.06          | 10.01          |
| FeO            | 6.96            | 6.96            | 9.59            | 9.32            | 8.54           | 8.24           | 8.14           | 8.16           |
| Fe₂O₃          | 1.76            | 1.82            | 2.54            | 2.63            | 2.32           | 2.11           | 2.14           | 2.05           |
| MnO            | 0.16            | 0.20            | 0.22            | 0.20            | 0.19           | 0.25           | 0.19           | 0.16           |
| MgO            | 2.55            | 2.15            | 3.46            | 3.48            | 3.86           | 2.47           | 4.77           | 4.79           |
| CaO            | 6.20            | 5.77            | 7.52            | 7.52            | 7.33           | 5.75           | 8.80           | 8.88           |
| Na₂O           | 4.37            | 4.65            | 3.38            | 3.50            | 3.30           | 3.84           | 3.89           | 4.00           |
| K₂O            | 0.44            | 0.55            | 0.37            | 0.36            | 0.38           | 0.57           | 0.35           | 0.36           |
| P₂O₅           | 0.26            | 0.28            | 0.17            | 0.16            | 0.21           | 0.29           | 0.20           | 0.20           |
| Total          | 98.44           | 99.55           | 98.66           | 98.47           | 97.82          | 98.03          | 98.92          | 98.72          |
| H₂O            | 1.72            | 2.10            | 1.82            | 2.27            | 1.84           | 2.46           | 1.89           | 1.93           |
| CO₂            | n.d.            | n.d.            | n.d.            | n.d.            | n.d.           | n.d.           | n.d.           | n.d.           |
| S              | 207             | 395             | 330             | 307             | 377            | 217            | 553            | 583            |
| Cl             | 1430            | 1775            | 1390            | 1350            | 1307           | 1533           | 953            | 960            |
| Fe³⁺/ΣFe       | 0.186           | 0.190           | 0.193           | 0.203           | 0.196          | 0.188          | 0.191          | 0.184          |
Table 1.3 (Electronic Appendix D): con’t...

| Sample       | MNB000100 | MNB000101 | MNB000102 | MNB000103 | MNB000104 | MNB000105 | MNB000106 | MNB000107 |
|--------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Latitude (°N)| 13.850    | 13.769    | 13.769    | 13.769    | 13.730    | 13.688    | 13.660    | 13.607    |
| Longitude (°E)| 143.520  | 143.488   | 143.488   | 143.488   | 143.437   | 143.384   | 143.355   | 143.219   |
| Depth (mbsl) | 3006      | 2891      | 2891      | 2891      | 2924      | 2880      | 3050      | 2918      |
| IGSN designation | MNB000100 | MNB000101 | MNB000102 | MNB000103 | MNB000104 | MNB000105 | MNB000106 | MNB000107 |

Normalized compositions:

- SiO₂: 58.04, 58.72, 55.35, 54.93, 55.06, 57.88, 52.49, 52.38
- TiO₂: 1.55, 1.33, 1.70, 1.77, 1.52, 1.68, 1.63, 1.65
- Al₂O₃: 16.07, 15.89, 14.14, 14.22, 15.47, 14.67, 15.87, 15.74
- FeO*: 8.52, 8.43, 11.80, 11.58, 10.64, 10.08, 9.97, 9.93
- FeO: 6.94, 6.83, 9.53, 9.23, 8.55, 8.19, 8.06, 8.10
- Fe₂O₃: 1.76, 1.78, 2.53, 2.61, 2.32, 2.10, 2.12, 2.03
- MnO: 0.16, 0.19, 0.22, 0.19, 0.19, 0.25, 0.18, 0.16
- MgO: 2.55, 2.11, 3.44, 3.44, 3.86, 2.46, 4.72, 4.75
- CaO: 6.18, 5.66, 7.47, 7.45, 7.35, 5.71, 8.72, 8.80
- Na₂O: 4.35, 4.56, 3.36, 3.46, 3.31, 3.81, 3.85, 3.97
- K₂O: 0.44, 0.54, 0.37, 0.36, 0.38, 0.56, 0.35, 0.36
- P₂O₅: 0.26, 0.28, 0.16, 0.16, 0.21, 0.29, 0.20, 0.20
- H₂O: 1.71, 2.06, 1.81, 2.25, 1.84, 2.44, 1.87, 1.91
- CO₂: n.d., n.d., n.d., n.d., n.d., n.d., n.d., n.d.
- S: 206, 388, 328, 304, 378, 215, 548, 579
- Cl: 1425, 1742, 1381, 1338, 1309, 1523, 944, 952
- Fe³+/ΣFe: 0.186, 0.190, 0.193, 0.203, 0.196, 0.188, 0.191, 0.184
| Sample     | TN273-13D-01-01 |
|------------|-----------------|
| Latitude (°N) | 13.505         |
| Longitude (°E) | 143.180        |
| Depth (mbsl) | 2639           |
| IGSN designation | MNB000108     |

|          | normalized compositions² |
|----------|---------------------------|
| SiO₂     | 53.37                     |
| TiO₂     | 0.90                      |
| Al₂O₃    | 16.42                     |
| FeO*     | 8.43                      |
| FeO      | 6.83                      |
| Fe₂O₃    | 1.78                      |
| MnO      | 0.21                      |
| MgO      | 5.64                      |
| CaO      | 10.51                     |
| Na₂O     | 2.89                      |
| K₂O      | 0.31                      |
| P₂O₅     | 0.07                      |
| Total    | 98.74                     |
| H₂O      | 1.49                      |
| CO₂      | n.d.                      |
| S        | 157                       |
| Cl       | 1077                      |
| Fe³⁺/ΣFe| 0.190                     |

n.d., not determined (no measured data).

¹mbsl, meters below sea level.

²normalized to 100 wt%, including H₂O, CO₂, S and Cl concentrations.
| Volcano | Agrigan | Pagan  | Alamagan | Guguan | Sarigan | NW     | Rota-1 | Mariana Trough |
|---------|---------|--------|----------|--------|---------|--------|--------|----------------|
| SiO₂    | -0.239  | -0.998¹ | -0.555   | -0.301 | 0.003   | -1.146 | -0.540 |                |
| TiO₂    | -0.017  | -0.429¹ | -0.023   | -0.024 | -0.030  | -0.190 | -0.163 |                |
| Al₂O₃   | -0.515  | 0.117   | -0.643   | -0.419 | -1.177  | 1.080  | 0.9110 |                |
| FeO     | 0.317¹  | -0.492¹ | 0.071¹   | -0.090¹| -0.323¹ | -0.530¹| -0.681¹|                |
| Fe₂O₃   | -0.073¹ | -0.116¹ | 0.108¹   | 0.009¹ | -0.004¹| -0.395¹| -0.234¹|                |
| MnO     | -0.005  | -0.024  | -0.006   | -0.005 | -0.003  | -0.030 | -0.004¹|                |
| CaO     | -0.329  | 1.395   | -0.466   | -0.314 | 0.413   | 0.002  | 0.201  |                |
| Na₂O    | -0.057  | -0.229  | -0.050   | -0.056 | -0.136  | -0.094 | -0.082 |                |
| K₂O     | -0.012  | -0.145  | -0.011   | -0.014 | -0.024  | -0.091 | -0.027¹|                |
| P₂O₅    | -0.003  | -0.039  | -0.004   | -0.004 | -0.007  | -0.024 | -0.008¹|                |

¹slopes of lines defined by the natural data for the given major oxide and 5-7 wt% MgO
| Volcano | Agrigan | Pagan | Alamagan | Guguan | Sarigan | NW Rota-1 | Mariana Trough |
|---------|---------|-------|----------|--------|---------|-----------|----------------|
| SiO₂    | 46.73   | 48.66 | 46.12    | 47.35  | 47.26   | 51.21     | 51.97          |
| TiO₂    | 0.61    | 0.42  | 0.59     | 0.57   | 0.61    | 0.69      | 0.64           |
| Al₂O₃   | 14.31   | 13.56 | 16.18    | 15.04  | 14.08   | 15.88     | 16.68          |
| FeO     | 8.91    | 8.74  | 6.92     | 6.70   | 7.25    | 1.54      | 6.18           |
| Fe₂O₃   | 2.20    | 2.30  | 2.15     | 2.38   | 2.21    | 7.18      | 1.38           |
| MnO     | 0.17    | 0.19  | 0.16     | 0.12   | 0.16    | 0.14      | 0.19           |
| MgO     | 13.43   | 13.18 | 10.44    | 10.09  | 10.93   | 10.82     | 9.31           |
| CaO     | 9.72    | 11.01 | 11.87    | 10.72  | 12.41   | 9.41      | 9.66           |
| Na₂O    | 1.72    | 1.63  | 1.51     | 2.00   | 1.45    | 1.99      | 2.62           |
| K₂O     | 0.42    | 0.47  | 0.39     | 0.44   | 0.27    | 0.48      | 0.25           |
| P₂O₅    | 0.11    | 0.09  | 0.10     | 0.08   | 0.08    | 0.14      | 0.06           |
Table 1.6A (Electronic Appendix G): Primary melt compositions for Northern Mariana Trough lavas

| Sample | 73-2-1 | 71-1-14 | 82-1-1 | 76-1-1 | 75-1-2 | 80-1-3 | 46-1-6 | 74-1-1 | 47-1-5 |
|--------|--------|---------|--------|--------|--------|--------|--------|--------|--------|
| SiO₂   | 50.93  | 50.80   | 50.42  | 51.07  | 51.19  | 48.94  | 50.59  | 50.70  | 50.59  |
| TiO₂   | 1.26   | 0.95    | 1.10   | 1.39   | 1.46   | 0.78   | 1.03   | 1.09   | 0.90   |
| Al₂O₃  | 16.17  | 16.22   | 16.01  | 13.67  | 14.84  | 16.68  | 15.59  | 17.16  | 15.60  |
| FeO    | 6.62   | 6.05    | 6.41   | 8.52   | 7.41   | 7.55   | 6.86   | 6.13   | 6.49   |
| Fe₂O₃  | 1.31   | 1.40    | 1.39   | 1.45   | 1.39   | 1.35   | 1.36   | 1.34   | 1.38   |
| MnO    | 0.14   | 0.14    | 0.15   | -      | -      | 0.15   | 0.14   | 0.14   | 0.15   |
| MgO    | 9.99   | 9.13    | 9.67   | 12.85  | 11.17  | 11.38  | 10.36  | 9.26   | 9.80   |
| CaO    | 9.71   | 10.97   | 10.39  | 8.92   | 9.60   | 10.74  | 10.63  | 11.39  | 11.39  |
| Na₂O   | 3.14   | 2.49    | 2.58   | 2.99   | 2.96   | 2.23   | 2.48   | 2.65   | 2.34   |
| K₂O    | 0.30   | 0.38    | 0.21   | 0.20   | 0.32   | 0.33   | 0.20   | 0.29   | 0.23   |
| P₂O₅   | 0.16   | 0.18    | 0.15   | 0.15   | 0.16   | 0.13   | 0.14   | 0.16   | 0.12   |

A "-" indicates that the calculation returned a negative value.
Table 1.7A (Electronic Appendix H): Trace element concentrations for screened melt inclusions

| Volcano Sample | Sari15-04 |
|----------------|-----------|
| Inclusion #    | 3         | 7         | 11        | 15        | 17        | 18        | 21        | 22        | 23        | 24        | 25        | 27        |
| Li             | 3.69      | 3.18      | -         | 4.26      | 4.00      | 3.88      | 4.37      | 4.72      | 4.19      | 4.03      | 3.34      | 3.70      |
| Be             | -         | -         | 0.32      | -         | 0.33      | -         | -         | 0.23      | -         | 0.32      | -         | -         |
| Sc             | 42.3      | 43.4      | 46.1      | 42.4      | 43.9      | 41.5      | 39.5      | 39.6      | 45.6      | 41.4      | 42.5      | 46.0      |
| V              | 244       | 229       | 241       | 320       | 290       | 267       | 310       | 322       | 280       | 242       | 260       | 270       |
| Cr             | 84.1      | 104       | 49.7      | 70.7      | 58.5      | 111       | 69.5      | 84.1      | 97.6      | 98.5      | 41.6      | 95.8      |
| Co             | 35.7      | 33.5      | 30.2      | 37.0      | 33.8      | 35.1      | 36.5      | 39.4      | 37.3      | 33.0      | 31.7      | 33.1      |
| Ni             | 32.8      | 26.7      | 29.4      | 28.7      | 26.4      | 31.1      | 27.9      | 29.9      | 30.4      | 28.1      | 24.2      | 30.1      |
| Cu             | 124       | 120       | 122       | 140       | 125       | 126       | 145       | 140       | 144       | 126       | 116       | 124       |
| Zn             | 73.3      | 66.1      | 68.2      | 91.5      | 75.1      | 81.1      | 86.5      | 99.0      | 85.1      | 69.6      | 73.1      | 76.0      |
| Rb             | 2.76      | 2.58      | 5.11      | 4.32      | 2.67      | 2.99      | 4.44      | 4.56      | 2.89      | 2.50      | 2.79      | 2.75      |
| Sr             | 283       | 274       | 345       | 311       | 270       | 258       | 295       | 305       | 276       | 300       | 281       | 264       |
| Y              | 14.0      | 14.2      | 15.5      | 12.6      | 12.3      | 12.7      | 11.5      | 12.9      | 13.4      | 12.5      | 12.8      | 13.0      |
| Zr             | 32.9      | 33.4      | 39.7      | 29.4      | 27.1      | 25.7      | 28.0      | 29.9      | 28.1      | 30.4      | 27.5      | 27.0      |
| Nb             | 0.65      | 0.75      | 0.79      | 0.84      | 0.62      | 0.58      | 0.82      | 0.85      | 0.68      | 0.60      | 0.63      | 0.63      |
| Cs             | -         | -         | -         | -         | -         | -         | 0.17      | -         | -         | -         | -         | -         |
| Ba             | 108       | 107       | 153       | 135       | 100       | 113       | 131       | 140       | 111       | 109       | 105       | 101       |
| La             | 2.17      | 2.24      | 4.99      | 3.22      | 2.02      | 2.08      | 3.04      | 3.27      | 2.10      | 2.19      | 2.26      | 1.94      |
| Ce             | 5.42      | 4.91      | 8.40      | 7.67      | 4.93      | 5.42      | 7.48      | 8.27      | 5.74      | 5.19      | 5.18      | 4.84      |
| Pr             | 0.88      | 0.84      | 1.46      | 1.17      | 0.79      | 0.87      | 1.11      | 1.15      | 0.89      | 0.84      | 0.87      | 0.83      |
| Nd             | 4.55      | 4.86      | 7.38      | 5.82      | 4.32      | 4.18      | 5.20      | 5.60      | 4.63      | 4.52      | 4.53      | 4.33      |
| Sm             | 1.66      | 1.63      | 2.27      | 1.87      | 1.47      | 1.53      | 1.63      | 1.76      | 1.40      | 1.41      | 1.46      | 1.51      |
| Eu             | 0.62      | 0.60      | 0.73      | 0.73      | 0.62      | 0.57      | 0.66      | 0.66      | 0.59      | 0.61      | 0.60      | 0.62      |
| Gd             | 2.27      | 2.17      | 3.06      | 2.13      | 1.98      | 2.00      | 2.03      | 2.01      | 1.97      | 1.95      | 2.05      | 2.06      |
| Inclusion # | Tb  | Dy  | Ho  | Er  | Tm  | Yb  | Lu  | Hf  | Ta  | Pb  | Th  | U   |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 3           | 0.38| 2.46| 0.51| 1.57| 0.28| 1.40| 0.26| 0.77| 0.04| 1.52| 0.19| 0.10|
| 7           | 0.45| 2.32| 0.61| 1.65| 0.22| 1.37| 0.22| 1.03| 0.04| 1.60| 0.27| 0.12|
| 11          | 0.42| 2.69| 0.61| 1.56| 0.21| 1.67| 0.25| 1.43| -   | 2.10| 0.75| 0.24|
| 15          | 0.38| 2.24| 0.51| 1.46| 0.22| 1.39| 0.21| 0.78| 0.06| 1.68| 0.38| 0.21|
| 17          | 0.34| 2.23| 0.51| 1.45| 0.20| 1.34| 0.22| 0.81| 0.04| 2.16| 0.17| 0.12|
| 18          | 0.31| 2.18| 0.46| 1.38| 0.20| 1.36| 0.21| 0.81| 0.04| 1.94| 0.19| 0.11|
| 21          | 0.34| 2.10| 0.45| 1.35| 0.20| 1.32| 0.19| 0.87| 0.05| 2.37| 0.19| 0.19|
| 22          | 0.37| 2.22| 0.49| 1.37| 0.20| 1.37| 0.21| 0.84| 0.05| 2.17| 0.41| 0.18|
| 23          | 0.36| 2.20| 0.53| 1.39| 0.23| 1.31| 0.24| 0.76| 0.04| 1.66| 0.42| 0.12|
| 24          | 0.36| 2.46| 0.50| 1.41| 0.24| 1.39| 0.22| 0.78| 0.04| 1.68| 0.21| 0.11|
| 25          | 0.35| 2.28| 0.50| 1.42| 0.22| 1.35| 0.22| 0.78| 0.04| 1.62| 0.23| 0.12|
| 27          | 0.37| 2.21| 0.53| 1.44| 0.22| 1.45| 0.22| 0.72| 0.05| 1.63| 0.17| 0.11|
| Inclusion # | 29 | 31A | 32A | 32B | 33 | 1 | 3 | 4 | 5 | 7 | 8 | 9 |
|------------|----|-----|-----|-----|----|---|---|---|---|---|---|---|
| Li         | 3.87 | 3.44 | 3.44 | 3.90 | 4.28 | 4.40 | - | 5.24 | 4.52 | 6.22 | 5.44 | 5.48 |
| Be         | -   | -   | -   | -   | -   | 0.26 | - | -   | -   | -   | -   | 0.28 |
| Sc         | 46.0 | 40.7 | 39.0 | 41.3 | 33.7 | 39.3 | 34.3 | 36.3 | 48.4 | 33.6 | 41.0 | 39.1 |
| V          | 279 | 232 | 211 | 224 | 214 | 264 | 207 | 211 | 237 | 222 | 245 | 254 |
| Cr         | 211 | 83.9 | 84.0 | 91.0 | 29.8 | 42.6 | 31.3 | 20.4 | 73.8 | 23.6 | 45.0 | 32.6 |
| Co         | 33.0 | 31.5 | 29.4 | 29.5 | 33.2 | 37.7 | 28.9 | 35.9 | 29.4 | 41.2 | 34.7 | 38.3 |
| Ni         | 35.3 | 25.2 | 25.8 | 28.0 | 23.9 | 35.3 | - | 31.6 | 17.8 | 38.3 | 31.0 | 28.9 |
| Cu         | 125 | 114 | 117 | 116 | 115 | 108 | 108 | 170 | 93.3 | 126 | 105 | 107 |
| Zn         | 78.4 | 66.4 | 60.3 | 57.5 | 78.5 | 86.8 | 64.7 | 87.1 | 60.0 | 89.2 | 72.0 | 71.5 |
| Rb         | 2.67 | 2.61 | 2.73 | 2.02 | 7.13 | 5.32 | 14.0 | 9.10 | 7.92 | 9.20 | 6.42 | 3.39 |
| Sr         | 266 | 288 | 256 | 253 | 394 | 267 | 285 | 313 | 277 | 342 | 271 | 227 |
| Y          | 13.0 | 12.8 | 13.2 | 12.5 | 14.9 | 12.5 | 18.8 | 14.5 | 14.3 | 13.5 | 12.5 | |
| Zr         | 26.3 | 31.0 | 32.9 | 30.5 | 53.1 | 27.3 | 60.2 | 50.5 | 31.6 | 42.1 | 29.5 | 25.4 |
| Nb         | 0.58 | 0.59 | 0.40 | 0.65 | 1.24 | 0.50 | 1.06 | 0.90 | 0.59 | 0.88 | 0.47 | 0.26 |
| Cs         | -   | -   | -   | -   | -   | 0.28 | 0.23 | -   | -   | -   | 0.46 | -   |
| Ba         | 104 | 110 | 102 | 95  | 225 | 108 | 194 | 156 | 106 | 138 | 108 | 94.6 |
| La         | 2.10 | 2.09 | 2.06 | 1.93 | 6.15 | 2.69 | 5.37 | 3.88 | 3.69 | 4.11 | 2.96 | 1.52 |
| Ce         | 4.87 | 4.96 | 4.52 | 4.19 | 12.2 | 6.66 | 11.1 | 9.28 | 7.84 | 9.71 | 6.82 | 4.43 |
| Pr         | 0.85 | 0.83 | 0.72 | 0.75 | 1.92 | 1.01 | 1.89 | 1.43 | 1.16 | 1.44 | 1.10 | 0.71 |
| Nd         | 4.63 | 4.47 | 4.12 | 4.13 | 8.92 | 4.79 | 9.39 | 6.77 | 6.12 | 6.80 | 5.54 | 3.91 |
| Sm         | 1.54 | 1.59 | 1.17 | 1.32 | 2.62 | 1.67 | 2.26 | 2.09 | 1.75 | 2.10 | 1.71 | 1.29 |
| Eu         | 0.62 | 0.58 | 0.63 | 0.59 | 0.88 | 0.58 | 0.68 | 0.69 | 0.71 | 0.57 | 0.57 | |
| Gd         | 2.20 | 1.79 | 2.37 | 2.09 | 2.64 | 1.94 | 2.96 | 2.34 | 2.32 | 2.13 | 1.98 | 1.79 |
| Volcano Sample | Sarigan Sari15-04 | Alamagan Ala02 |
|----------------|-------------------|----------------|
| Inclusion #    | 29    | 31A | 32A | 32B | 33 | 1 | 3 | 4 | 5 | 7 | 8 | 9 |
| Tb             | 0.37  | 0.34 | 0.22 | 0.37 | 0.44 | 0.30 | 0.57 | 0.40 | 0.39 | 0.39 | 0.34 | 0.27 |
| Dy             | 2.32  | 2.17 | 2.26 | 3.09 | 2.73 | 2.06 | 3.27 | 2.32 | 2.43 | 2.57 | 2.18 | 1.77 |
| Ho             | 0.50  | 0.53 | 0.44 | 0.46 | 0.58 | 0.48 | 0.79 | 0.48 | 0.53 | 0.59 | 0.48 | 0.44 |
| Er             | 1.52  | 1.47 | 1.33 | 1.26 | 1.57 | 1.29 | 1.96 | 1.35 | 1.43 | 1.40 | 1.33 | 1.28 |
| Tm             | 0.21  | 0.24 | 0.16 | 0.21 | 0.22 | 0.19 | 0.24 | 0.22 | 0.24 | 0.27 | 0.26 | 0.24 |
| Yb             | 1.37  | 1.44 | 1.39 | 1.23 | 1.43 | 1.28 | 2.01 | 1.44 | 1.41 | 1.55 | 1.54 | 1.31 |
| Lu             | 0.21  | 0.22 | 0.14 | 0.12 | 0.20 | 0.21 | 0.22 | 0.22 | 0.33 | 0.23 | 0.19 | 0.25 |
| Hf             | 0.82  | 0.92 | 1.11 | 0.74 | 1.36 | 0.88 | 1.78 | 1.27 | 0.90 | 1.19 | 0.83 | 0.75 |
| Ta             | 0.04  | 0.04 | -    | -    | 0.08 | 0.04 | -   | 0.06 | 0.03 | 0.06 | 0.05 | -   |
| Pb             | 1.64  | 1.69 | 1.39 | 1.19 | 2.63 | 1.93 | 3.37 | 2.86 | 1.78 | 2.31 | 1.90 | 1.64 |
| Th             | 0.18  | 0.23 | 0.18 | 0.12 | 0.93 | 0.21 | 0.63 | 0.48 | 0.41 | 0.50 | 0.27 | 0.11 |
| U              | 0.13  | 0.12 | 0.06 | 0.07 | 0.29 | 0.12 | 0.38 | 0.26 | 0.14 | 0.26 | 0.12 | 0.09 |
### Electronic Appendix H con’t

| Volcano Sample Inclusion # | Alamagan Ala02 |   |   | Guguan Gug11 |   |   | Pagan Paga8 |   | Agr05 |   | Agr04 |   |
|----------------------------|----------------|---|---|--------------|---|---|--------------|---|-------|---|-------|---|
| Li                         | -              | 4.52 | 5.34 | -            | 3.63 | 6.91 | 3.67 | 3.81 | 3.27 | 6.52 | -  | 5.16 | -  |
| Be                         | -              | 0.29 | -   | -            | -   | 0.41 | 0.31 | -   | -   | 0.46 | -  | 0.48 | -  |
| Sc                         | 40.9           | 48.2 | 39.8 | 42.3         | 40.0 | 33.7 | 40.7 | 36.1 | 36.0 | 35.1 | 43.1 | 40.2 | 38.1 |
| V                          | 241            | 272 | 254 | 242          | 222 | 373  | 275  | 261  | 267  | 421  | 421 | 322  | 283 |
| Cr                         | 27.0           | 147.0 | 35.5 | -            | 38.1 | 57.8  | 20.3 | 8.65 | 12.1 | 7.45  | 7.45 | 7.45 | 23.8 |
| Co                         | 33.0           | 34.3 | 37.2 | 26.6         | 28.0 | 33.3  | 26.1 | 34.4 | 35.7 | 26.0  | 7.45 | 28.2 | 28.5 |
| Ni                         | 21.3           | 35.0 | 27.6 | -            | 17.7 | 24.0  | 7.96  | 7.87 | 7.74 | 2.48  | -   | 12.8 | -   |
| Cu                         | 111            | 99.2 | 206 | 70.4         | 171 | 190  | 91.3  | 137  | 143  | 78.6  | 113 | 107  | 119 |
| Zn                         | 65.9           | 75.1 | 73.0 | 46.6         | 66.2 | 115  | 67.6  | 73.2 | 76.8 | 99.5  | 90.9 | 88.0 | 89.7 |
| Rb                         | -              | 8.40 | 7.78 | 8.17         | 3.90 | 12.0  | 11.4  | 14.2 | 15.6 | 21.8  | 13.2 | 17.4 | 14.9 |
| Sr                         | 315            | 247 | 343 | 340          | 326 | 294  | 310  | 341  | 353  | 371  | 305 | 306  | 339 |
| Y                          | 12.4           | 12.9 | 12.3 | 16.6         | 19.2 | 18.1  | 17.0  | 18.6 | 18.2 | 23.6  | 16.0 | 18.7 | 13.3 |
| Zr                         | 27.3           | 30.1 | 25.1 | 50.5         | 24.1 | 41.5  | 33.2  | 41.1 | 41.5 | 52.5  | 33.6 | 46.7 | 29.3 |
| Nb                         | 0.72           | 0.68 | 0.85 | 0.84         | 0.55 | 0.76  | 0.65  | 1.03 | 0.80 | 1.18  | 0.66 | 1.00 | 0.71 |
| Cs                         | -              | 0.26 | -   | -            | -   | 0.51  | 0.32  | -   | -   | 0.47  | -   | 0.43 | -   |
| Ba                         | 94.5           | 125 | 107 | 106          | 117 | 190  | 113   | 124 | 128  | 170  | 118 | 157  | 98.3 |
| La                         | 3.09           | 3.84 | 4.74 | 5.25         | 2.43 | 4.22  | 4.78  | 6.16 | 6.78 | 8.56  | 4.36 | 6.47 | 4.77 |
| Ce                         | 7.12           | 9.45 | 10.2 | 11.5         | 5.48 | 10.5  | 10.1  | 12.0 | 13.6 | 18.3  | 9.95 | 13.3 | 10.0 |
| Pr                         | 0.89           | 1.35 | 1.44 | 1.53         | 0.85 | 1.62  | 1.60  | 1.84 | 2.15 | 2.46  | 1.57 | 2.08 | 1.52 |
| Nd                         | 5.21           | 6.36 | 6.13 | 7.77         | 4.53 | 7.79  | 7.71  | 9.49 | 8.86 | 12.5  | 7.33 | 9.55 | 7.85 |
| Sm                         | 2.37           | 1.87 | 1.95 | 2.07         | 1.84 | 2.46  | 2.05  | 2.24 | 2.60 | 3.24  | 1.95 | 2.86 | 2.09 |
| Eu                         | 0.61           | 0.70 | 0.70 | 0.65         | 0.62 | 0.86  | 0.81  | 1.03 | 1.06 | 1.31  | 0.93 | 1.05 | 0.74 |
| Gd                         | 2.06           | 2.25 | 2.25 | 2.83         | 2.44 | 2.81  | 2.74  | 3.01 | 3.03 | 3.45  | 2.54 | 3.37 | 2.25 |
### Electronic Appendix H con’t

| Volcano Sample | Alamagan | Guguan | Pagan | Agr05 | Agri04 |
|----------------|----------|--------|-------|-------|--------|
| Inclusion #    |          |        |       |       |        |
|                | Ala02    | Ala03  | Gug11 | Paga8 |        |
|                | 11       | 15     | 16A   | 1     | 2      |
| Tb             | 0.41     | 0.34   | 0.29  | 0.52  | 0.46   |
| Dy             | 2.34     | 2.30   | 2.30  | 2.18  | 2.89   |
| Ho             | 0.47     | 0.47   | 0.50  | 0.81  | 0.68   |
| Er             | 1.48     | 1.40   | 1.32  | 1.76  | 2.02   |
| Tm             | 0.26     | 0.22   | 0.26  | -     | 0.32   |
| Yb             | 1.11     | 1.34   | 1.07  | 1.69  | 1.87   |
| Lu             | 0.20     | 0.22   | 0.18  | 0.20  | 0.33   |
| Hf             | 0.76     | 0.89   | 0.66  | 1.09  | 0.77   |
| Ta             | 0.05     | 0.05   | 0.05  | -     | 0.04   |
| Pb             | 1.88     | 2.19   | 1.82  | 1.19  | 2.18   |
| Th             | 0.17     | 0.35   | 0.45  | 0.46  | 0.26   |
| U              | 0.15     | 0.17   | 0.21  | 0.09  | 0.12   |

A "-" indicates a measured value below the detection limit of the analysis.
Table 1.8 (Electronic Appendix I): Trace element concentrations for Mariana Trough glasses

| Sample     | TN273-02W-01 | TN273-03W-02 | TN273-04W-01 | TN273-05W-01 | TN273-06W-01 | TN273-01D-01-01 | TN273-02D-01-02 | TN273-04D-01-02 | TN273-05D-01-01 |
|------------|--------------|--------------|--------------|--------------|--------------|-----------------|-----------------|-----------------|-----------------|
| Li         | 7.90         | 10.2         | 8.02         | 11.8         | 7.78         | 7.53            | 11.4            | 7.43            | 12.2            |
| Be         | 0.393        | 0.469        | 0.535        | 0.617        | 0.512        | 0.574           | 0.681           | 0.797           | 0.970           |
| Sc         | 29.9         | 31.1         | 27.3         | 27.0         | 29.5         | 24.2            | 24.8            | 26.6            | 23.6            |
| V          | 323          | 355          | 296          | 260          | 316          | 192             | 221             | 248             | 154             |
| Cr         | 96.1         | 61.0         | 14.5         | 8.08         | 15.6         | 4.15            | 24.5            | 8.54            | -               |
| Co         | 32.1         | 29.0         | 27.4         | 23.5         | 29.7         | 16.8            | 19.5            | 25.8            | 14.7            |
| Ni         | 44.0         | 25.4         | 8.56         | 8.69         | 12.2         | 0.406           | 11.9            | 10.5            | -               |
| Cu         | 72.0         | 73.0         | 40.1         | 36.8         | 38.8         | 7.40            | 23.3            | 48.7            | 8.55            |
| Zn         | 96.6         | 105          | 98.2         | 112          | 97.1         | 118             | 123             | 84.9            | 124             |
| Rb         | 2.51         | 2.97         | 2.30         | 3.48         | 2.53         | 4.06            | 4.91            | 5.80            | 5.77            |
| Sr         | 143          | 138          | 119          | 122          | 134          | 152             | 140             | 129             | 164             |
| Y          | 18.7         | 22.5         | 29.9         | 35.0         | 30.4         | 42.1            | 35.6            | 30.0            | 45.3            |
| Zr         | 52.0         | 65.5         | 95.4         | 111          | 99.4         | 171             | 119             | 105             | 155             |
| Nb         | 1.09         | 1.32         | 2.26         | 2.86         | 2.82         | 5.13            | 3.91            | 2.76            | 4.97            |
| Cs         | 0.095        | -            | -            | 0.112        | -            | 0.105           | 0.140           | -               | 0.142           |
| Ba         | 38.0         | 43.9         | 33.6         | 42.7         | 32.9         | 56.6            | 58.3            | 44.9            | 64.5            |
| La         | 2.29         | 2.69         | 3.47         | 4.25         | 3.95         | 7.73            | 5.51            | 4.60            | 6.88            |
| Ce         | 7.83         | 9.24         | 10.6         | 13.4         | 11.5         | 22.5            | 16.3            | 11.8            | 19.3            |
| Pr         | 1.29         | 1.52         | 1.81         | 2.28         | 1.93         | 2.95            | 2.50            | 2.00            | 3.00            |
| Nd         | 6.77         | 8.35         | 9.97         | 12.3         | 10.4         | 14.0            | 13.0            | 10.3            | 16.2            |
| Sm         | 2.27         | 2.76         | 3.51         | 4.19         | 3.58         | 4.20            | 4.36            | 3.33            | 5.16            |
| Eu         | 0.969        | 1.12         | 1.26         | 1.45         | 1.32         | 1.44            | 1.50            | 1.22            | 1.78            |
| Gd         | 3.01         | 3.57         | 4.68         | 5.31         | 4.91         | 5.64            | 5.45            | 4.72            | 6.98            |
### Electronic Appendix I con’t

| Sample | TN273-02W-01 | TN273-03W-02 | TN273-04W-01 | TN273-05W-01 | TN273-06W-01 | TN273-01D-01-01 | TN273-02D-01-02 | TN273-04D-01-02 | TN273-05D-01-01 |
|--------|---------------|---------------|---------------|---------------|---------------|-----------------|-----------------|-----------------|-----------------|
| Tb     | 0.522         | 0.629         | 0.851         | 0.910         | 0.864         | 0.942           | 0.966           | 0.867           | 1.15            |
| Dy     | 3.43          | 4.12          | 5.46          | 6.04          | 5.52          | 6.12            | 6.21            | 5.44            | 7.68            |
| Ho     | 0.710         | 0.850         | 1.23          | 1.30          | 1.20          | 1.36            | 1.30            | 1.21            | 1.64            |
| Er     | 2.02          | 2.46          | 3.52          | 3.72          | 3.60          | 3.76            | 3.73            | 3.53            | 4.81            |
| Tm     | 0.308         | 0.387         | 0.550         | 0.574         | 0.552         | 0.575           | 0.563           | 0.563           | 0.725           |
| Yb     | 2.05          | 2.68          | 3.52          | 3.88          | 3.42          | 3.45            | 3.84            | 3.54            | 4.67            |
| Lu     | 0.302         | 0.371         | 0.555         | 0.572         | 0.535         | 0.561           | 0.573           | 0.549           | 0.707           |
| Hf     | 1.39          | 1.73          | 2.53          | 2.88          | 2.65          | 3.18            | 2.94            | 2.88            | 3.82            |
| Ta     | 0.069         | 0.082         | 0.144         | 0.188         | 0.178         | 0.261           | 0.251           | 0.171           | 0.331           |
| Pb     | 0.903         | 1.06          | 0.900         | 1.09          | 0.788         | 0.876           | 1.26            | 0.757           | 1.30            |
| Th     | 0.131         | 0.163         | 0.214         | 0.257         | 0.247         | 0.449           | 0.388           | 0.365           | 0.511           |
| U      | 0.087         | 0.107         | 0.096         | 0.131         | 0.102         | 0.175           | 0.186           | 0.148           | 0.218           |
| Sample  | TN273-06D-01-03 | TN273-06D-02-02 | TN273-06D-03-03 | TN273-07D-01-01 | TN273-08D-01-01 | TN273-09D-01-03 | TN273-12D-01-01 | TN273-13D-01-01 |
|---------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Li      | 16.0           | 9.97           | 10.8           | 9.34           | 11.1           | 8.47           | 9.62           | 4.82           |
| Be      | 1.29           | 0.562          | 0.621          | 0.910          | -              | 0.697          | 0.666          | 0.357          |
| Sc      | 23.4           | 29.4           | 30.6           | 27.8           | 24.0           | 28.7           | 28.3           | 30.8           |
| V       | 178            | 416            | 413            | 332            | 168            | 301            | 297            | 296            |
| Cr      | -              | 4.87           | 3.24           | 8.43           | -              | 60.7           | 58.3           | 84.3           |
| Co      | 21.8           | 28.2           | 24.0           | 25.6           | 17.5           | 31.0           | 26.6           | 31.6           |
| Ni      | 2.27           | 2.97           | 3.26           | 4.50           | -              | 24.7           | 23.2           | 27.3           |
| Cu      | 16.4           | 69.7           | 63.21          | 26.9           | 13.9           | 42.4           | 37.5           | 98.6           |
| Zn      | 144            | 121            | 128            | 95.4           | 108            | 94.8           | 94.2           | 92.4           |
| Rb      | 10.01          | 5.06           | 5.07           | 3.70           | 7.68           | 4.36           | 4.71           | 4.22           |
| Sr      | 134            | 128            | 130            | 161            | 156            | 185            | 192            | 232            |
| Y       | 56.7           | 32.0           | 30.4           | 38.5           | 38.7           | 29.7           | 30.3           | 17.8           |
| Zr      | 240            | 101            | 95.4           | 143            | 140            | 111            | 108            | 73.3           |
| Nb      | 6.56           | 3.33           | 3.03           | 3.63           | 3.57           | 3.26           | 2.90           | 1.65           |
| Cs      | -              | -              | 0.135          | 0.054          | -              | -              | 0.079          | 0.095          |
| Ba      | 77.3           | 55.9           | 59.5           | 37.8           | 69.7           | 49.5           | 50.3           | 68.9           |
| La      | 10.53          | 4.35           | 4.49           | 5.86           | 6.21           | 5.62           | 5.19           | 4.71           |
| Ce      | 29.3           | 12.2           | 12.7           | 15.7           | 17.2           | 15.7           | 14.3           | 13.8           |
| Pr      | 4.52           | 2.04           | 2.04           | 2.65           | 2.71           | 2.42           | 2.31           | 1.68           |
| Nd      | 23.1           | 11.0           | 10.6           | 14.2           | 14.0           | 12.4           | 12.2           | 7.36           |
| Sm      | 7.10           | 3.83           | 3.75           | 4.58           | 4.64           | 3.89           | 3.94           | 2.14           |
| Eu      | 2.10           | 1.33           | 1.31           | 1.61           | 1.45           | 1.41           | 1.44           | 0.78           |
| Gd      | 9.27           | 4.95           | 4.55           | 6.16           | 6.21           | 5.01           | 4.84           | 2.53           |
### Electronic Appendix I con’t

| Sample | TN273-06D-01-03 | TN273-06D-02-02 | TN273-06D-03-03 | TN273-07D-01-01 | TN273-08D-01-01 | TN273-09D-01-03 | TN273-12D-01-01 | TN273-13D-01-01 |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Tb     | 1.60           | 0.913          | 0.816          | 1.04           | 1.01           | 0.874          | 0.825          | 0.427          |
| Dy     | 10.3           | 5.82           | 5.58           | 6.77           | 6.40           | 5.46           | 5.45           | 2.80           |
| Ho     | 2.29           | 1.32           | 1.19           | 1.46           | 1.44           | 1.20           | 1.13           | 0.590          |
| Er     | 6.65           | 3.72           | 3.50           | 4.19           | 4.54           | 3.47           | 3.21           | 1.64           |
| Tm     | 1.03           | 0.580          | 0.522          | 0.637          | 0.596          | 0.523          | 0.483          | 0.256          |
| Yb     | 6.51           | 3.69           | 3.49           | 4.12           | 4.25           | 3.31           | 3.33           | 1.52           |
| Lu     | 0.982          | 0.581          | 0.525          | 0.609          | 0.550          | 0.506          | 0.477          | 0.231          |
| Hf     | 6.13           | 2.64           | 2.47           | 3.50           | 3.59           | 2.82           | 2.76           | 1.52           |
| Ta     | 0.420          | 0.194          | 0.207          | 0.270          | 0.246          | 0.204          | 0.197          | 0.078          |
| Pb     | 1.79           | 1.21           | 1.19           | 0.983          | 1.46           | 1.03           | 1.05           | 0.950          |
| Th     | 0.844          | 0.327          | 0.347          | 0.422          | 0.588          | 0.451          | 0.452          | 0.461          |
| U      | 0.371          | 0.168          | 0.162          | 0.159          | 0.226          | 0.183          | 0.182          | 0.212          |

A "-" indicates a measured value below the detection limit of the analysis.
Table 1.9A (Electronic Appendix J): GeoROC references for whole rock data from Figs. A2-A6

| Volcanoes                | Citation                                                                 |
|-------------------------|--------------------------------------------------------------------------|
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|--------------|---------------------------------------------------------------------------------------------------|
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|              | backarc basin mantle. Earth Planet. Sci. Lett. 100. p. 251-264.                                   |
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| Agrigan,     | processes. Chem. Geol. 76. p. 1-24.                                                               |
| Sarigan,     | Gill J. B., Williams Ross W. [1990] Th isotope and U-Series studies of subduction related volcanic   |
| Pagan        | rocks. Geochem. Cosmochim. Acta. 54. p. 1427-1442.                                                 |
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| Agrigan,     | studies. Geophys. Res. Lett. 4. p. 465-468.                                                       |
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|              | 141. p. 453-472.                                                                                  |
| Volcanoes | Citation |
|-----------|----------|
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| Volcanoes | Citation |
|-----------|----------|
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Table 1.10A (Electronic Appendix K): Photomicrographs of melt inclusions to accompany the manuscript, “$\text{Fe}^{3+}/\Sigma\text{Fe}$ in Mariana Arc basalts and primary $fO_2$”.

| Sample | Plane polarized | Cross polarized | Reflected |
|--------|----------------|----------------|-----------|
| Sarigan |                |                |           |
| Sari15-04-01 | 300 µm |                |           |
| Sari15-04-03 | 300 µm |                |           |
| Sari15-04-04 | 300 µm |                |           |
| Sari15-04-07 | 300 µm |                |           |
| Sari15-04-10 | 300 µm |                |           |
| Sari15-04-11 | 300 µm |                |           |
| Sari15-04-13 | 300 µm |                |           |
| Sample      | Image 1 | Image 2 | Image 3 |
|-------------|---------|---------|---------|
| Sari15-04-15| ![Image](https://example.com/image1.png) | 300 µm |         |
| Sari15-04-17| ![Image](https://example.com/image2.png) | 300 µm |         |
| Sari15-04-18| ![Image](https://example.com/image3.png) | 300 µm |         |
| Sari15-04-19| ![Image](https://example.com/image4.png) | 300 µm |         |
| Sari15-04-21| ![Image](https://example.com/image5.png) | 300 µm |         |
| Sari15-04-22| ![Image](https://example.com/image6.png) | 300 µm |         |
| Sari15-04-23| ![Image](https://example.com/image7.png) | 300 µm |         |
| Sari15-04-24| ![Image](https://example.com/image8.png) | 300 µm |         |
|                | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
|----------------|----------------------|----------------------|----------------------|
| **Sari15-04-34** | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| **Sari15-04-35** | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |
| **Sari15-04-36** | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |

**Alamagan**

| Ala02-01 | No photos |
|----------|-----------|
| Ala02-02 | No photos |
| Ala02-03 | No photos |
| Ala02-04 | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) |
| Ala02-05 | ![Image](image16.png) | ![Image](image17.png) | ![Image](image18.png) |
| Ala02-06 | ![Image](image19.png) | ![Image](image20.png) | ![Image](image21.png) |
| Ala02-07 | ![Image](image22.png) | ![Image](image23.png) | ![Image](image24.png) |
| Ala02-08 | ![Image](image25.png) | ![Image](image26.png) | ![Image](image27.png) |
| Sample     | Images | Scale |
|------------|--------|-------|
| Gug23-02-03 | ![Image](image1.png) | 300 µm |
| Gug23-02-04 | ![Image](image2.png) | 300 µm |
| Gug11-02    | ![Image](image3.png) | 300 µm |
| Gug11-04    | ![Image](image4.png) | 300 µm |
| Gug11-05    | ![Image](image5.png) | 300 µm |
| Gug11-06    | ![Image](image6.png) | 300 µm |
| Gug11-08    | ![Image](image7.png) | 300 µm |
| Pagan       | ![Image](image8.png) | 300 µm |
| Paga8-02    | ![Image](image9.png) | 300 µm |
| Agrigan     | ![Image](image10.png) | No photos |
| Agri07-01   | ![Image](image11.png) | No photos |
| Agri07-04   | ![Image](image12.png) | No photos |
| Agri07-05 | ![Image](163) | ![Image](163) | ![Image](163) |
|-----------|----------------|----------------|----------------|
| Agri07-06 | ![Image](163) | ![Image](163) | ![Image](163) |
| Agri07-07 | ![Image](163) | ![Image](163) | ![Image](163) |
| Agri07-09 | ![Image](163) | ![Image](163) | ![Image](163) |
| Agri07-10 | ![Image](163) | ![Image](163) | ![Image](163) |
| Agri07-11 | ![Image](163) | ![Image](163) | ![Image](163) |
| Agri07-12 | ![Image](163) | ![Image](163) | ![Image](163) |
| Agri07-13 | ![Image](163) | ![Image](163) | ![Image](163) |
| Image     | Description |
|-----------|-------------|
| Agri07-14 |             |
| Agri07-15 |             |
| Agri05-01 |             |
| Agri05-04 |             |
| Agri04-03 |             |
| Agri04-05 |             |
| Agri04-07 |             |
| Agri04-11 |             |

300 µm
| Agri04-12 | 300 µm |
|-----------|--------|
| Agri04-13 | 300 µm |
| Agri04-14 | 300 µm |
| Agri04-15 | 300 µm |
MANUSCRIPT 2: TEMPORAL EVOLUTION OF MANTLE WEDGE OXYGEN FUGACITY DURING SUBDUCTION INITIATION

In preparation for submission to Nature

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Arc basalts have a higher proportion of oxidized Fe (Fe$^{3+}$) relative to reduced Fe (Fe$^{2+}$) compared to mid-ocean ridge basalts (MORB), likely because slab-derived fluids oxidize the mantle wedge where subduction zone magmas originate$^{1-7}$. Yet, the timescales over which oxygen fugacity of the mantle wedge changes during subduction initiation and margin evolution are unknown. Here, we show that mantle melts produced during the early stages of subduction initiation in the Mariana arc are ~3.5 times more oxidized than MORB and that mantle wedge oxygen fugacity rises as slab fluids become more dominant, increasing ~1.5 orders of magnitude, to conditions equivalent to the modern arc, in just 2-4 million years. These results constrain existing models for the geochemical evolution of the mantle wedge and suggest that oxidation commences upon subduction initiation and matures rapidly to a steady state. This further implies that sulfide or other reduced phases with the potential to oxidize are not present in the mantle wedge in high enough abundance to prevent oxidation of the resultant magmas upon subduction initiation. The arc mantle source is oxidized for the majority of a subduction zone’s lifetime, influencing the mobility of multi-valent elements during recycling, degassing of oxidized volcanic volatiles, and mechanisms for generating continental crust from the immediate onset of subduction.

Oxygen fugacity ($f_{O_2}$) is an intrinsic thermodynamic property that records the chemical activity of oxygen and controls the speciation of multi-valent elements in the solid Earth. The ratios of oxidized to total Fe (expressed as Fe$^{3+}$/ΣFe) in unaltered, basaltic samples from the modern Mariana arc reflect mantle wedge $f_{O_2}$ that is up to
1.8 orders of magnitude higher than for MORBs\textsuperscript{5,6,8}, which is linked to the influence of aqueous fluids released from the oxidized subducting oceanic lithosphere on the mantle wedge beneath the arc volcanoes\textsuperscript{2-7}. The timescales and material flux required to oxidize the wedge have been modeled\textsuperscript{9,10}, but lack observational constraints and thus the results of these models have big uncertainties. Here, we present the Fe\textsuperscript{3+}/ΣFe ratios of pristine submarine glass from basaltic pillow lavas that record the initiation and evolution of subduction along the Izu Bonin-Mariana (IBM) convergent margin, from 52 Ma to the modern Mariana arc. We use these data to determine the timescales over which the Mariana mantle wedge \( f_{O_2} \) became more oxidized than MORB source mantle. We also report the Fe\textsuperscript{3+}/ΣFe ratios of pristine, Jurassic age Pacific MORB glasses recovered from ODP Site 801C (Fig. 1a)\textsuperscript{11} as a reference showing the uniformity of the \( f_{O_2} \) of MORB source mantle over the past ~170 Ma.

Mafic pillow lavas from the IBM forearc south of Guam, from DSDP site 458 (central Mariana fore-arc), and from along the Bonin Ridge (Fig. 1a) record the initiation of the subduction of the Pacific plate 52-51 Ma and the subsequent temporal evolution of IBM arc volcanism\textsuperscript{12-14}. The volcanic section from oldest to youngest comprises fore-arc basalt pillow lavas (FAB; 51-52 Ma), transitional pillow lavas (48-49 Ma), boninitic pillow lavas (43-48 Ma), and “normal” arc lavas\textsuperscript{14} (<43 Ma, Fig. 1b). The FAB lavas reflect decompression melting that occurred as mantle rose to accommodate the sinking of the Pacific plate at the immediate onset of subduction\textsuperscript{12}. As the lavas become younger, they reflect increasing influence of aqueous slab fluids in the mantle wedge\textsuperscript{12}. The youngest group of lavas (<43 Ma) record the transition to normal arc lavas, similar in composition to the modern IBM volcanic arc\textsuperscript{12}. These
lavas were erupted in the submarine environment and samples included in this study have pristine glass along quench margins (Fig. 1b). We measured high precision Fe$^{3+}$/ΣFe ratios (±0.005) of five FAB, three boninite, and two Site 801 pillow glasses by micro-x-ray absorption near-edge structure (µ-XANES) spectroscopy (see supplement). Four early transitional pillow glasses from DSDP Site 458 were too micro-crystalline to obtain µ-XANES spectra free from crystal interference. For these samples, Fe$^{2+}$O determinations were done using micro-colorimetric procedures and combined with bulk glass FeO* concentrations to calculate Fe$^{3+}$/ΣFe ratios (1σ±0.02, see supplement). Although less precise, the results from micro-colorimetry are comparable to the results from µ-XANES (see supplement).

Jurassic-aged MORB glasses (Site 801; ~170 Ma) have Fe$^{3+}$/ΣFe ratios of 0.167 and fall within the modern MORB field in both major element composition and Fe redox (Fig. 2). The FAB glasses have Fe$^{3+}$/ΣFe ratios that range from 0.165 (overlapping with MORB) to 0.195 (slightly more oxidized than MORB) and span a wide range in compositions from 7.56-2.75 wt% MgO (Fig. 2). Early transitional glasses are more oxidized, with Fe$^{3+}$/ΣFe ratios that range from 0.202-0.249 at 4.56 – 7.56 wt% MgO, which overlap entirely with modern Mariana arc basalts and are significantly more oxidized than MORB or Mariana trough glasses (Fig. 2). The boninite glasses have slightly lower Fe$^{3+}$/ΣFe ratios (0.210-0.220), consistent with the transitional glass with the lowest MgO content. The black and gray lines in figure 2 are modeled liquid lines of descent that show the expected change in Fe$^{3+}$/ΣFe ratios during crystal fractionation in a system closed to oxygen (unbuffered) for modern back-arc and arc magmas (see supplement). It is apparent from Fig. 2 that although
fractionation undoubtedly played a small role in modifying the Fe\textsuperscript{3+}/\Sigma Fe ratios of these glasses (Fig. 2, see supplement), the elevated Fe\textsuperscript{3+}/\Sigma Fe ratios of boninite and transitional glasses are unrelated to the Fe\textsuperscript{3+}/\Sigma Fe ratios of FAB or MORB, and cannot be generated by shallow level crystal fractionation of a reduced primary melt. This is similar to the case of modern Mariana back-arc and arc samples\textsuperscript{6} and suggests that there were fundamental differences in the fO\textsubscript{2} of the mantle sources that produced these magmas.

The major element relationships for these samples indicate that a simple linear correction is valid to account for variations during differentiation down to relatively low MgO concentrations, so we calculated primary melt compositions and Fe\textsuperscript{3+}/\Sigma Fe ratios for all samples with MgO>4.5 wt\% (see supplement). Using the corrected major element compositions, we calculate primary melt fO\textsubscript{2} relative to the quartz-fayalite-magnetite (QFM) buffer at pressure and temperature according to Frost (1991) using the algorithm of Kress and Carmichael (1991). We pair the calculated primary melt fO\textsubscript{2}s with the measured Ba/La ratio in each sample in order to assess the influence that aqueous, slab-derived fluids have had on mantle wedge fO\textsubscript{2} through time. Barium is mobilized in aqueous fluids preferentially over melt-mobile La, such that the ratio of Ba to La in erupted subduction-related lavas reflects the influence of slab-derived fluids in the mantle wedge. During subduction initiation, the increasingly important role of slab-derived fluids in melt generation processes is recorded in the increasing Ba/La ratios of FAB, transitional, and boninite lavas from the Mariana forearc.

Primary Jurassic-aged MORBs from ODP Site 801C have Ba/La ratios that range from 3.8 to 4.5 and fO\textsubscript{2} from QFM to +0.08, similar to modern MORB primary
melts. This indicates that there has been no change in the $f_O^2$ of MORB source mantle from Jurassic to present day (Fig. 3a). Primary FAB melts have Ba/La ratios that range from 4.3-10.3 and $f_O^2$ from QFM+0.05 to +0.4, which overlaps MORB primary melts at the low end but extends to slightly higher Ba/La ratios and $f_O^2$. This suggests that there are small additions from the subducted slab during melt generation processes at the immediate onset of subduction in the Marianas (Fig 3a, b). Primary transitional melts have high Ba/La ratios (24-39) and $f_O^2$ (QFM+1.4-QFM+1.6), demonstrating that within 2-4 my of FAB eruption, slab fluids play a significant role in melt generation processes and are capable of producing melts with $f_O^2$ ~QFM+1.5, which are as oxidized as lavas erupted at the modern Mariana arc. Primary boninite melts have Ba/La ratios and $f_O^2$ (19-26, QFM+1.4) that are consistent with those of transitional melts.

Recent studies show a positive correlation between Ba/La ratio and primary melt $f_O^2$ from the modern Mariana back-arc to the arc (pale symbols, Fig. 3a), linking the oxidation conditions of back-arc and arc basalts to slab fluid influence$^{4,6}$. The positive relationship between Ba/La ratio and primary melt $f_O^2$ for samples in this study (Fig. 3a) is consistent with observations for the modern Mariana subduction system, demonstrating that slab fluids play an important role in oxidizing the portion of the mantle wedge that produces arc magmas, from the onset of subduction. Recent studies have calculated “redox budgets”, or fluxes for multivalent elements in subduction systems, by comparing the bulk (average) oxidation state and rate of input of downgoing materials (altered oceanic lithosphere + sediments) to the bulk oxidation state and rate of output of erupted arc lavas$^{9,10}$. Because redox budget is an extensive
parameter that can change when oxidized or reduced species are added to the mantle wedge, these studies relate redox budget to mantle source \( fO_2 \) and to changes in this \( fO_2 \) through time\(^9,10\). There is a wide range of possible model outcomes that arise due to variability in the composition and distribution of seafloor sediments and the extent of alteration in oceanic lithosphere, due to uncertainties in the rate of arc crustal growth and due to mechanisms of fluid or melt migration in the mantle wedge. For example, in Phanerozoic mantle, these models predict that the mantle wedge becomes 0-3 orders of magnitude more oxidized than QFM (the \( fO_2 \) of MORB source mantle\(^8\)) on 10,000 to several million year time scales\(^9,10\). Results from our study place observational constraints on these model outcomes, yielding first-order agreement with redox budget models for a hydrous, sulfur free mantle wedge (Fig. 3b)\(^9,10\). This supports the conclusion that portions of the mantle wedge in subduction zones become oxidized as the result of influence from subducting slabs, specifically from transferring oxidized species (e.g., \( S^{6+}, Fe^{3+} \)) from downgoing slabs in aqueous slab fluids. It also suggests that sulfur may not be present in the mantle wedge in high enough abundance (e.g., 1 wt %, see thick dashed line, Fig. 3b) to inhibit slab fluids from oxidizing the mantle wedge during subduction.

The rapid timescales of slab material transfer and subsequent oxidation of the zone of melt generation in the mantle wedge that we have constrained here (14x increase in \( fO_2 \) in 2-4 my) have implications for the mechanisms of generating oxidized arc basalts and for the lifetime of redox sensitive volcanic processes during active subduction. We show that there is negligible delay between the onset of slab fluid transfer and the eruption of oxidized arc basalts. In the 2-4 my between the
eruption of FAB and transitional basalts, the slab may have achieved pressure-
temperature conditions that enable the transfer of slab fluids into the mantle wedge
that is analogous to the modern Mariana subduction system. This may also signal the
start of true down-dip subduction, such that the next magmas to erupt, the boninites,
show a similar relationship between slab fluid influence (e.g., Ba/La) and oxidation as
the modern subduction system. These observations show that mechanisms for material
transfer from the subducted slab, specifically the communication of oxidizing
conditions in subducting plates through the subduction system, develop rapidly upon
the initiation of subduction. Subduction zone processes that depend upon oxidized
mantle wedge conditions, such as the production of Fe-depleted continental crust\(^{20}\), are
likely active for the entire lifetime of a subduction zone.

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Figure 2.1 (a) Individual symbols along the Mariana arc and trough show the sample locations for modern (zero-age) samples. The white diamond is the location of ODP Site 801, where pristine Jurassic aged MORB glass was recovered\textsuperscript{11}. The basemap was created using GeoMapApp (http://www.geomapapp.org)\textsuperscript{21}. 

**Volcanic stratigraphy**

- "Normal" arc lavas
- boninites
- Transitional basalt
- FAB
- Gabbro
- Peridotite

![Volcanic stratigraphy diagram](image)
Figure 2.2 A plot of Fe$^{3+}$/ΣFe ratios vs. MgO concentrations for samples in this study. The black field represents a global set of fresh MORB glass. The gray and yellow fields represent modern Mariana trough and arc (respectively) samples. The black and gray lines are modeled liquid lines of descent (see supplement) that demonstrate the expected variation in Fe redox during crystal fractionation in a system closed to oxygen.
Figure 2.3 Mantle $f_O^2$ relative to the QFM oxygen buffer vs. (a) Ba/La ratio and (b) time (millions of years) since subduction initiation. Semi-transparent symbols are modern MORB, Mariana trough, and Mariana arc volcanic glasses. The dashed black line is a linear regression through the modern glasses ($R^2 = 0.86$). The heavy solid and dashed black lines are redox budget models for Phanerozoic mantle$^9$. Symbols are as in Figures 1 and 2.
Supplementary text to accompany the manuscript, “The evolution of mantle wedge oxygen fugacity during subduction initiation”

Methods Summary

We determined Fe$^{3+}$/ΣFe ratios of pillow glass by micro-x-ray absorption near-edge structure (µ-XANES) spectroscopy at beamline X26A, National Synchrotron Light Source, Brookhaven National Laboratory\textsuperscript{1}. Spectra were collected in fluorescence mode from 7020 eV to 7220 eV using a Si [311] monochromator and a nominal beam size of 9x5 µm. LW-0 was monitored continuously during each experimental session to correct for instrument drift. Spectra were scrutinized for any influence from phenocrysts or micro-phenocrysts in the glass chips and inclusions. Determinations of Fe$^{3+}$/ΣFe ratios following these methods have an associated precision of ±0.005\textsuperscript{1}.

In some cases, pillow glasses were too micro-crystalline to obtain optically clear paths of glass and µ-XANES was unsuitable for determination of Fe$^{3+}$/ΣFe ratios. For these samples, Fe$^{2+}$O\textsubscript{(actual)} determinations were done using micro-colorimetric procedures\textsuperscript{2,3}. Four USGS powdered rock standards were run during each analytical session. Analyses of these USGS standards never deviated from the certified Fe$^{2+}$O\textsubscript{(actual)} content by more than 0.20 wt% (absolute), within the established analytical precision of ±0.22 wt% (absolute). Whole glass FeO* determinations were then used with Fe$^{2+}$O\textsubscript{(actual)} concentrations to calculate Fe$^{3+}$/ΣFe ratios\textsuperscript{4}.

We take the results from both techniques to be equivalent and directly comparable. Other studies have observed an offset between these methods in natural
MORB glasses, where micro-colorimetric determinations yield more reduced Fe$^{3+}$/ΣFe ratios than XANES determinations$^5$. The origin of this offset in MORB glasses may arise due to the inclusion of olivine in the wet chemical dissolutions, or to an interfering redox couple (e.g., Fe-S) that affects the wet chemical determinations of natural basalts. The samples that we performed micro-colorimetry on, DSDP 458 glasses, have a mineral mode that is dominated by plagioclase, however, which should have no effect on the bulk Fe$^{3+}$/ΣFe ratios of these samples. We are combining bulk glass FeO* determinations from$^4$ with bulk glass Fe$^{2+}$O$_{\text{actual}}$ determinations on the same glass chips, so we expect no offset to arise as the result of combining FeO* determinations on glass with bulk glass Fe$^{2+}$O$_{\text{actual}}$ determinations that represent a mixture of true glass and microphenocrysts. The sulfur content of these glasses are not known, although the sum of their major element concentrations (>98.3 wt%) indicates that they are significantly degassed by the time of eruption. Although the influence of sulfur on wet chemical determinations of Fe$^{2+}$ is tenuous, if the sulfur contents of these glasses are high enough to influence the wet chemistry results, we would expect wet chemistry to yield more reduced Fe$^{3+}$/ΣFe ratios than μ-XANES results. In this case, our determinations of the Fe$^{3+}$/ΣFe ratios for the DSDP glasses are a lower limit estimate of their true magmatic Fe$^{3+}$/ΣFe ratios.

Subduction influence

Basaltic lavas from the Izu-Bonin-Mariana forearc record subduction initiation and the evolution of melt generation, from primarily decompression melting and minor traces of slab fluid influence to significant slab fluid influence and flux
melting. This is evident in their trace element compositions (S. Fig. 1). The trace element signatures of FAB glasses are similar to NMORB, with enrichments in elements typical of influence from fluids released from subducting slabs (Fig. 1a; e.g., Rb, Ba, Th, U). They overlap with modern Mariana trough basalts in Figure 1b, potentially mixing to a fluid composition that is similar to the composition of fluids that influence modern back-arc magmatism in the Marianas. Transitional basalts are uniformly depleted from Nb to Lu relative to FAB and NMORB, suggesting that these magmas represent the generation of higher melt fractions in the mantle wedge at this time. Fluid mobile trace elements in these samples, such as Rb, K, Ba, Pb, and U are enriched over NMORB and FAB, and significantly enriched relative to trace elements more compatible than Nb in the same samples. The transitional glasses with the highest Ba/La ratio overlap distinctly with modern Mariana arc glasses, and may mix to fluids of broadly similar compositions. The transitional glass with the lowest Ba/La ratio looks more similar to Mariana trough samples, but extends to higher Ba/La and Sm/La ratios. The boninite glasses are the most similar of all fore arc samples to the trace element patterns of modern arc basalts (S. Fig. 1a, yellow field). Their Ba/La and Sm/La ratios are consistent with modern arc basalts. Jurassic aged glass from ODP Site 801C have trace element contents that are slightly enriched over NMORB, entirely consistent with the composition of enriched basalts from the Pacific seafloor.

**Liquid lines of descent**

Figure 2 in the main text shows model liquid lines of descent (LLD) for two parental melt compositions, generated using PetroLog3. The white star is a naturally
glassy, olivine-hosted melt inclusion composition from Sarigan volcano (Sari15-04-27)\(^7\). The gray star is the composition of a submarine pillow glass (80-1-3)\(^9\). Both models replicate major element trends for available published data from Sarigan volcano (black line) and the Mariana trough (dashed gray line) as closely as possible. To model the extent to which Fe redox varies as the result of crystal fractionation, these models are generated as systems closed to oxygen. Details related to these models can be found in the supplementary material from Brounce et al (submitted). Broadly, the model represented by the black line demonstrates the expected variation in magmatic \(\text{Fe}^{3+}/\Sigma \text{Fe}\) ratios during olivine ± clinopyroxene ± plagioclase fractionation from hydrous arc magmas. The gray dashed line demonstrates the expected variation in magmatic \(\text{Fe}^{3+}/\Sigma \text{Fe}\) ratios during olivine ± plagioclase ± clinopyroxene ± magnetite fractionation from back-arc magmas. Similar to the modern Mariana back-arc and arc, none of the compositions of FAB, transitional, or boninite glasses are consistent with these models. Instead of the pattern of fractionation-induced oxidation, transitional and boninite samples appear to become more reduced as MgO concentrations decrease.

**Reconstructing primary melt compositions**

Primary melt compositions (i.e., in equilibrium with mantle olivine at Fo90), were reconstructed using data defined liquid lines of descent (Supplementary figure 2). Major element relationships for FAB, transitional, and boninite glasses were used to calculate the primary magma compositions for each sample with MgO > 4.5 wt% (black dashed line in supplementary figure 2 marks the position of MgO = 4.5 wt%).
Each composition was projected back to MgO = 7.0 wt% using the slope defined by the natural data between 5 and 7 wt% MgO for all major elements (S. Fig. 2). For Fe, FeO\textsubscript{(actual)} and Fe\textsubscript{2}O\textsubscript{3(actual)} concentrations were plotted versus MgO concentration and projected back along the slopes of lines defined by the natural data for each sample suite. The slopes of these lines are shown for each element on supplementary figure 2. FAB compositions were corrected along the slope of a line defined by only FAB samples. Transitional basalt and boninite samples were corrected back along the slope of a line defined by transitional basalt compositions. Once at MgO = 7.0 wt%, olivine of equilibrium composition was added to each composition in 0.1% increments until in equilibrium with Fo\textsubscript{90} olivine. Primary $f$O\textsubscript{2} was calculated relative to the QFM buffer calculated at 1200°C, 1 atm, and at 1300°C, 1 GPa (Supplementary Table 1)\textsuperscript{10,11}.

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Figure 2.1A (a) Spider diagram for FAB, transitional, boninite, and ODP Site 801C glasses. All samples are normalized to NMORB\(^{12}\). The yellow field represents the trace element patterns of modern Mariana arc basalts\(^{7}\). (b) Plot of Ba/La ratios vs. Sm/La ratios. The light gray field represents Pacific MORB data\(^{13}\), the dark gray and yellow fields represent modern Mariana back-arc and arc data, respectively\(^{7}\). The dashed black lines represent approximate mixing lines to slab fluids of unknown composition.
**Figure 2.2A** Major element variations for samples in this study. Dark and light gray triangles are data for the modern Mariana trough for comparison. The black, purple, and green lines are linear regressions through data with MgO >4.5 wt%. Their slopes and $R^2$ values are shown on the plot in corresponding font color. The black dashed line marks the position of MgO = 4.5 wt%. Samples with MgO lower than this value were not considered in the calculation of primary melt composition.
Table 2.1 (Supplementary Table 1). Fe$^{3+}$/ΣFe ratios for Mariana forearc submarine glasses

| Sample          | Type             | age (my) | Method         | Fe$^{3+}$/ΣFe | 1σ   | primary f$O_2$ at 1200°C, 1 atm (ΔQFM) | primary f$O_2$ at 1350°C, 1 GPa (ΔQFM) | Ba/La |
|-----------------|------------------|----------|----------------|---------------|------|----------------------------------------|----------------------------------------|-------|
| 801C28R2-118    | MORB             | ~170     | Fe-µ-XANES     | 0.167         | 0.001| -0.17                                  | 0.08                                   | 4.5   |
| 801C46R1-45     | MORB             | ~170     | Fe-µ-XANES     | 0.168         | 0.001| -0.25                                  | 0.00                                   | 3.8   |
| 459-65B-1g      | FAB              | 51-52    | Fe-µ-XANES     | 0.195         | 0.004| -                                      |                                        |       |
| 974-R9g         | FAB              | 51-52    | Fe-µ-XANES     | 0.181         | 0.003| 0.13                                   | 0.38                                   | 9.3   |
| 974-R10g        | FAB              | 51-52    | Fe-µ-XANES     | 0.182         | 0.004| 0.12                                   | 0.37                                   | 9.0   |
| 975-R22g        | FAB              | 51-52    | Fe-µ-XANES     | 0.173         | 0.002| 0.04                                   | 0.29                                   | 4.6   |
| 6K1153-R09      | FAB              | 51-52    | Fe-µ-XANES     | 0.165         | 0.008| -0.21                                  | 0.05                                   | 4.3   |
| 458-28-1g       | early transitional | 48-49 | colorimetry    | 0.238         | 0.019| 1.21                                   | 1.46                                   | 39.1  |
| 458-43-1g       | early transitional | 48-49 | colorimetry    | 0.249         | 0.023| 1.30                                   | 1.55                                   | 24.0  |
| 458-43-2g       | early transitional | 48-49 | colorimetry    | 0.202         | -    | 1.10                                   | 1.35                                   |       |
| 458-39-1g       | early transitional | 48-49 | colorimetry    | 0.246         | 0.006| 1.22                                   | 1.47                                   | 35.0  |
| GUM02-35        | transitional (late transitional) | 43-46 | Fe-µ-XANES     | 0.220         | 0.003| 1.12                                   | 1.38                                   | 22.8  |
| GUM02-06        | transitional (late transitional) | 43-46 | Fe-µ-XANES     | 0.210         | 0.001| -                                      |                                        | 25.8  |
| GUM02-32        | transitional     | 43-46    | Fe-µ-XANES     | 0.221         | 0.009| 1.16                                   | 1.41                                   | 18.8  |
MANUSCRIPT 3: A review of transition row element proxies for mantle source oxygen fugacity

In preparation for submission to Earth and Planetary Science Letters

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Abstract

Several proxies exist for quantifying mantle oxygen fugacity ($fO_2$) from the chemistry of erupted basalts. Each proxy, however, presents a contrasting view of the $fO_2$ of the upper mantle when applied to lavas from a range of tectonic settings, such that the fundamental questions of the magnitude of upper mantle oxygen fugacity and whether it varies across tectonic settings remain a matter of significant debate. We use $Fe^{3+}/ΣFe$ ratios and trace element compositions of natural melt inclusions, their olivine hosts, and submarine glasses to compare several proxies (Cu, $D_V^{ol/melt}$, and $Zn/Fe^*$, $V/Sc$, $V/Yb$, and $Fe^{3+}/ΣFe$ ratios) for calculating mantle source oxygen fugacity for mid-ocean ridge, Mariana trough, and Mariana arc basalts using a common sample suite. For MORB and Mariana trough samples, results from $Fe^{3+}/ΣFe$ ratios, $V/Sc$ ratios, $V/Yb$ ratios and primary melt Cu concentrations are consistent with a source mantle between QFM-1 and QFM+0.8. The $Zn/Fe^*$ proxy is highly sensitive to mantle source composition (i.e., $Zn/Fe^*$ of mantle source rocks) and as a result, can only be applied to a small number of MORB and none of the Mariana trough samples in our dataset. For these few MORB samples, the $Zn/Fe^*$ ratio proxy suggests that MORB primary melts have $Fe^{3+}/ΣFe$ ratios that are between 0.12 and 0.19, broadly consistent with results from Fe-XANES measurements. In the case of the Mariana arc, these proxies yield a variety of results. The $Fe^{3+}/ΣFe$ ratio proxy suggests that arc magmas originate from a mantle source with $fO_2$ of QFM+1– QFM+2. The $D_V^{ol/melt}$ proxy, applied to olivine hosted melt inclusions from sub-aerially erupted tephras, indicates that Mariana arc magmas have $fO_2 > QFM+2.0$ at the time of olivine crystallization. These results are systematically offset to higher magmatic $fO_2$ than
those calculated from the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios measured on the inclusions, suggesting that the relationship between vanadium partitioning and magmatic $f_{O_2}$ is not well constrained for natural basalt compositions. The trace element compositions of Mariana arc magmas suggest that V, Sc, Zn, and Cu all behave more incompatibly during melting in the mantle wedge than during melting in MOR settings, and that the mantle wedge may have different initial bulk concentrations of these elements, independent of $f_{O_2}$. Variations in the mantle source composition do not significantly affect the results of the V/Sc ratio proxy for $f_{O_2}$, however variations in the mineral mode that change the bulk partition coefficients for V and Sc can be important, particularly as clinopyroxene mode decreases (i.e., during melting). We show that low V/Sc ratios of arc basalts need not preclude oxidized conditions in the mantle source for Mariana arc lavas. Unlike Sc, Yb is incompatible in all mantle phases and as a result, the V/Yb ratio proxy records source mantle for arc magmas with $f_{O_2}$ between QFM and QFM+2, regardless of model variations. The Cu proxy is sensitive to both Cu and S contents of the source, which are not well constrained for subduction zone mantle. Depending on the values chosen, the Cu proxy suggests that arc basalts originate from a source mantle between QFM and QMF+2. The Zn/Fe* proxy cannot be applied to any arc samples in this study unless the source mantle has greater heterogeneity in Zn/Fe* ratios than previously thought. After comparing these proxies on a common sample suite, we find that each consistently records mantle source $f_{O_2}$ of ~QFM for global MORB and Mariana trough basalts. The mantle source $f_{O_2}$ for Mariana arc magmas varies from QFM+1 to QFM+3 for Fe-based and $D_v^{\text{oliv/melt}}$ proxies, from QFM to QFM+2 for the V/Yb and Cu proxies, and $\geq$QFM for the V/Sc proxies.
proxy. To improve these estimates for arc mantle, more work on the mobility of transition row elements during subduction is necessary.

1. INTRODUCTION

Oxygen fugacity ($f_{O_2}$) is a fundamental thermodynamic property that represents the availability of oxygen to govern reduction-oxidation (redox) equilibria in the solid Earth. For example, Fe in silicate melts exists as a mixture of reduced ($Fe^{2+}$) and oxidized ($Fe^{3+}$) species (expressed as $Fe^{3+}/ΣFe$), where the proportion of each species present in the melt can be related to $f_{O_2}$ using the simple equilibrium,

$$2Fe^{2+}O + \frac{1}{2}O_2 = Fe^{3+}O_3$$

(1).

By governing the proportions of multi-valent species in magmatic systems, $f_{O_2}$ can influence elemental partitioning behaviors during melting, crystallization, and degassing (Canil, 2002; Frost and McCammon, 2008; Kelley and Cottrell, 2012; Stagno et al., 2013).

Despite its key importance in petrogenetic processes, $f_{O_2}$ has been difficult to constrain in natural igneous systems because it cannot be directly measured. Instead, we rely on calibrated proxies, such as the direct speciation or crystal/liquid partitioning behavior of multi-valent elements, as records of magmatic and mantle $f_{O_2}$.

Classically, Fe redox ratios (i.e., $Fe^{3+/ΣFe}$) recorded in erupted basaltic lavas have been used to constrain mantle source $f_{O_2}$ in mid-ocean ridge and arc settings (e.g., Carmichael, 1991; Christie et al., 1986), showing that the mantle source for mid-ocean ridge basalts (MORB) have $f_{O_2}$ ~ one to two log units more reduced than the quartz-fayalite-magnetite oxygen buffer (QFM-1 to QFM-2) and QFM+1 to QFM+4 for the mantle source of arc basalts. These Fe redox ratios were obtained using wet chemical
titration techniques on whole rock erupted lavas, which present significant analytical challenges (e.g., Bezos and Humler, 2005) and natural bulk samples analyzed using wet chemical titrations may not yield magmatic Fe$^{3+}$/ΣFe ratios due to crystal accumulation or other analytical interferences (e.g., Cottrell and Kelley, 2011). Given the potential for composition changes in crustal magma chambers, the relevance of whole-rock Fe$^{3+}$/ΣFe ratios to the fO$_2$ of the mantle source has also been questioned (e.g., Lee et al., 2005). More recently, trace element proxies (e.g., V-based, Cu, and Zn/Fe*) have been developed to avoid the challenges of magmatic redox changes during differentiation processes and alteration of Fe$^{3+}$/ΣFe ratios during weathering, and provide ease of use by exploiting commonly-measured trace elements (Jackson et al., 2010; Laubier et al., 2014; Lee et al., 2005; Lee et al., 2012; Lee et al., 2010; Mallmann and O'Neil, 2013). These proxies are designed to avoid the effects of differentiation, such that the measured trace element composition of the lava reflects only information related to the mantle source. They require knowledge of the mantle source composition, mineral mode, and mechanism for melting, all of which can be difficult to constrain in some tectonic settings (e.g., subduction zones). Considering all of these proxies, the current view of fO$_2$ in the upper mantle varies widely. The V/Sc, Zn/Fe*, and Cu-based proxies all suggest that the fO$_2$ of the upper mantle is homogeneous and independent of tectonic setting, though the specific value for upper mantle fO$_2$ varies with each proxy. The V/Sc ratio predicts fO$_2$ for the upper mantle between QFM-1 and QFM+1 (Lee et al., 2005), Zn/Fe* ratio predicts fO$_2$ between QFM-2 and QFM+2 (Lee et al., 2010), and the Cu-based proxy predicts fO$_2$ between QFM-2 and QFM (Lee et al., 2012; Fig. 1a). Like the Fe-based proxy, the V/Yb ratio
and $D_{V}^{\text{olv/melt}}$ proxies suggest instead that the $f_{O_2}$ of the upper mantle is heterogeneous, though each of these proxies presents a wide range in values for $f_{O_2}$, particularly in subduction settings. According to the V/Yb proxy, MORB mantle has $f_{O_2} \approx \text{QFM-1}$ and arc mantle is between QFM-1 and QFM+3 (Laubier et al., 2014). Much less data exists for assessing the $D_{V}^{\text{olv/melt}}$ proxy in natural settings, but the few existing data suggest that MORB mantle has $f_{O_2}$ between QFM and QFM+1, while arc mantle is between QFM+1.5 and QFM+3 (Kelley and Cottrell, 2012; Mallmann and O'Neill, 2013; Fig. 1a).

Across these various proxies, we find an uncertainty of four orders of magnitude for the $f_{O_2}$ of MORB source mantle and uncertainty of five or more orders of magnitude for arc source mantle. A fundamental motivating question thus remains, what is the $f_{O_2}$ of the upper mantle, and is it heterogeneous with respect to tectonic setting? Here, we test several proxies for constraining mantle $f_{O_2}$ in basaltic systems by applying the proxies to the same set of samples. We compare the $f_{O_2}$ derived via these proxies on basaltic samples from MORB, the Mariana trough back-arc spreading center, and Mariana arc volcanoes in order to trace the origins of discrepancies between transition element proxies for $f_{O_2}$. We show that careful accounting of model uncertainties related to element mobility in subduction zones and variations in partition coefficients in concert with examination of large datasets on a volcano-to-volcano basis, may reconcile the perceived discrepancies between many of these proxies. Our assessment taken as sum points towards an upper mantle that is heterogeneous in $f_{O_2}$ as a function of tectonic setting.
2. METHODS AND DATA TREATMENT

Terry Plank generously donated bulk tephra powders from several Mariana arc volcanoes (Agrigan, Alamagan, Sarigan, Pagan, Guguan, Uracas, Anatahan, and Maug) to this study. These tephras were originally collected by an NSF-MARGINS joint field expedition to the Marianas (http://sio.ucsd.edu/marianas) and powders were made following the techniques outlined by Wade et al. (2005).

This work makes use of previously published major, trace, and volatile element concentrations and Fe\(^{3+}/\Sigma\)Fe ratios (Fe-\(\mu\)-XANES) for submarine glass and olivine hosted melt inclusions. The arc dataset consists of olivine hosted melt inclusions that originate from eight Mariana arc tephra samples from five volcanoes (Sarigan, Guguan, Alamagan, Agrigan, Pagan). We also include submarine glasses from Pagan and NW Rota-1 volcanoes (Brounce et al., revised; Tamura et al., 2013; Tamura et al., 2011). We use submarine glasses from the Malaguana-Gadao segment of the southern Mariana trough (Brounce et al., revised) and from the northern Mariana trough (18.1° - 20.9°N; Kelley and Cottrell, 2009; Newman et al., 2000; Pearce et al., 2005; Stolper and Newman, 1994) for the back-arc basin basalt dataset. For MORB, we use a global distribution of samples (Cottrell and Kelley, 2011 and references therein; Cottrell and Kelley, 2013). The Fe\(^{3+}/\Sigma\)Fe ratios and trace element concentrations were all determined using the same analytical procedures in the same laboratories, thus producing an internally consistent compiled data set.

2.2 Analytical methods

We present new minor and trace element analyses collected on the olivine hosts of the melt inclusions discussed in section 2.1. The concentrations of minor and
trace elements were determined using laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) at the Graduate School of Oceanography, University of Rhode Island. Details on analytical procedures and complete data tables are provided in the electronic supplement.

We also present new wet chemical titrations for Fe$_2^+$O$_{\text{actual}}$ using micro-colorimetric techniques outlined by Wilson (1960) and modified by Carmichael (2014) at the Smithsonian Institution. Four USGS powdered rock standards (W-2, QLO-1, BCR-1, and BIR-1) were run during each analytical session. Analyses of these USGS standards never deviated from the certified Fe$_2^+$O$_{\text{actual}}$ content by more than 0.35 wt% (absolute) for standards with Fe$_2^+$O$_{\text{actual}}$ >8 wt%, and by more than 0.46 wt% (absolute) for QLO-1 (Fe$_2^+$O$_{\text{actual}}$ = 3.43 wt%). These errors are slightly higher than the analytical precision of ±0.22 w% (absolute) reported by Christie et al. (1986), and we attribute this to random error introduced during the weighing of powders and transfer to Teflon digestion vials. The mass of sample required for micro-colorimetry is small (2-6 mg) and must be known precisely (±10 µg). For QLO-1, misreporting the mass of sample by 0.1 mg translates into differences of 0.08 wt% in the calculated Fe$_2^+$O$_{\text{actual}}$ concentrations. Therefore, if sample is lost during transfer of the powder from the weigh boat into the Teflon vial, or if powder is lost at any time from the Teflon vial, large errors can be introduced. The calculated error for each batch is reported in Table 1 and representative error bars are shown on figures where the data appear. These data were combined with whole rock FeO* determinations on the same powders (Plank, unpublished ICP-AES data) to calculate Fe$^{3+}$/ΣFe ratios.

2.3 Data Treatment
2.3.1 Determining inclusion/olivine equilibrium and post-entrapment crystallization

We use only olivine host-melt inclusion pairs that satisfy the screening tests of Brounce et al. (revised), the results of which we summarize briefly here. Further details can be found in the supplementary material. Equilibrium host forsterite contents (Fo) were calculated for melt inclusions and compared to the measured Fo for the olivine host of each inclusion using a FeO/MgO $K_{\text{olv/liq}}^\text{Fo} = 0.3$ (Roeder and Emslie, 1970). We use only those melt inclusions that have $F_{\text{oinclusion}}$ that are within 2% of the value of the $F_{\text{ohost}}$. Melt inclusion compositions that reflect $F_{\text{oinclusion}} < F_{\text{ohost}}$, but within the 2% difference limit, were subject to the mathematical addition of calculated equilibrium olivine to the inclusion major element composition in 0.1% increments until the $F_{\text{oinclusion}}$ and $F_{\text{ohost}}$ were equal. Additionally, each melt inclusion suite was compared to published whole rock and melt inclusion major element data for each volcano. Inclusion compositions that deviate significantly from the major element relationships defined by the available published data were excluded.

2.3.2 Model liquid lines of descent and primary melt calculations

Arc and back-arc LLDs

Variations in major element concentrations due to fractional crystallization for melt inclusion and submarine glass suites were constrained either using Petrolog3 (Danyushevsky and Plechov, 2011) or empirical trends in the natural data and presented by Brounce et al. (revised). Melt compositions in equilibrium with mantle olivine at Fo$_{90}$, which we refer to here as primary melt compositions, were reconstructed for each sample with MgO > 5 wt%, using methods modified after Klein and Langmuir (1987). Each composition was projected back in composition to MgO =
7.0 wt% using the slope of the fractionation model or the natural data between 5 and 7 wt% MgO for all major elements. Where the fractionation model was poorly fit to the most incompatible elements (e.g., P₂O₅), and FeO(actual) and Fe₂O₃(actual), the slope of a line defined by the natural data between 5 and 7 wt% MgO was used instead. Once at MgO = 7 wt%, each composition was subject to the addition of equilibrium composition olivine in 0.1% increments until in equilibrium with Fo₉₀ olivine. Details of these models and primary melt composition calculations can be found in Brounce et al. (revised).

Trace elements V, Sc, Yb, and Zn were not corrected for the effects of fractional crystallization in arc and back-arc basalts. Their respective proxies for fO₂ are designed to be unaffected by low-pressure crystal fractionation and volcanic degassing and, accordingly, there is little systematic variation in V/Sc and Zn/Fe* ratios with decreasing MgO (Fig. 2b, d) for samples with >5 wt% MgO. This is not as clear for V/Yb ratios, which will be discussed later. Copper concentrations, however, either increase with decreasing MgO due to its incompatibility in fractionating silicate phases or decrease strongly with decreasing MgO if the magma reaches sulfide saturation. To correct for these processes, we projected the Cu concentration of each sample with MgO between 5 and 7 wt% back to MgO = 7.0 wt% using the slope of a line defined by the natural data for samples from Sarigan, Alamagan, Agrigan volcanoes and the southern and northern Mariana trough. We did not include Pagan and Guguan samples in this calculation because the data were too few to define variation in Cu vs. MgO with confidence. Once at MgO = 7.0 wt%, each composition was subject to the addition of equilibrium composition olivine until in equilibrium.
with Fo90 olivine, assuming a $D_{Cu}^{olv/melt} = 0$. This technique differs from that presented by Lee et al. (2010), who project whole rock lava compositions along lines that model changes in Cu concentration with melt Mg#. The model lines used by Lee et al. (2010) assume that Cu is incompatible in all phases except for sulfide, such that variations in Cu concentration during volcanic differentiation are tied to sulfide saturation and thus to magmatic $fO_2$. Then, they apply these model lines to the available whole rock data at several subduction zones and correct the whole rock data back to Mg#72. We do not use this method for several reasons. First, it assumes that arc magmas are sulfide saturated, which for arc melt inclusions and submarine glasses in this study, is not the case (Brounce et al., in revision). It also neglects evidence that Cu may behave as a volatile element in the presence of CO2-rich fluids (Collins et al., 2009; Zajacz and Halter, 2009) and thus cannot account for any change in Cu contents as the result of volcanic degassing. Additionally, for the Marianas in particular, there is not good agreement between the model lines presented by Lee et al. (2010) and the whole rock data, which suggests that sulfide saturation does not control the Cu concentrations of Mariana arc lavas. Finally, upon examination of the Cu concentrations of submarine glass and melt inclusions from this study, we find that variations in Cu concentrations are different at each volcanic center, necessitating a flexible technique that can be applied to each sample set accurately.

**MORB LLDs**

To calculate primary MORB melts, we correct the major element compositions of MORB glasses that have only olivine on the liquidus (i.e., glasses with MgO > 8.5 wt%) by adding equilibrium olivine compositions back until the melt composition is in...
equilibrium with Fo$_{90}$ olivine (Cottrell and Kelley, 2011, Cottrell and Kelley, 2013). Trace elements V, Sc, Yb, and Zn were not corrected for crystal fractionation for the reasons described above. Copper is compatible in sulfide phases, however, and MORB are likely saturated with a sulfide phase from the onset of crystallization (Fig. 2e; Peach et al., 1990) causing Cu concentrations to decrease with decreasing MgO. To correct for this effect, we calculated the equilibrium olivine Fo number for each glass composition (FeO/MgO $K_{D_{olv/liq}} = 0.3$; Roeder and Emslie, 1970). We use this value as the index of increasing crystallization, such that Cu concentrations decrease with decreasing equilibrium Fo number, then project Cu concentrations back to Fo$_{90}$ along the slope of a line defined by the natural data (Fig. 3). Although there is scatter in the Cu contents of the global MORB data set, Figure 3 shows an individual segment of the East Pacific Rise from 8.3°N – 13.7°N that shows coherent fractionation trends in major elements (Langmuir et al., 1992), as well as a clear liquid line of descent for Cu. We use the slope of this EPR data set to correct all MORB Cu concentrations back to equilibrium with Fo$_{90}$.

2.3.3 Conditions of melt generation

Temperatures and pressures of last equilibration of primary melt with peridotite were calculated using the thermobarometer of Lee et al. (2009). Melt fractions were calculated from primary melt TiO$_2$ concentrations ($\text{TiO}_2^{\text{Fo}_{90}}$) using the expression from Kelley et al. (2006) and Kelley et al. (2010):

$$ F = \left( \frac{c_{\text{Ti}}^0}{c_{\text{Ti}}^l} \right)^{-D_{\text{Ti}}} (1-D_{\text{Ti}}) $$

(2)
where $C^{o}_{Ti}$ is the concentration of TiO$_2$ in the mantle source (0.133), $C^{l}_{Ti}$ is the calculated concentration of TiO$_2$ in primary melts, and $D_{Ti}$ is the bulk distribution coefficient for Ti during mantle melting (0.04; Kelley et al., 2006).

3. RESULTS

In order to assess each proxy on our dataset, first we apply each proxy for $fO_2$ as developed in the published literature on our sample set, using the new and compiled data presented here. In this section we report these initial model outcomes, and in the Discussion section that follows we explore sources of model uncertainty and explanations for disagreements among the various proxies.

3.1 Fe$^{3+}$/ΣFe ratios

The relationship between Fe speciation and $fO_2$ has been experimentally calibrated for a wide range of natural basaltic melt compositions, temperatures, and pressures (Kilinc et al., 1983; Kress and Carmichael, 1991), such that direct measurements of Fe$^{3+}$/ΣFe ratios in erupted basalts can be used to calculate magmatic $fO_2$. Whole rock wet chemistry is a classic method for determining Fe redox in erupted lavas, which we apply here to the bulk tephras that provide the source material for melt inclusions from the Mariana arc.

Bulk tephras from eight Mariana arc volcanoes have Fe$^{3+}$/ΣFe ratios that vary widely from 0.203 (04Urac5a, Uracas volcano) to values that plot off of the scale of Fig. 2a (0.560, 04Maug5, Maug volcano). The bulk tephra samples have comparatively low MgO concentrations (6.60-1.17 wt%) relative to in situ glass and melt inclusion analyses from the same volcano (Fig. 2a), which is likely because whole rock samples represent the average final composition of magma erupted during
a particular eruptive event, whereas some melt inclusions have the potential to record magmatic compositions that represent some pre-eruptive condition in the magma chamber. The bulk samples from Agrigan, Pagan, Guguan, and Alamagan volcanoes are also offset to significantly higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios than recorded in melt inclusions or submarine glasses from the same volcano that were analyzed using Fe-XANES techniques. An offset between wet chemical methods and Fe-XANES techniques is observed for natural MORB samples, where wet chemical methods yield more reduced $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios than Fe-XANES. This is the opposite relationship than what is observed in this study, where wet chemical determinations of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios on bulk tephras are more oxidized than Fe-XANES measurements on glasses. We hypothesize that this arises due to varying degrees of post-eruptive chemical weathering in the bulk samples (i.e., rounded clasts, red alteration surfaces) and that bulk rock $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in these cases were affected as a result. Because of this, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios determined on these samples are likely to be unsuitable for discussion of magmatic or mantle source $f\text{O}_2$ conditions.

Recent application of Fe-XANES techniques on basaltic glasses has made it possible to measure in situ, on small scales (9x5 $\mu$m) the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of pristine volcanic glass (Brounce et al., revised; Cottrell and Kelley, 2011; Cottrell and Kelley, 2013; Kelley and Cottrell, 2009). These studies have shown that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of MORB glasses range from 0.13-0.17, with an average value of 0.16±0.01 (Fig. 2a). Mariana trough glasses overlap with the most oxidized MORB and extend to more oxidized values, with $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios that range from 0.15-0.21 (Fig. 2a). Mariana arc samples have significantly higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (0.20-0.34) than Mariana trough or
MORB glasses (Fig. 2a). This is consistent with previous observations from the whole rock record, that arc basalts erupt with a higher proportion of Fe\textsuperscript{3+} than do MORB (Carmichael, 1991). We calculate magmatic $f$O\textsubscript{2} for each sample (i.e., the $f$O\textsubscript{2} of the magma as recorded by naturally quenched volcanic glasses) relative to the quartz-fayalite-magnetite oxygen buffer (QFM; Frost, 1991) using the major element compositions and Fe\textsuperscript{3+}/\textgreek{e}\textsubscript{Fe} ratios measured for each sample, with the algorithm of Kress and Carmichael (1991), at 1 atm, 1200°C. These magmatic $f$O\textsubscript{2}s range from QFM-0.4 – QFM+0.4 for MORB, QFM – QFM+1 for Mariana trough basalts, and QFM+0.9 - QFM+1.7 for Mariana arc basalts (Tables 1, 2). We calculate primary melt $f$O\textsubscript{2} in the same way as magmatic $f$O\textsubscript{2}, using calculated primary melt major element compositions and Fe\textsuperscript{3+}/\textgreek{e}\textsubscript{Fe} ratios at 1 GPa, 1350°C. These calculations yield primary melt $f$O\textsubscript{2}s of QFM-0.2 - QFM+0.3 for MORB, QFM+0.1 – QFM +0.8 for the Mariana trough, and QFM+0.7 - QFM+1.8 for the Mariana arc.

3.2 Vanadium

Vanadium is a multi-valent trace element in the range of $f$O\textsubscript{2} relevant to the solid Earth. As $f$O\textsubscript{2} increases, the oxidation state of V increases and V becomes more incompatible during melting and crystallization. The relationships between $D_{V}^{\text{mineral/melt}}$ and $f$O\textsubscript{2} have been calibrated experimentally for olivine, orthopyroxene, clinopyroxene, and spinel (Canil, 1997, 2002; Mallmann and O'Neill, 2009), providing the foundation of three proxies for calculating mantle source $f$O\textsubscript{2} – V/Sc ratios in basalts and komatiites (Canil, 1997, Lee et al., 2005, Mallmann and O’Neill, 2009), V/Yb ratios in basalts (Laubier et al., 2014), and $D_{V}^{\text{olivine/melt}}$ (Mallmann and O'Neill, 2013).
The V/Sc proxy assumes similar behavior of V and Sc early in shallow level differentiation processes (i.e., at MgO > 8.0 wt%) to create an $f_O^2$-sensitive ratio that should not be affected by volcanic degassing or olivine crystallization (Lee et al., 2005). Because $D_{V \text{mantle/melt}}$ is sensitive to $f_O^2$, the measured V/Sc ratio in a primitive basalt may be related directly to the $f_O^2$ of its mantle source, provided the mantle source composition and the extent of mantle melting are known. For fixed source concentrations of V and Sc, and melt fraction (F), a mantle with high $f_O^2$ should yield erupted magmas with high V/Sc ratios relative to a mantle with low $f_O^2$ (Fig. 4; Lee et al., 2005).

It is uncommon to find volcanic glass with MgO > 8.0 wt% in subduction settings, so we extend our consideration of samples to 5.0 wt% MgO, taking care to examine each sample suite for the effects of crystal fractionation on V/Sc ratios. The distribution of measured V/Sc ratios in MORB, Mariana trough, and Mariana arc basalts with MgO > 5.0 wt% are similar, ranging from ~5 to 12 (Fig. 2b). This is consistent with previous observations using whole rock data from literature databases GEOROC and PetDB (Lee et al., 2005) and supports the notion that V/Sc ratios are not significantly affected by shallow level differentiation (Fig. 4a). Following the procedure of Lee et al. (2005) for calculating mantle source $f_O^2$, we use uniform mantle abundance for $V = 83$ ppm and $Sc = 16.5$ ppm (equivalent to primitive mantle composition, McDonough and Sun, 1995), bulk $D_{Sc} = 0.458$ at 1350°C, and parameterizations of $D_V$ for mantle minerals described by Canil (2002). The model assumes that basalts erupted in all three tectonic regions are best represented as accumulated fractional melts. Using these conditions, the measured V/Sc ratios in
MORB, Mariana trough, and Mariana arc basaltic glasses correspond to mantle source \( \text{fO}_2 \) between QFM and QFM+2 (Fig. 4a).

Laubier et al. (2014) proposed the V/Yb ratio proxy with the goal of minimizing the impact of crystal fractionation on the ratio used to calculate mantle source \( \text{fO}_2 \) because unlike Sc, which is compatible in clinopyroxene, Yb is incompatible in all silicate mineral phases that are likely to fractionate from basaltic magmas (e.g., olivine, plagioclase, clinopyroxene; Laubier et al., 2014; Lee et al., 2005). The V/Yb ratios of samples in this study are clearly affected by magnetite saturation in samples with MgO < 5.0 wt\%, which causes a sharp decrease in \( V_{\text{melt}} \) (Fig. 2c) with decreasing MgO. Above 5.0 wt\% MgO, most MORB and northern Mariana trough samples appear to have relatively constant V/Yb ratios centered about a value between 70-100, consistent with data presented by Laubier et al. (2014). In contrast to models of shallow level crystal fractionation presented by Laubier et al. (2014), however, Mariana arc samples with MgO > 5.0 wt\% have widely variable V/Yb ratios from 102 to 237, with most of this range represented by melt inclusions within a single eruptive event at individual volcanic centers (Fig. 2c; i.e., Sarigan and Alamagan samples). The range in V/Yb ratios observed for samples in this study is consistent with recent observations from the literature database GeoROC, however it is also not clear if crystal fractionation or magma mixing play roles in generating the very wide range in V/Yb ratios observed by Laubier et al. (2014). We emphasize the importance of examining samples on a volcano-to-volcano basis at a minimum, for a thorough assessment of the level of variation in trace element ratios that may be expected from subduction-related lavas. In the case of our samples from the Mariana
arc, we cannot say with confidence that V/Yb ratios are constant prior to the point of magnetite fractionation (Fig. 2c). Nonetheless, there is a fundamental offset in V/Yb ratios between MORB/northern Mariana trough basalts and Mariana arc melt inclusions that may reflect variation in mantle source $fO_2$, so we apply the V/Yb ratio proxy to these samples. We use a uniform mantle abundance of $V = 83$ ppm and Yb = 0.401, $D_{Yb}$ equal to 0.147, reported by Laubier et al. (2014), parameterizations of $D_V$ for mantle minerals described by Canil (2002) and a fractional melting model. The V/Yb ratio proxy predicts a mantle source $fO_2$ of $\sim$QFM-1 to QFM for MORB and northern Mariana trough basalts, and $fO_2$ of $\sim$QFM to QFM+2 for southern Mariana trough and Mariana arc basalts (Fig. 5).

The $D_V^{\text{oliv/melt}}$ proxy requires less knowledge of the mantle source and mechanisms for melt generation, relying solely on the calibration of the partitioning of V between olivine and melt as a function of $fO_2$, the major element composition of melt and olivine pairs, and the magmatic temperature during olivine crystallization (Mallmann and O'Neill, 2013). Melt inclusions are ideal samples for the application of this proxy on magmatic systems, since V concentrations in melt inclusions and olivine should not be affected by shallow level differentiation or post-entrapment melt inclusion processes prior to the onset of magnetite crystallization, provided that magmatic timescales are short relative to V diffusivity. By examining high forsterite content olivine phenocrysts in particular, the $D_V^{\text{olivine/melt}}$ proxy can record magmatic $fO_2$ prior to extensive magmatic differentiation.

The $D_V^{\text{oliv/liq}}$ proxy for magmatic $fO_2$ requires knowledge of the magmatic temperature at the time of olivine fractionation. For consistency with the published
model, we used the Sc/Y thermometer of Mallmann and O'Neill (2013), who show that Sc/Y exchange between olivine and melt is temperature sensitive in the same experimental samples against which the $D_V^{\text{oliv/liq}} fO_2$ proxy is calibrated. This thermometer is also shown to be relatively consistent with MgO olivine thermometers (Mallmann and O'Neill, 2013; Putirka et al., 2007). The log $D_V^{\text{oliv/liq}}$ calculated for each melt inclusion-olivine host pair range from -1.68 to -1.97, corresponding to a range in magmatic $fO_2$ at the time of the melt inclusion entrapment from QFM+2.3 to QFM+3.0 for arc magmas (Table 3). We did not examine olivine phenocrysts in submarine glass samples, so we cannot apply this proxy to Mariana trough or MORB magmas. Three MORB olivines were included in Kelley and Cottrell (2012), yielding magmatic $fO_2$ between QFM-0.5 and QFM.

3.3 Zn/Fe* ratios

Zinc occurs only as Zn$^{2+}$ in the solid Earth and may have similar partitioning behavior as Fe$^{2+}$ during mantle melting (Le Roux et al., 2010). When $fO_2$ is low and most of the Fe in a system exists as Fe$^{2+}$ (i.e., Fe$^{3+}/\Sigma$Fe ratios are low), Zn may not be significantly fractionated from Fe during mantle melting. As mantle source $fO_2$ increases, the proportion of Fe$^{3+}$ in the source increases, and Zn and Fe* (i.e., Fe* is total Fe, regardless of valence state) may be fractionated from one another as a result of the greater incompatibility of Fe$^{3+}$ in silicate mineral phases. A mantle with a higher Fe$^{3+}/\Sigma$Fe ratio may produce melts with lower Zn/Fe* ratios than that of a mantle with low Fe$^{3+}/\Sigma$Fe ratios. The Zn/Fe* proxy was developed to calculate directly the Fe$^{3+}/\Sigma$Fe ratio of primary melts, for a mantle with given Zn/Fe* and Fe$^{3+}/\Sigma$Fe ratio (Lee et al., 2010).
The Zn/Fe* ratios in MORB, Mariana trough, and Mariana arc basalts with MgO > 5.0 wt% are similar, ranging from ~8 to 14 (Fig. 2d, Tables 1, 2), consistent with observations from published whole rock data (Lee et al., 2010). Above 5 wt% MgO, there is no variation in Zn/Fe* ratios with MgO concentrations for MORB, Mariana trough and Mariana arc glasses (Fig. 2d). The total variation at any one MgO value is large for all samples (MORB, Mariana trough, and Mariana arc glasses), however, which may potentially reflect differences in source composition and Fe$^{3+}$/ΣFe ratios, and/or differences in the temperature of melting that may lead to variation in Fe* concentrations. Nonetheless, we conclude that the effects of crystal fractionation on the Zn/Fe* ratio in samples in this study are small enough to be negligible. Because Zn/Fe* ratios of magmas are expected to decrease as Fe$^{3+}$ concentration in the source increases, the maximum Zn/Fe* ratio in a mantle melt is tied to the Zn/Fe* ratio of a solid mantle assemblage that has no Fe$^{3+}$ present. The higher the $f$O$_2$ of the mantle source, the more Fe$^{3+}$ is present, and upon melting, the lower the Zn/Fe* ratio of the melt. Thus, an undifferentiated mantle melt cannot have a Zn/Fe* ratio that is greater than the Zn/Fe* ratio of the source mantle. Using a mantle source Zn/Fe* of 9-10, mantle source Fe$^{3+}$/ΣFe ratio = 0.03 (Lee et al., 2010), and a K$_{d(perid/melt)}^{Zn/Fe^{2+}}$ of 0.84 (Davis et al., 2013), there are only a few MORB samples to which the Zn/Fe* proxy can be applied (gray box, Fig. 7a) because these have Zn/Fe* ≤ 10, which yield magmatic Fe$^{3+}$/ΣFe ratios > 0. These samples have Zn/Fe* ratios that correspond to primary melt Fe$^{3+}$/ΣFe ratios ~0.12-0.19. The remaining samples in this study have Zn/Fe*>10, and thus the model cannot be applied as published because it would yield melt Fe$^{3+}$/ΣFe ratios < 0. We use a
$K_d(\text{perid/melt})^{Zn/Fe^{2+}} = 0.84$ rather than Lee et al.’s recommended value of 1, because it is calculated from measurements of olivine, clinopyroxene, orthopyroxene, and spinel and their equilibrium melt composition in experimental charges rather than inferring a value based on the limited mineral-mineral partitioning data from natural peridotite xenoliths (Le Roux et al., 2010) that was available at the time. For a primary melt with given $Zn/Fe^*$ ratio, using a lower $K_d(\text{perid/melt})^{Zn/Fe^{2+}}$ produces calculated $Fe^{3+}/\sum Fe$ ratios that are higher than when $K_d(\text{perid/melt})^{Zn/Fe^{2+}} = 1$ is used.

### 3.4 Cu concentration

Like Zn, Cu exists in only one oxidation state ($Cu^{1+}$) in the range of $f_O^2$ typical of igneous rocks. As a chalcophile element, Cu partitioning during mantle melting can be dramatically altered by the presence of sulfide phases in the mantle. The speciation of sulfur is very sensitive to changes in $f_O^2$ in the range of QFM to QFM+2, where sulfide ($S^{2-}$) is the dominant species of S at $f_O^2$ lower than QFM, and as $f_O^2$ increases from QFM to QFM+2, S species change to sulfate. A change in mantle $f_O^2$ from QFM to QFM+2 and the consequent disappearance of sulfides will affect bulk Cu partitioning during mantle melting, making Cu more incompatible in an oxidized mantle with no sulfide phase present. For a mantle with a given Cu content and sulfide mode, a mantle above QFM+2 will produce melts with higher primary melt Cu concentrations than a mantle below QFM+2 (Lee et al., 2012). It is important to note that this is only true if sulfide phases are not exhausted during melting. The effect of sulfides on Cu partitioning is erased if the sulfide mode is small and melt fraction is large.
Measured Cu concentrations in MORB and northern Mariana trough lavas decrease with decreasing MgO, likely because they reflect saturation of the magma with a sulfide phase (Fig. 2e). Agrigan melt inclusions and southern Mariana trough lavas also have decreasing Cu concentrations with decreasing MgO (Fig. 2e), although these samples show no other evidence of sulfide saturation; for example, there are no sulfides present either as included phases in olivine phenocrysts or as separate phases present in the erupted tephra or in the pillow lava (for southern Mariana trough samples; Brounce et al., revised). The sulfur concentrations of these samples are much lower than experimentally calibrated estimates of the sulfur content at sulfide saturation, at the $f_{O_2}$ indicated by measured $Fe^{3+}/\Sigma Fe$ ratios of the glasses (Jenner et al., 2012; Jugo et al., 2010; O'Neil and Mavrogenes, 2002), and there is evidence that sulfur has partitioned into a vapor phase (Brounce et al., revised; Kelley and Cottrell, 2012). Copper has been shown to partition into vapor phases during shallow level volcanic degassing in both mafic and felsic magmas (Collins et al., 2009; Zajacz and Halter, 2009) and it is possible that the complex degassing behaviors recorded in the volatile element concentrations in Agrigan inclusions and southern Mariana trough lavas (Brounce et al., revised) also reflect copper loss into a S- or CO$_2$-rich vapor phase. In contrast, the Cu contents in melt inclusions from Alamagan and Sarigan do not appear to vary significantly with decreasing MgO concentrations (Fig. 2e). In particular, we find that upon examination of volcano-specific liquid lines of descent for Mariana glass compositions, there is little variation in Cu concentrations in glasses with MgO > 5.0 wt%, consistent with the previous observation that these melts are not sulfide saturated (Brounce et al., revised).
Calculated primary Cu concentrations of MORB range from 69 to 117 ppm. Some northern Mariana trough samples extend to lower primary Cu concentrations, but most of the northern and southern Mariana trough samples overlap with MORB, with primary Cu concentrations ranging from 51 to 104 ppm. The Mariana arc samples range from 66 to 182 ppm, partially overlapping with MORB and Mariana trough samples, although some Sarigan, Alamagan, and Agrigan samples extend to higher primary Cu concentrations (gray field, Fig. 8). Assuming uniform upper mantle conditions of 1350°C and 1 GPa, and source concentrations of S and Cu of 200 and 28 ppm, respectively, the arc samples are consistent with a source mantle with $f_{O_2}$ between QFM (dashed black line, Fig. 8) and QFM+1.3 (solid black line, Fig. 8). Mariana trough and MORB samples representative of melt fractions <0.15 are most consistent with mantle $f_{O_2}$ of QFM to QFM+0.5 (gray line, Fig. 8). Above melt fraction~0.15, Mariana trough, MORB, and most of the Mariana arc melts have similar Cu concentrations that are consistent with mantle $f_{O_2}$ of ~QFM to QFM+0.5. A small subset of Mariana arc primary melts have elevated Cu concentrations that are more consistent with mantle $f_{O_2}$ of ~QFM+1.3 (gray shaded region, Fig. 8).

3.5 Comparison

Each proxy yields slightly different results when applied to samples in this study. The V/Sc ratio proxy suggests that the $f_{O_2}$ of the upper mantle is heterogeneous on a small scale (i.e., within MORB; Cottrell and Kelley, 2011, Mariana trough, or Mariana arc samples), ranging from QFM to QFM+2, but homogeneous at the largest scale (i.e., all MORB, Mariana trough, and Mariana arc V/Sc ratios correspond to the same range in mantle source $f_{O_2}$). This range in $f_{O_2}$ is broadly consistent with calculated primary
melt $f$/O$_2$s from the Fe$^{3+}$/∑Fe ratio proxy, although unlike the Fe$^{3+}$/∑Fe ratio proxy, there is no distinction between mantle source $f$/O$_2$ for MORB, the Mariana trough, and the Mariana arc (Fig. 4a). In contrast to V/Sc, the V/Yb proxy reflects a heterogeneous upper mantle, and the ranges of $f$/O$_2$ for MORB, Mariana trough, and Mariana arc mantle are broadly consistent with the Fe-based proxy, where the mantle sources for MORB and the northern Mariana trough basalts have $f$/O$_2$ between QFM-1 and QFM+1, between QFM and QFM+1 for the southern Mariana trough, and between QFM and QFM+2 for the Mariana arc. The $D_V^{\text{olivine/melt}}$ proxy, a simplified application of the V partitioning principle, yields magmatic $f$/O$_2$s that are an average of 1.4 log units more oxidized than the magmatic $f$/O$_2$ values calculated from the Fe$^{3+}$/∑Fe ratios measured on the same melt inclusions (Table 2). However, the log $D_V^{\text{olivine/melt}}$ calculated directly from trace element measurements on the melt inclusions and their olivine hosts, paired with their magmatic $f$/O$_2$ calculated from measured Fe$^{3+}$/∑Fe ratios (Fe-XANES) are consistent with the experimental dataset upon which the $D_V^{\text{olivine/melt}}$ model is calibrated (Fig. 6). The Zn/Fe$^*$ proxy yields primary melt Fe$^{3+}$/∑Fe ratios (0.15-0.19) that are broadly consistent with Fe$^{3+}$/∑Fe ratios reconstructed from Fe-XANES measurements (0.12-0.16) on the few MORB samples to which the proxy can be applied. The Cu-based proxy is also consistent with Fe-, V/Sc-, and Zn/Fe-based proxies when applied to MORB and Mariana trough glasses, predicting a mantle source $f$/O$_2$ of ~QFM and ~QFM+0.5 respectively. For Mariana arc samples, the Cu proxy predicts mantle $f$/O$_2$ between ~QFM and QFM+1.3.

4. DISCUSSION

4.1. Fe$^{3+}$/∑Fe ratios in basaltic glasses versus whole rock analyses
Iron is a major element. Magmatic differentiation can change its concentration, and differentiation and post-eruption chemical weathering can change its redox ratios. For these reasons, it can be difficult to be certain that measurements of Fe\(^{3+}/\sum\)Fe ratios on erupted lavas reflect magmatic values, and even more difficult to reconstruct the Fe\(^{3+}/\sum\)Fe ratios of undifferentiated mantle melts. This is apparent from the comparison of Fe\(^{3+}/\sum\)Fe ratios determined from bulk tephra and from melt inclusions from the same tephra (Fig. 2a). Most of the tephras have slightly lower MgO contents than their melt inclusions, representing more evolved magma compositions, and are also more oxidized. The tephra powders are all visibly weathered and their bulk Fe\(^{3+}/\sum\)Fe ratios may not be entirely representative of the magmatic redox state.

The application of Fe-XANES techniques to determining Fe\(^{3+}/\sum\)Fe ratios in basaltic glasses presents the opportunity to address many of the main concerns regarding Fe redox proxies for magmatic and mantle source fO\(_2\). Although some sample suites display excellent coherence between magmatic and whole rock redox determinations (e.g., Crabtree and Lange, 2011), by measuring Fe\(^{3+}/\sum\)Fe ratios in situ in pristine volcanic glass, we can avoid any potential effects of alteration that may occur under the relatively oxidizing conditions at the Earth’s surface (e.g., Grocke et al., submitted). We also avoid the large and potentially random error that may occur during the weighing and transfer of powders in micro-colorimetry procedures for samples with relatively low FeO* concentrations (MgO < 5.0 wt%). While micro-colorimetry can be precise, for example in the study of MORB glasses (less than 1% relative; Christie et al., 1986), when FeO* contents are low and the samples are more oxidized, the Fe\(^{2+}\)O\(_{\text{actual}}\) concentration can be very low and small weighing errors
correspond to large errors in the calculated Fe$^{3+}$/$\Sigma$Fe ratios (see error bars, Fig. 2a).

Finally, by applying Fe-XANES techniques to carefully chosen melt inclusions, we can measure Fe$^{3+}$/$\Sigma$Fe ratios in samples that potentially record changing magmatic compositions during crystallization and degassing. This information can be used to determine the effects of these processes on magmatic Fe$^{3+}$/$\Sigma$Fe ratios and if necessary, to correct for these variations. Once this is done, the algorithm of Kress and Carmichael (1991) can be used to calculate magmatic and mantle source $f$O$_2$ to $\pm$ 0.5 log units.

The range in possible mantle source $f$O$_2$ calculated from Fe$^{3+}$/$\Sigma$Fe ratios determined via Fe-XANES is much smaller than that calculated from Fe$^{3+}$/$\Sigma$Fe ratios determined via micro-colorimetric techniques (Fig. 1) and indicates that primary arc melts are more oxidized than MORBs (Brounce et al., revised). Additionally, no study has yet demonstrated an oxidizing differentiation process in natural magmas that could create the very oxidized Fe$^{3+}$/$\Sigma$Fe ratios observed in arc lavas (Brounce et al., revised; Crabtree and Lange, 2011; Frost and Lindsley, 1992; Kelley and Cottrell, 2009; Kelley and Cottrell, 2012, Moussalam, 2014). Thus we conclude that the Fe$^{3+}$/$\Sigma$Fe ratio proxy strongly suggests that the upper mantle is heterogeneous with respect to $f$O$_2$, where the mantle source for arc volcanism is more oxidized than that of MORB.

4.2 Ratios of vanadium to other trace elements

Application of the V/Sc proxy for determining mantle source $f$O$_2$ from the composition of erupted basalts involves making several assumptions or inferences about the mechanisms for melt generation and the composition of the source itself. First, it is necessary to distinguish between mechanisms for melt generation in various
tectonic settings. Mantle melts at mid-ocean ridge and back-arc basin settings exist because the mantle is upwelling passively in response to divergent plate motions; these melts are best modeled as accumulated fractional melts (Langmuir et al., 2006; Langmuir et al., 1992). Under an arc however, melt generation takes place due to a shift in the position of the peridotite solidus towards lower temperatures because of the addition of water to the mantle wedge from subducting slabs. The melting column under arc volcanoes integrates melts formed over a relatively focused depth range corresponding to the hot core of the mantle wedge (England and Katz, 2010).

Although there remains much to understand about melt generation and transport processes in this part of the mantle wedge, arc lavas may be better modeled as equilibrium batch melts (e.g., Kelley et al., 2010). When modeling the behavior of mildly incompatible elements such as Sc, and V in settings with \( f_{O_2} < QFM+2 \) during melting, at a fixed mantle source composition, the difference between accumulated fractional melts (black lines, Fig. 4a) and batch melts (gray lines, Fig. 4b) for the calculated mantle source \( f_{O_2} \) is small. At \( f_{O_2} \) higher than QMF+2, V becomes increasingly incompatible (\( D_{\text{bulk}}^V < 0.1 \)) and the difference between batch and fractional melting processes for calculated mantle source \( f_{O_2} \) increases. In particular, at \( f_{O_2} > QFM+2 \) and \( F > 0.10 \), a batch melting model yields a slightly lower source \( f_{O_2} \) than a fractional melting model at a given V/Sc ratio.

The ranges in possible source concentrations for V and Sc are also important to consider. Lee et al. (2005) use estimates for bulk silicate Earth (\( V_o = 83 \) ppm, \( Sc_o = 16.5 \) ppm, McDonough and Sun, 1995) for both mid-ocean ridge and arc mantle sources (black lines, Fig. 4a). Here, we used the average compositions for NMORB,
EMORB, and DMORB reported by Gale et al. (2013) to calculate the range of $V_{\text{source}}$ and $Sc_{\text{source}}$ for mantle that feeds the mid-ocean ridge system. We calculated primary melt $V$ and $Sc$ concentrations for these three representative MORB compositions by adding equilibrium olivine back to the major element composition each type of MORB until in equilibrium with $Fo_{90}$ olivine, using a starting $Fe^{3+}/\sum Fe$ ratio of 0.16 (average global MORB; Cottrell and Kelley, 2011), assuming a system closed to oxygen (i.e., $Fe^{3+}$ is conserved during fractionation). To calculate $V_{\text{source}}$ and $Sc_{\text{source}}$, we assumed that MORB represent 10% fractional melts of the mantle and used the same partition coefficient parameterizations described previously, specifically $D_{\text{Bulk}}^{Sc} = 0.45$ (at 1350°C) and $D_{\text{Bulk}}^{V} = 0.35$ (at QFM). For EMORB, this calculation yields $Sc_{\text{source}}=14$ and $V_{\text{source}}=88$, for DMORB $Sc_{\text{source}}=16$ and $V_{\text{source}}=99$, and for NMORB $Sc_{\text{source}}= 15.9$ and $V_{\text{source}}=94.6$.

The full range of expected $V/Sc$ ratios during melting of a source mantle within the range of $V$ and $Sc$ concentrations calculated for each MORB group at QFM is small (thick gray line, Fig. 4a) but offset to higher $V/Sc$ ratios than when a BSE source is used. Whichever compositions are used, the $V/Sc$ model shows that MORB are consistent with extraction from a source mantle at ~ QFM. The mantle source for Mariana trough lavas unmodified by subduction is NMORB to EMORB mantle in composition (Langmuir et al., 2006; Stolper and Newman, 1994), and for southern Mariana trough samples with the highest $V/Sc$ ratio, using the NMORB source composition calculated here, suggest mantle $fO_2 > QFM+1$.

In the case of the Mariana arc, the mantle source under the arc is the residue of melt extraction at the Mariana trough (Plank, 2005, Stolper and Newman, 1994). We
model this composition by assuming that 10% fractional melt is extracted from the source composition at the back arc, yielding a source mantle with 14.9 ppm Sc and 86.2 ppm V if melting at the back arc took place at QFM, or 76.5 ppm V if melting at the back arc took place at QFM+1. We take the first composition and use a batch melting model to calculate the range of V/Sc ratios expected during melting beneath the arc at QFM, QFM+1, and QFM+2 (gray solid lines, Fig. 4b), and find that this model is not significantly different from models using MORB type mantle compositions (compare to gray field in Fig. 4b). We find, however, that if we take any of the source Sc concentrations discussed here, to generate the Sc abundances observed in Mariana trough and Mariana arc lavas with the highest MgO concentrations, it would require $D_{\text{Bulk}}^{\text{Sc}} < 0.3$, which occurs at mantle temperatures in excess in 1500°C (calculated from Beattie et al., 1991, Lee et al., 2005), This temperature is likely too hot to be reasonable for melting in the mantle wedge (England and Katz, 2010). At ~1350°C, to generate Sc abundances in mafic arc magmas from this study requires either (1) a mantle source with higher Sc concentrations, (2) Sc addition to the mantle by aqueous fluids or melts from the subducting slab, or (3) a lower bulk partition coefficient for Sc during melting than is used in the V/Sc model, or (3) . The mantle under the Mariana arc is more refractory and depleted than mantle under the Mariana trough, so it is unlikely that the mantle source has higher Sc content than outlined here (Plank, 2005, Stolper and Newman, 1994). Scandium is not present in abundance in experimental liquids and melts found to be in equilibrium with altered oceanic crust at P and T relevant for subducting slabs, so it is also unlikely that Sc is added to the mantle wedge from the subducting slab.
It may be that our $D_{\text{Bulk}}^{\text{Sc}}$ should reflect more incompatible behavior for Sc during melting in arc settings, relative to MOR settings. Figure 9 shows the relationship between Sc/La, V/La, Zn/La, and Cu/La and Sm/La ratios in MORB (light gray field, Liu, 1997), Mariana trough, and Mariana arc samples. The MORB data define the relationship between each of these elements and Sm during melting of the MOR source upper mantle. Mariana trough samples from this study overlap the MORB field, suggesting that, to a first order, similar models for melt generation can be used to calculate source $f_O^2$ in these regions. However, the Mariana arc data do not plot with MORB data, instead they have higher Sc/La, V/La, Zn/La, and Cu/La ratios than MORB samples with the same Sm/La ratio. This suggests that there is a fundamental difference in the behavior and abundance of these elements during melting between arc and MOR settings. In the case of V, the difference between MORB and Mariana arc samples in Fig. 9b potentially reflects elevated source $f_O^2$ conditions in arc settings relative to MOR. For Sc, Zn, and Cu, it may be that the bulk partition coefficients for these elements are lower during melting in arc settings than in MOR settings. Peridotites found in the forearc of subduction zones, are commonly harzburgites with modal abundances of ~70% olivine, up to 30% orthopyroxene, and 1-3% each of clinopyroxene and spinel (e.g., Pearce et al., 1984). These harzburgites are thought to reflect significant degrees of melt extraction that takes place during hydrous melting of forearc and arc mantle sources, depleting the source rock significantly of clinopyroxene. This has an important effect on the relative partitioning of V and Sc, because $D_{\text{Sc}}^{\text{cpx/melt}} \sim 1.2$ and at $f_O^2 \geq \text{QFM}$, $D_{\text{V}}^{\text{cpx/melt}} < 1$. As $f_O^2$ increases, V becomes increasingly more incompatible in clinopyroxene, while Sc remains
compatible. At any constant $fO_2 \geq QFM$, the bulk $D_V$ will increase and bulk $D_{Sc}$ will decrease as the modal abundance of clinopyroxene decreases. The result is that melts of a mantle depleted in trace elements (because of prior melt extraction at the back-arc) that is 1% clinopyroxene, 70% olivine, 3% spinel, and 26% orthopyroxene (in the style of forearc peridotites described in Pearce et al., 1984) have lower V/Sc ratios at a given $fO_2$ than the same depleted trace element composition mantle that has 18% clinopyroxene, 55% olivine, 2% spinel, and 25% orthopyroxene (the modal composition used by Lee et al., 2005). The red dash-dot line in figure 4b illustrates this effect for the depleted mantle composition discussed above, which becomes more pronounced as $fO_2$ increases above QFM. Additionally, as melt fraction increases above 20%, lines of constant $fO_2$ converge and it becomes difficult to distinguish between QFM and QFM+1 (Fig. 4b). If clinopyroxene is completely eliminated from the mantle assemblage at 20% melt fraction, a depleted mantle with $fO_2$ of ~QFM+1 will produce a melt with V/Sc = 6.4. From this, we conclude that the V/Sc ratios of Mariana arc basalts in this study need not preclude oxidized conditions in the mantle wedge if the mantle source is depleted in trace elements and has a lower modal abundance of clinopyroxene than MORB or Mariana trough source mantle.

Normalizing V to another trace element that is not compatible in clinopyroxene or other mantle phases may avoid the potential problems outlined above. Examining variations in V/Yb ratios on a volcano-to-volcano basis and choosing samples that have not clearly fractionated V/Yb ratios via magnetite crystallization limits the range of V/Yb ratios that are used to infer mantle source $fO_2$ significantly when compared to the range in V/Yb ratios examined by Laubier et al. (2014), and thus yield a narrower
range for the possible \( fO_2 \) of arc mantle (Fig. 1). However, even within samples from a single volcano, we observe significant variation in \( V/Yb \) ratios in samples with \( MgO > 5.0 \) wt\%, suggesting that there is more work to be done in understanding the relationship between \( V/Yb \) ratios and mantle source \( fO_2 \).

4.3 Vanadium partitioning

The \( D_V^{olv/melt} \) proxy avoids many potential problems associated with complex subduction zone magmatism because it relies simply on the relationship between magmatic \( fO_2 \) and V partitioning between olivine and melt. The calibration of \( D_V^{olv/melt} \) as function of \( fO_2 \) developed by Mallmann and O'Neill (2013) yields magmatic \( fO_2 \)s that are systematically higher than given by other proxies for both MORB and arcs, and are notably offset from \( Fe^{3+}/\sum Fe \) ratios measured on the same inclusions (Fig. 6). Although Mallmann and O'Neill (2013) base their calibration on a large experimental dataset, many of these experiments are at 1 atm, anhydrous conditions and use synthetic starting compositions that lack Fe, or use natural compositions (i.e., komatiites) that are unusual in the geologic record and not necessarily appropriate matches for normal MORB and arc basalts. Natural basaltic magmas contain dissolved volatiles and differentiate at pressures between 1 and 10 kbar (e.g., Plank et al., 2013) and these factors may impact the relationship between V partitioning and \( fO_2 \).

Alternatively, it is possible that the \( Fe^{3+}/\sum Fe \) ratios recorded in arc melt inclusions are reduced during some post-entrapment process and therefore represent a minimum estimate for magmatic \( fO_2 \). However, the \( fO_2 \) predicted for MORB olivine-pillow glass pairs from \( D_V^{olv/melt} \) are also more oxidized than other proxies, suggesting that the bias is not a melt inclusion phenomenon. Additionally, we observe that the calculated
$D_{\text{ol/melt}}^v$ values for melt inclusions and magmatic $fO_2$ calculated from the melt inclusions’ measured $\text{Fe}^{3+}/\sum \text{Fe}$ ratios are entirely consistent with those of the experimental conditions upon which the empirical relationship is derived. This suggests that there may be a bias in the empirical parameterization that describes the relationship between $D_{\text{ol/melt}}^v$ and magmatic $fO_2$. Whatever the cause of the offset between the $D_{\text{ol/melt}}^v$ and $\text{Fe}^{3+}/\sum \text{Fe}$ ratio proxies, the two proxies are consistent with one another in that they both suggest that the upper mantle is heterogeneous with respect to $fO_2$, specifically that the mantle source at arc volcanoes is more oxidized than MORB.

4.4 Broader application of the Zn/Fe* proxy

The Zn/Fe* proxy is consistent with measured $\text{Fe}^{3+}/\sum \text{Fe}$ ratios for the four MORB samples with Zn/Fe* $\leq 10$, assuming a mantle source Zn/Fe* $= 9 \pm 1$. The remaining MORB, Mariana trough, and Mariana arc samples have Zn/Fe* ratios higher than $\sim 11$, a value too high to be the result of melting a mantle with Zn/Fe* $= 9$, even when there is no Fe$^{3+}$ present. Zinc and iron may be fractionated from one another as the result of crystal fractionation in the shallow crust, in particular at the point of clinopyroxene saturation, causing the magmatic Zn/Fe* ratio to increase (Lee et al., 2010). The Zn/Fe* ratios measured in samples with MgO $> 5.0$ wt% do not correlate significantly with decreasing MgO (Fig. 2d), however, which suggests that Zn/Fe* $= 9 \pm 1$ does not encompass the full range of possible mantle source compositions relevant to samples in this study. If the highest Zn/Fe* ratios measured in this study ($\sim 14$; MORB, southern Mariana trough, Pagan) are controlled mostly by melting, it would require a mantle source with Zn/Fe* as high as 14, significantly
higher than the recommended Zn/Fe* = 9 ± 1. Allowing for source variation in Zn/Fe*
of this magnitude would render the model more applicable. In Fig. 7b, we show the
distribution of whole rock measurements of Zn/Fe* ratios in peridotites sampled from
oxenoliths and exhumed terranes. The blue bars show values measured on xenoliths
from the western USA and Tanzanian craton, which are the basis for Zn/Fe*_source = 9 ±
1 (Le Roux et al., 2010; Lee et al., 2010), although this data set actually ranges from 7
to 13. We also show the range for abyssal peridotites (Niu, 2004) and xenoliths
erupted in serpentine mud volcanoes from the Mariana forearc (Parkinson and Pearce,
1998; Savov et al., 2005). One sample each from the Mariana forearc and western
USA/Tanzanian craton have Zn/Fe* ratios as high as 13, and several abyssal
peridotites have Zn/Fe* ratios as high as 15, demonstrating that the full range of
Zn/Fe* ratios in the upper mantle is greater than Zn/Fe* = 9 ± 1. To explain the full
range of Zn/Fe* ratios observed in MORB and arc basalts with MgO > 5 wt% would
require variation in mantle source Zn/Fe* ratios from ~8 to 14, which is consistent
with observations from figure 7b. If this level of variation is allowed, then the
Fe³⁺/∑Fe ratios of primary melts calculated using the Zn/Fe* proxy are entirely
consistent with those calculated from direct measurements of Fe³⁺/∑Fe ratios in
basaltic glasses (Fig. 1b), although we lack a means to constrain independently the
Zn/Fe* ratio of the source based solely on melt composition. The Mariana forearc
xenoliths with Zn/Fe* ratios > 9 are among the most heavily serpentinized xenoliths
from Conical Seamount (Savov et al., 2005), suggesting that slab-derived fluids
responsible for serpentinization may have increased the Zn/Fe* ratios of the
peridotites. If true, then Zn mobility in slab-derived fluids and melts is also a key factor to consider for accurate application of the Zn/Fe* proxy.

4.5 Primary melt Cu contents

In the case of the Cu proxy for mantle source fO₂, MORB and Mariana trough samples are clearly consistent with a mantle source fO₂ between QFM and QFM+0.5. Above 15% melt fraction, however, sulfide phases are exhausted during melting, vastly diminishing the sensitivity of the model to mantle fO₂. The range in F observed for Mariana trough basalts and MORB are mostly between 5 and 15%, although the range of F in all arc samples is between 15 and 25% melt fraction, making it especially difficult to apply the Cu-based proxy to accurately predict mantle source fO₂ in these locations. The difference in primary melt Cu concentrations at 20% melt fraction between QFM and QFM+0.5 is <4 ppm, and <20 ppm between QFM and QFM+1.3. These values are either within or just outside of the limit of the confidence interval of our calculation of primary Cu concentrations in Mariana arc samples (± 10ppm).

Despite these uncertainties, the Cu contents of Mariana arc basalts reflect melting of a mantle source with fO₂ between QFM and QFM+1.3 (Fig. 1b). There is a significant impact of varying the Cu_source (green dash-dotted line, QFM+1.3) for the case where melt extraction in the back-arc depletes the source composition of Cu by 8 ppm, to a value of 20 ppm. This model also relies heavily upon knowledge of the S content of the source mantle, which is difficult to know in subduction zones because of the possibility for S recycling in slab fluids or sediment melts (e.g., Alt et al., 2013). If sulfur is added to the mantle wedge in slab fluids or sediment melts, increasing the S content of the mantle source and by extension the sulfide mineral mode, sulfide phases
in the wedge may persist to higher melt fractions. This would make Cu more compatible in the mantle mineral assemblage at higher melt fractions, decreasing the Cu content of arc magmas at a given \( f_{O_2} \). More work towards understanding the mobility of sulfur and abundance of Cu in the mantle wedge must be done before the Cu proxy can be used to accurately predict mantle source \( f_{O_2} \) in subduction settings, though we note that like the V/Sc and Zn/Fe* proxies, reasonable constraints can be used with the Cu proxy to yield oxidized mantle conditions at arc volcanoes.

4.6 The oxygen fugacity of the upper mantle

We have presented an assessment of several proxies for mantle source \( f_{O_2} \) and tested each proxy on a global set of MORB submarine glasses, submarine glasses from the Mariana trough and Mariana arc, as well as olivine hosted melt inclusions from several volcanic centers along the Mariana arc. After testing a range of different constraints that affect the outcome of each proxy, the results of this study suggest that these proxies converge upon an upper mantle that is heterogeneous with respect to \( f_{O_2} \), and that this heterogeneity is a function of tectonic setting.

For MORB and Mariana trough samples, results from \( \text{Fe}^{3+}/\sum \text{Fe} \) ratios, V/Sc ratios, and primary melt Cu concentrations are consistent with a source mantle in these locations of QFM and between QFM and QFM+1, respectively (Fig. 1b). The Zn/Fe* ratios of a small subset of our MORB dataset are entirely consistent with \( \text{Fe}^{3+}/\sum \text{Fe} \) ratios determined via Fe-XANES if source Zn/Fe* is fixed at a value of 9, suggesting that MORB primary melts have \( \text{Fe}^{3+}/\sum \text{Fe} \) ratios \( \sim 0.12-0.19 \) (\( \sim \text{QFM-0.5 to QFM+0.5} \), Fig. 1b).
In the case of the Mariana arc, it is important to consider the full range in possible modal compositions of the mantle wedge, as decreasing clinopyroxene abundance has a significant impact on the application of the V/Sc ratio proxy to arc basalts. If the mantle source for arc magmas is depleted in bulk V and Sc abundances due to melt extraction at the back-arc and has a low clinopyroxene mode due to the generation of high melt fractions during hydrous melting, the V/Sc ratios of Mariana arc basalts need not preclude oxidized mantle wedge conditions. We emphasize the importance of examining the composition of arc basalts on a volcano-to-volcano basis when assessing the potential for compositional variability, as it can impact the application of certain trace element proxies for $f$O$_2$. For example, we demonstrate that variation in V/Yb ratios in Mariana arc samples with MgO > 5.0 wt% is significant, suggesting that work remains to be done to fully understand the relationship between V/Yb ratios and mantle source $f$O$_2$. In the simplified case of vanadium partitioning between melt and olivine, we show that mafic Mariana arc magmas have significantly elevated magmatic $f$O$_2$ (>QFM+2) over MORB, although we note that $f$O$_2$s determined using $D_V^{\text{ol/melt}}$ are systematically higher than those determined using Fe$^{3+}/\Sigma$Fe ratios (Fig. 1b). Finally, the Cu contents of some Mariana arc primary magmas reflect melting at QFM+1.3, consistent with constraints from Fe$^{3+}/\Sigma$Fe ratios, although we demonstrate that this proxy is also sensitive to starting mantle Cu and S content, which, for S in particular, is not well constrained in subduction zone settings. Similar to the case of V/Sc ratios, the Cu contents of Mariana arc primary magmas need not preclude oxidized mantle source conditions. In total, the Fe redox, V/Sc, V/Yb, and Cu proxies for mantle source $f$O$_2$ in this study are consistent with the $f$O$_2$ of
the arc mantle source between QFM and QFM+3, and in particular, that each of these proxies yield source $fO_2 > \text{QFM+1}$ for some portion of the arc samples in this study (Fig. 1b).

These results are summarized in Figure 1b. Overall, we recommend that any study seeking to constrain mantle source $fO_2$ from any proxy discussed here take full and careful consideration of each model before applying. In particular, considering the potential differences between petrogenesis at the mid-ocean ridge, back-arc spreading centers, and arc volcanoes may impact results from each proxy significantly.

5. CONCLUSIONS

We have tested six transition element proxies for mantle source $fO_2$ on an internally consistent dataset of MORB, Mariana trough, and Mariana arc basalts with the goal of presenting a summarized view of $fO_2$ in the upper mantle, as recorded by erupted basalts. After careful consideration of the application of each model, we find that the upper mantle is heterogeneous with respect to $fO_2$. The Fe redox, Zn/Fe*, V/Sc, and Cu proxies all suggest that the source mantle for MORB has $fO_2$ of ~QFM. The Fe redox, V/Sc, and Cu proxies source mantle for Mariana trough basalts is between QFM and QFM+1. The complicated nature of subduction zone magmatism presents several challenges to the application of trace element proxies in this study, although the Fe redox, V/Yb, and $D_v^{\text{ol/melt}}$ proxies all reflect a mantle source with $fO_2$ between QFM+1 and QFM+3. The V/Sc and Cu proxies suggest a mantle source with $fO_2$ between QFM and QFM+2, dependent upon the mantle source composition and extent of influence from subduction components in the Marianas.
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Figure 3.1 Mantle source $f_{O_2}$ (relative to QFM) for global suites of MORB, back-arc, and arc basalts, as determined from $Fe^{3+}/\Sigma Fe$ ratios (Bezos and Humler, 2005; Brounce et al., revised; Carmichael, 1991; Christie et al., 1986; Cottrell and Kelley, 2011; Cottrell and Kelley, 2013), V/Sc ratios (Lee et al., 2005), $D_{V^{oIv/melt}}$ (this study; Mallmann and O’Neill, 2013), Zn/Fe* ratios (Lee et al., 2010), and Cu abundances (Lee et al., 2012). Panel (a) shows results from the application of each model as recommended. Panel (b) summarizes the conclusions of this work.
Figure 3.2 Variations in (a) Fe$^{3+}$/∑Fe ratios, (b) V/Sc ratios, (c) V/Yb ratios, (d) Zn/Fe$^*$ ratios, and (e) Cu concentration with MgO for MORB (Cottrell and Kelley, 2011, 2013), Mariana trough (Kelley and Cottrell, 2009; Stolper and Newman, 1994), and Mariana arc basalts (Brounce et al., revised). The Fe$^{3+}$/∑Fe ratios of MORB and Mariana trough submarine glasses are determined via Fe-XANES. The Fe$^{3+}$/∑Fe ratios of Mariana arc melt inclusions (filled symbols) are also determined via Fe-XANES. The Fe$^{3+}$/∑Fe ratios of whole rock samples are determined via micro-colorimetry. The vertical dashed line marks MgO = 5.0 wt%.
Figure 3.2 con’t Variations in (a) Fe$^{3+}$/∑Fe ratios, (b) V/Sc ratios, (c) V/Yb ratios, (d) Zn/Fe* ratios, and (e) Cu concentration with MgO for MORB (Cottrell and Kelley, 2011), Mariana trough (Kelley and Cottrell, 2009; Stolper and Newman, 1994), and Mariana arc basalts (Brounce et al., in review). The Fe$^{3+}$/∑Fe ratios of MORB and Mariana trough submarine glasses are determined via Fe-XANES. The Fe$^{3+}$/∑Fe ratios of Mariana arc melt inclusions (filled symbols) are also determined via Fe-XANES. The Fe$^{3+}$/∑Fe ratios of whole rock samples are determined via micro-colorimetry. The vertical dashed line marks MgO = 5.0 wt%.
Figure 3.3 Variations in copper contents measured in MORB glass with the forsterite content of equilibrium composition olivine, calculated using a $K_D$ FeO/MgO = 0.3 (Roeder and Emslie, 1970). The black line is a simple linear regression with slope of 306, along which Cu contents were projected back to Fo90.
Figure 3.4 The variation in V/Sc ratios of samples from this study with calculated melt fraction from primary melt TiO$_2$ concentrations. Black model lines in (a) are for a fractional melting model and illustrate the relationship between V/Sc ratio, melt fraction, and mantle source $f$O$_2$ for V and Sc abundance estimates for bulk silicate earth at QFM, QFM+1, and QFM+2 (Lee et al., 2005). The thick gray line shows the sensitivity of the model to changing the V and Sc mantle source abundance at QFM. In (b), a batch melting model; the black solid lines show the relationship between V/Sc ratios, melt fraction, and mantle source $f$O$_2$ using the same mantle source V and Sc compositions as in panel (a) (also at QFM, QFM+1, and QFM+2). The black dashed lines show a batch melting model for the case where melt extraction along the Mariana trough brings a depleted mantle composition into the Mariana arc source, for QFM, QFM+1, and QFM+2 cases. The red dash-dot lines use the same mantle source compositions as in the black dashed lines, but with a mantle mineral mode of 1% cpx, 70% olv, 3% spinel, and 26% opx, also at QFM, QFM+1, and QFM+2. Symbols are as in Figure 2.
Figure 3.5 The variation in V/Yb ratios of samples from this study with calculated melt fraction from primary melt TiO$_2$ concentrations. The solid black lines show the relationship between V/Yb ratio, melt fraction, and $f$/O$_2$ for a depleted source composition, V = 86.2 (this study) and Yb = 0.401 (Salters and Stracke, 2004), using a fractional melting model. The red dash-dot lines have the same mantle source V and Yb concentrations, but use mantle mineral mode of 1% cpx, 70% olv, 3% spinel, and 26% opx in a batch melting model. Symbols are as in figure 2.
Figure 3.6 Variation in measured V partitioning between olivine and melt with \( fO_2 \) for experiments (gray circles; Mallmann and O'Neill, 2013, and references therein), three MORB glass-olivine pairs (black circles; Kelley and Cottrell, 2012), and olivine hosted melt inclusions (colored samples, symbols as in Figure 2). Magmatic \( fO_2 \) for olivine hosted melt inclusions are calculated using the \( Fe^{3+}/\sum Fe \) ratios (Fe-XANES) measured directly on the melt inclusions, and the algorithm of Kress and Carmichael (1991) relative to the QFM oxygen buffer at 1200°C, 1 atm (Frost, 1991). The 1 sigma error bar represents the confidence interval for magmatic \( fO_2 \) calculated using the Kress and Carmichael (1991) algorithm. The orange line is an example calibration line for the relationship between log \( D_{V}^{\text{ol/liq}} \) and magmatic \( fO_2 \) using melt inclusion composition Sari15-04-03.
Figure 3.7 (A) Relationship between primary melt Fe$^{3+}$/∑Fe ratios and measured Zn/Fe* ratios for MORB, Mariana trough and Mariana arc basalts. Symbols are as in Figure 2. Results for the Mariana trough and Mariana arc are plotted here as average values for each geographic location. The black line is the expected relationship for a Zn/Fe* mantle source ratio = 9, a K$_D$ Zn/Fe* = 0.84, and source mantle Fe$^{3+}$/∑Fe ratio = 0.03. The gray and blue dashed lines demonstrate the impact of changing the mantle source Zn/Fe* ratio to 8 and 14, respectively. (B) A histogram showing the range in measured Zn/Fe* ratios in mantle rocks from various tectonic locations.
Figure 3.8 Plot of primary Cu concentrations calculated for MORB, Mariana trough, and Mariana arc samples versus melt fraction calculated from primary melt TiO$_2$ concentrations. The black dashed line, solid gray line, and solid black lines demonstrate the results from fractional melting models at QFM, QFM+0.5, and QFM+1.3 respectively, using mantle source Cu = 28 ppm and S = 200 ppm. The green dashed lines show the results of a fractional melting model at QFM+1.3 using mantle source Cu = 20 ppm and S = 200 ppm.
Figure 3.9 Plot of (a) Sc/La, (b) V/La, (c) Zn/La, and (d) Cu/La ratios versus Sm/La ratios for MORB (gray field; Niu and Batiza, 1997), Mariana trough (this study), and Mariana arc (this study) samples. Symbols are as in figure 2.
Table 3.1. \( Fe^{2+}O \) and \( FeO^* \) for Mariana arc bulk tephra

| Volcano | \( Fe^{2+}O_{\text{actual}} \) (wt%, measured) | \( FeO^* \) (wt%) | \( Fe^{3+}/\Sigma Fe \) (1σ) |
|---------|-----------------------------------------------|------------------|----------------------------|
| Maug    |                                               |                  |                            |
| 04MAUG3 | 6.36                                          | 12.08            | 0.470 (0.023)              |
|         | 6.38                                          |                  |                            |
| 04MAUG5 | 5.10                                          | 11.5             | 0.560 (0.031)              |
| MAUG1   | 7.04                                          | 10.36            | 0.320 (0.030)              |
| Pagan   |                                               |                  |                            |
| 04PAGA10| 7.99                                          | 11.64            | 0.310 (0.024)              |
| Anatahan|                                               |                  |                            |
| ANAT26-02| 4.94                                         | 8.13             | 0.393 (0.013)              |
| ANAT9   | 4.67                                          | 6.77             | 0.310 (0.016)              |
| ANAT26-01| 5.40                                         | 7.71             | 0.300 (0.313)              |
| 04ANAT4 | 5.78                                          | 7.82             | 0.261 (0.014)              |
| 04ANAT1 | 5.32                                          | 7.34             | 0.276 (0.014)              |
| Sarigan |                                               |                  |                            |
| SARI15-04| 6.53                                         | 8.64             | 0.244 (0.036)              |
| Agrigan |                                               |                  |                            |
| AGRI19-02| 7.37                                         | 10.44            | 0.294 (0.030)              |
| Guguan  |                                               |                  |                            |
| 04GUG11 | 6.37                                          | 9.38             | 0.321 (0.033)              |
| Uruacas |                                               |                  |                            |
| 04URAC5a| 7.36                                          | 9.24             | 0.203 (0.034)              |
| Asuncion|                                               |                  |                            |
| ASUN20-02| 6.62                                         | 9.04             | 0.268 (0.035)              |
| Alamagan|                                               |                  |                            |
| ALA01   | 6.17                                          | 9.03             | 0.317 (0.035)              |

\(^1\)Plank, unpublished data
| USGS standard powders | Fe\(^{2+}\)O\(_{(\text{actual})}\) (wt\% measured) | Fe\(^{2+}\)O\(_{(\text{actual})}\) (wt\% published) |
|----------------------|-----------------------------------------------|-----------------------------------------------|
| W-2                  | 8.32                                          | 8.34                                          |
|                      | 8.69                                          |                                               |
| QLO-1                | 3.28                                          | 2.97                                          |
|                      | 3.43                                          |                                               |
| BCR-1                | 9.05                                          | 8.8                                           |
|                      | 8.87                                          |                                               |
| BIR-1                | 8.39                                          | 8.34                                          |
|                      | 8.73                                          |                                               |
Table 3.2. Fe redox, trace element compositions, and calculated values for mid-ocean ridge and Mariana trough basalts

| Sample               | $\text{Fe}^{3+}/\Sigma\text{Fe}_{\text{measured}}$ | magmatic $f_O^2$ (1 atm, 1200°C) | V/Sc measured | Zn/Fe* measured | $\text{Cu}_{\text{measured}}$ (ppm) | $\text{Fe}^{3+}/\Sigma\text{Fe}_{\text{primary}}$ | primary $f_O^2$ (1 Gpa, 1350°C) | Cu primary (ppm) | F (TiO$_2$) |
|----------------------|---------------------------------|---------------------------------|----------------|-----------------|---------------------------------|---------------------------------|---------------------------------|-----------------|-----------|
| **Mid-ocean ridge basalts** |                                 |                                 |                |                 |                                |                                |                                 |                 |           |
| East Pacific Rise    |                                 |                                 |                |                 |                                |                                |                                 |                 |           |
| D12-5                | 0.163                           | 0.16                            | 8.8            | 13.1            | 89                             | 0.140                           | 0.22               | 100             | 0.08      |
| CH 19-3              | 0.158                           | 0.06                            | 8.4            | 11.8            | 85                             | 0.140                           | 0.17               | 93              | 0.08      |
| CH 21-1              | 0.150                           | -0.05                           | 6.4            | 10.5            | 76                             |                                 |                    |                 |           |
| CH 30-1              | 0.167                           | 0.28                            | 11.6           | 13.8            | 71                             |                                 |                    |                 |           |
| CH 5-1               | 0.166                           | 0.20                            | 7.6            | 11.3            | 63                             |                                 |                    |                 |           |
| CH 6-1               | 0.162                           | 0.14                            | 7.3            | 10.6            | 58                             |                                 |                    |                 |           |
| CH 61-1              | 0.163                           | 0.12                            | 7.9            | 12.5            | 74                             |                                 |                    |                 |           |
| CH 84-2              | 0.160                           | 0.10                            | 6.8            | 10.9            | 63                             |                                 |                    |                 |           |
| CH 15-2              | 0.172                           | 0.28                            | 8.1            | 12.2            | 76                             |                                 |                    |                 |           |
| CH 33-1              | 0.153                           | 0.06                            | 7.3            | 9.8             | 59                             |                                 |                    |                 |           |
| 975 5-1              | 0.165                           | 0.20                            | 8.3            | 11.8            | 65                             |                                 |                    |                 |           |
| RAIT 02-D120         | 0.178                           | 0.56                            | 6.6            | 8.9             | 42                             |                                 |                    |                 |           |
| RAIT 02-D122         | 0.166                           | 0.27                            | 7.5            | 11.6            | 65                             |                                 |                    |                 |           |
| RISE 3-D30           | 0.172                           | 0.38                            | 7.9            | 10.3            | 51                             |                                 |                    |                 |           |
Table 3.2. continued

| Sample                  | $\text{Fe}^{3+}/\Sigma\text{Fe}$ | $f_O^2$ (1 atm, 1200°C) | V/Sc measured | Zn/Fe* measured | $\text{Cu}_{\text{measured}}$ (ppm) | $\text{Fe}^{3+}/\Sigma\text{Fe}$ | $f_O^2$ primary | $\text{Cu}_{\text{primary}}$ (ppm) | F (TiO$_2$) |
|-------------------------|----------------------------------|-------------------------|----------------|-----------------|-------------------------------------|----------------------------------|----------------|-----------------------------------|------------|
| **Mid-ocean ridge basalts** |                                  |                          |                |                 |                                     |                                  |                |                                   |            |
| **Siqueiros Fracture Zone** |                                  |                          |                |                 |                                     |                                  |                |                                   |            |
| RAIT 02 D 12-1          | 0.159                            | 0.14                     | 6.2            | 9.9             | 72                                  | 0.140                            | 0.26           | 92                                | 0.07       |
| SIQ D3-1                | 0.157                            | 0.07                     | 6.0            | 9.3             | 83                                  | 0.140                            | 0.13           | 98                                | 0.10       |
| TW74-D7-1               | 0.159                            | 0.13                     | 5.4            | 10.5            | 73                                  | 0.160                            | 0.34           | 98                                | 0.10       |
| SIQ D3-3                | 0.162                            | 0.15                     | 7.1            | 10.2            | 89                                  | 0.150                            | 0.22           | 86                                | 0.11       |
| **Galapagos Spreading Center** |                                  |                          |                |                 |                                     |                                  |                |                                   |            |
| K 10-34                 | 0.149                            | -0.02                    | 4.8            | 8.6             | 76                                  | 0.140                            | 0.14           | 85                                | 0.10       |
| K 14-3                  | 0.167                            | 0.32                     | 11.7           | 13.4            | 85                                  |                                  |                |                                   |            |
| K 18-21                 | 0.168                            | 0.36                     | 10.4           | 14.3            | 65                                  |                                  |                |                                   |            |
| KK78-D17-14             | 0.151                            | 0.02                     | 6.4            | 10.3            | 97                                  | 0.140                            | 0.16           | 95                                | 0.13       |
| KK78-D17-4              | 0.146                            | -0.05                    | 5.5            | 9.8             | 82                                  | 0.140                            | 0.10           | 79                                | 0.13       |
| KK78-D17-32             | 0.144                            | -0.07                    | 7.0            | 10.8            | 104                                 | 0.130                            | 0.07           | 100                               | 0.13       |
| KK78-D17-3              | 0.141                            | -0.16                    | 6.2            | 10.4            | 92                                  | 0.130                            | -0.02          | 88                                | 0.13       |
| KK78-D21-2              | 0.154                            | 0.11                     | 5.0            | 8.1             | 97                                  | 0.140                            | 0.21           | 101                               | 0.12       |
| **Indian Ocean**        |                                  |                          |                |                 |                                     |                                  |                |                                   |            |
| V33-7-3                 | 0.155                            | -0.04                    | 6.5            | 10.3            | 52                                  |                                  |                |                                   |            |
| V33-8-8,7               | 0.147                            | -0.16                    | 5.8            | 10.0            | 59                                  |                                  |                |                                   |            |
| Sample          | Fe$^{3+}$/ΣFe measured | magmatic $f_O^2$ (1 atm, 1200°C) | V/Sc measured | Zn/Fe* measured | Cu$_{measured}$ (ppm) | Fe$^{3+}$/ΣFe primary | Cu$_{primary}$ (1 Gpa, 1350°C) | Cu$_{primary}$ (ppm) | F (TiO$_2$) |
|-----------------|------------------------|---------------------------------|---------------|----------------|----------------------|----------------------|----------------------------|----------------------|-------------|
| Mid-ocean ridge basalts |                       |                                 |               |                |                      |                      |                            |                      |             |
| *Juan de Fuca*  |                       |                                 |               |                |                      |                      |                            |                      |             |
| VG-2            | 0.164                  | 0.26                            | 8.3           | 13.2           | 56                   |                      |                            |                      |             |
| JDF C6-1        | 0.163                  | 0.27                            | 10.6          | 13.6           | 73                   |                      |                            |                      |             |
| JDF D11-2       | 0.167                  | 0.19                            | 5.4           | 10.0           | 90                   |                      |                            |                      |             |
| JDF D5-2        | 0.159                  | 0.15                            | 7.2           | 12.1           | 59                   |                      |                            |                      |             |
| JDFD2           | 0.167                  | 0.34                            | 7.9           | 14.2           | 57                   |                      |                            |                      |             |
| Mid-Atlantic Ridge |                     |                                 |               |                |                      |                      |                            |                      |             |
| MAPCO CH98      |                       |                                 |               |                |                      |                      |                            |                      |             |
| DR12            | 0.152                  | 0.05                            | 7.0           | 11.8           | 57                   |                      |                            |                      |             |
| All 92-29-1F    | 0.163                  | 0.18                            | 8.2           | 12.7           | 61                   |                      |                            |                      |             |
| 2πD47-1         | 0.159                  | 0.11                            | 7.4           | 12.4           | 71                   |                      |                            |                      |             |
| 523-1           | 0.152                  | -0.03                           | 6.3           | 10.8           | 64                   |                      |                            |                      |             |
| 523-2-1         | 0.143                  | -0.14                           | 7.1           | 11.9           | 59                   | 0.120                | -0.10                     | 69                   | 0.07        |
| ALV 527 1-1     | 0.128                  | -0.41                           | 5.9           | 9.6            | 105                  | 0.120                | -0.27                     | 105                  | 0.17        |
| TR138 11D-1     | 0.155                  | 0.05                            | 8.9           | 13.3           | 79                   |                      |                            |                      |             |
| TR138 2D-2      | 0.143                  | -0.15                           | 6.3           | 11.2           | 73                   | 0.140                | -0.01                     | 95                   | 0.11        |
| TR138 9D-4      | 0.145                  | -0.15                           | 7.5           | 11.7           | 70                   |                      |                            |                      |             |
| TK 2-10         | 0.169                  | 0.41                            | 8.5           | 14.8           | 80                   |                      |                            |                      |             |
| Sample          | Fe$_{3+}$/$\Sigma$Fe \(\text{measured} \) | magmatic f$_{O_2}$ (1 atm, 1200°C) | V/Sc \(\text{measured} \) | Zn/Fe* \(\text{measured} \) | Cu \(\text{measured} \) (ppm) | Fe$_{3+}$/$\Sigma$Fe \(\text{primary} \) | primary f$_{O_2}$ (1 Gpa, 1350°C) | Cu \(\text{primary} \) (ppm) | F \((\text{TiO}_2)\) |
|-----------------|-----------------------------------------|----------------------------------|----------------------------|----------------------------|----------------------------|---------------------------------|-------------------------------|----------------------------|-----------------|
| Mid-Atlantic Ridge |                                         |                                  |                            |                            |                            |                                 |                                |                            |                 |
| TK 3-1          | 0.159                                   | 0.10                             | 7.4                        | 10.9                       | 59                         |                                 |                                |                            |                 |
| TR119 6D-1      | 0.150                                   | -0.06                            | 6.8                        | 11.4                       | 84                         |                                 |                                |                            |                 |
| TR119 6D-4      | 0.159                                   | 0.15                             | 7.5                        | 10.6                       | 66                         |                                 |                                |                            |                 |
| EN25 6D-4       | 0.165                                   | 0.29                             | 9.0                        | 14.3                       | 99                         |                                 |                                |                            |                 |
| EN25 6D-3       | 0.155                                   | 0.19                             | 7.8                        | 10.8                       | 101                        |                                 |                                |                            |                 |
| 2πD43           | 0.146                                   | -0.13                            | 8.8                        | 14.9                       | 68                         |                                 |                                |                            |                 |
| MAPCO CH98      |                                         |                                  |                            |                            |                            |                                 |                                |                            |                 |
| DR11            | 0.154                                   | 0.09                             | 8.1                        | 12.2                       | 69                         | 0.130                           | 0.12                          | 69                          | 0.07            |
| Mariana trough basalts |                                         |                                  |                            |                            |                            |                                 |                                |                            |                 |
| Northern        |                                         |                                  |                            |                            |                            |                                 |                                |                            |                 |
| 76-1-1          | 0.160                                   | 0.12                             | 8.3                        | 11.1                       | 61                         | 0.133                           | 0.03                          | 51                          | 0.06            |
| 75-1-2          | 0.165                                   | 0.17                             | 7.2                        | 11.9                       | 59                         | 0.145                           | 0.17                          | 51                          | 0.05            |
| 80-1-3          | 0.152                                   | 0.05                             | 4.9                        | 9.3                        | 89                         | 0.139                           | 0.14                          | 70                          | 0.14            |
| 73-2-1          | 0.171                                   | 0.23                             | 6.8                        | 11.6                       | 58                         | 0.151                           | 0.27                          | 56                          | 0.07            |
| 46-1-6          | 0.170                                   | 0.25                             | 7.1                        | 10.7                       | 67                         | 0.151                           | 0.28                          | 61                          | 0.09            |
| 74-1-1          | 0.174                                   | 0.29                             | 6.8                        | 11.0                       | 74                         | 0.165                           | 0.44                          | 65                          | 0.09            |
| 71-1-14         | 0.191                                   | 0.48                             | 6.9                        | 9.9                        | 75                         | 0.173                           | 0.57                          | 77                          | 0.10            |
| 82-1-1          | 0.184                                   | 0.43                             | 6.9                        | 12.0                       | 65                         | 0.164                           | 0.49                          | 65                          | 0.08            |
| 47-1-5          | 0.175                                   | 0.29                             | 6.8                        | 10.6                       | 74                         | 0.160                           | 0.38                          | 67                          | 0.11            |
| Sample            | Fe\(^{3+}\)/ΣFe measured | magmatic fO\(_2\) (1 atm, 1200°C) | V/Sc measured | Zn/Fe* measured | Cu\(_{measured}\) (ppm) | Fe\(^{3+}\)/ΣFe primary | primary fO\(_2\) (1 Gpa, 1350°C) | Cu\(_{primary}\) (ppm) | F (TiO\(_2\)) |
|-------------------|----------------------------|----------------------------------|---------------|----------------|-------------------------|------------------------|--------------------------|------------------------|--------------|
| Mariana trough basalts |
| **Southern**      |                            |                                  |               |                |                         |                        |                          |                        |              |
| TN273-02W-01      | 0.185                      | 0.57                             | 10.8          | 14.4           | 72                      | 0.160                  | 0.52                     | 76                     | 0.11         |
| TN273-03W-02      | 0.189                      | 0.65                             | 11.4          | 14.1           | 73                      | 0.158                  | 0.55                     | 80                     | 0.11         |
| TN273-04W-01      | 0.188                      | 0.78                             | 10.8          | 13.3           | 40                      |                        |                          |                        |              |
| TN273-05W-01      | 0.194                      | 0.82                             | 9.6           | 14.8           | 37                      |                        |                          |                        |              |
| TN273-06W-01      | 0.178                      | 0.58                             | 10.7          | 12.7           | 39                      |                        |                          |                        |              |
| TN273-01D-01-01   |                            |                                  |               |                |                         |                        |                          |                        |              |
| TN273-02D-01-02   | 0.171                      | 0.49                             | 7.9           | 15.0           | 7                       |                        |                          |                        |              |
| TN273-04D-01-02   | 0.207                      | 1.01                             | 8.9           | 17.0           | 23                      |                        |                          |                        |              |
| TN273-05D-01-01   | 0.186                      | 0.67                             | 6.5           | 18.9           | 9                       |                        |                          |                        |              |
| Sample               | Fe$^{3+}$/ΣFe measured | magmatic $f_O^2$ (1 atm, 1200°C) | V/Sc measured | Zn/Fe* measured | Cu measured (ppm) | Fe$^{3+}$/ΣFe primary | primary $f_O^2$ (1 Gpa, 1350°C) | Cu primary (ppm) | F (TiO$_2$) |
|----------------------|------------------------|---------------------------------|----------------|----------------|-------------------|---------------------|-------------------------------|-----------------|------------|
| Mariana trough basalts |                        |                                 |                |                |                   |                     |                               |                 |            |
| Southern             |                        |                                 |                |                |                   |                     |                               |                 |            |
| TN273-06D-01-03      | 0.190                  | 0.73                            | 7.6            | 23.5           | 16                |                     |                               |                 |            |
| TN273-06D-02-02      | 0.193                  | 0.87                            | 14.2           | 14.1           | 70                |                     |                               |                 |            |
| TN273-06D-03-03      | 0.203                  | 0.99                            | 13.5           | 14.2           | 63                |                     |                               |                 |            |
| TN273-07D-01-01      | 0.196                  | 0.94                            | 12.0           | 12.0           | 27                |                     |                               |                 |            |
| TN273-08D-01-01      | 0.188                  | 0.81                            | 7.0            | 13.8           | 14                |                     |                               |                 |            |
| TN273-09D-01-03      | 0.191                  | 0.67                            | 10.5           | 12.7           | 42                |                     |                               |                 |            |
| TN273-12D-01-01      | 0.184                  | 0.53                            | 10.5           | 12.4           | 37                |                     |                               |                 |            |
| TN273-13D-01-01      | 0.190                  | 0.60                            | 9.6            | 13.4           | 99                | 0.167               | 0.60             | 104            | 0.17       |
Table 3.3  Fe redox, trace element compositions, and calculated values for Mariana arc olivine hosted melt inclusions

| Sample       | Fe$^{3+}$/ΣFe$^{2+}$ measured | magmatic $f$O$_2$ (Fe$^{3+}$/ΣFe$^{2+}$ measured, 1 atm, 1200°C) | V/Sc measured | Zn/Fe* measured | D $V_{\text{vol}/\text{liq}}$ | Temperature (Sc/Y) | magmatic $f$O$_2$ (from D $V_{\text{vol}/\text{liq}}$) | Cu$_{\text{measured}}$ (ppm) |
|--------------|-------------------------------|---------------------------------------------------------------|----------------|-----------------|-----------------|-------------------|-------------------|-------------------|
| Sarigan      |                               |                                                               |                |                 |                 |                   |                   |                   |
| SARI15-04-03 | 0.274                         | 1.57                                                          | 5.8            | 9.8             | 0.013           | 1331              | 2.86              | 124               |
| SARI15-04-07 | 0.250                         | 1.25                                                          | 5.3            | 9.0             | 0.012           | 1323              | 2.56              | 120               |
| SARI15-04-11 | 0.248                         | 1.29                                                          | 5.2            | 10.7            | 0.013           | 1353              | 2.68              | 122               |
| SARI15-04-15 | 0.233                         | 1.10                                                          | 7.5            | 14.2            | 0.012           | 1380              | 2.85              | 140               |
| SARI15-04-17 | 0.234                         | 1.14                                                          | 6.6            | 11.9            | 0.014           | 1375              | 2.73              | 125               |
| SARI15-04-18 | 0.240                         | 1.15                                                          | 6.4            | 12.2            | 0.012           | 1358              | 2.84              | 126               |
| SARI15-04-21 | 0.256                         | 1.41                                                          | 7.8            | 13.4            | 0.012           | 1370              | 2.96              | 145               |
| SARI15-04-22 | 0.237                         | 1.15                                                          | 8.1            | 14.4            | 0.013           | 1395              | 2.76              | 140               |
| SARI15-04-23 | 0.275                         | 1.58                                                          | 6.1            | 12.8            | 0.011           | 1404              | 3.01              | 144               |
| SARI15-04-24 | 0.258                         | 1.39                                                          | 5.9            | 9.8             | 0.011           | 1362              | 2.87              | 126               |
| SARI15-04-25 | 0.281                         | 1.71                                                          | 6.1            | 11.2            | 0.012           | 1418              | 2.74              | 116               |
| SARI15-04-27 | 0.218                         | 0.90                                                          | 5.9            | 12.0            | 0.012           | 1378              | 2.54              | 124               |
| SARI15-04-29 | 0.244                         | 1.16                                                          | 6.1            | 12.8            | 0.010           | 1372              | 2.85              | 125               |
| SARI15-04-31A| 0.245                         | 1.23                                                          | 5.7            | 9.0             | 0.013           | 1340              | 2.57              | 114               |
| SARI15-04-33 | 0.195                         | 0.69                                                          | 6.4            | 10.3            | 0.016           | 1300              | 2.66              | 115               |
Table 3.3 continued

| Sample    | Fe$^{3+}$/ΣFe measured | magmatic fO$_2$ (fFe$^{3+}$/ΣFe measured, 1 atm, 1200°C) | V/Sc measured | Zn/Fe* measured | D$_{\text{olv/liq}}$ | Temperature (Sc/Y) | magmatic fO$_2$ (from D$_{\text{olv/liq}}$) | Cu$_{\text{measured}}$ (ppm) |
|-----------|------------------------|----------------------------------------------------------|---------------|-----------------|---------------------|-------------------|---------------------------------|-------------------------------|
| **Guguan**|                        |                                                           |               |                 |                     |                   |                                 |                               |
| GUG11-02  | 0.263                  | 1.43                                                     | 5.5           | 10.2            | 0.015               | 1319              | 2.60                            | 171                           |
| **Pagan** |                        |                                                           |               |                 |                     |                   |                                 |                               |
| PAGA8-2   | 0.222                  | 1.17                                                     | 11.1          | 13.5            | 0.018               | 1390              | 2.74                            | 190                           |
| **Alamagan**|                       |                                                           |               |                 |                     |                   |                                 |                               |
| ALA-02-01 | 0.258                  | 1.53                                                     | 6.7           | 13.2            | 0.014               | 1385              | 2.52                            | 108                           |
| ALA-02-03 | 0.243                  | 1.33                                                     | 6.0           | 10.2            | 0.021               | 1303              | 2.36                            | 108                           |
| ALA-02-04 | 0.244                  | 1.41                                                     | 5.8           | 13.6            | 0.020               | 1320              | 2.30                            | 170                           |
| ALA-02-05 | 0.259                  | 1.36                                                     | 4.9           | 9.3             | 0.011               | 1368              | 2.74                            | 93                            |
| ALA-02-07 | 0.244                  | 1.35                                                     | 6.6           | 12.6            | 0.018               | 1281              | 2.61                            | 126                           |
| ALA-02-08 | 0.245                  | 1.34                                                     | 6.0           | 10.8            | 0.012               | 1372              | 2.85                            | 105                           |
| ALA-02-09 | 0.230                  | 1.21                                                     | 6.5           | 10.4            | 0.012               | 1360              | 3.01                            | 107                           |
| ALA02-11  | 0.221                  | 1.06                                                     | 5.9           | 9.7             | 0.016               | 1335              | 2.62                            | 111                           |
| ALA02-15  | 0.244                  | 1.08                                                     | 5.6           | 11.7            | 0.013               | 1412              | 2.24                            | 99                            |
| ALA02-16A | 0.238                  | 1.30                                                     | 6.4           | 10.4            | 0.016               | 1334              | 2.38                            | 206                           |
| ALA-03-01 | 0.212                  | 0.75                                                     | 5.7           | 7.7             | 0.015               | 1300              | 2.82                            | 70                            |
| **Agrigan**|                       |                                                           |               |                 |                     |                   |                                 |                               |
| AGR07-15A | 0.254                  | 1.49                                                     | 7.2           | 9.2             | 0.015               | 1304              | 2.89                            | 137                           |
| AGR07-15B | 0.242                  | 1.33                                                     | 7.4           | 9.9             | 0.015               | 1307              | 2.95                            | 143                           |
| AGRI04-14 | 0.243                  | 1.35                                                     | 7.4           | 12.4            | 0.018               | 1410              | 2.64                            | 119                           |
**Table 3.3 continued**

| Sample       | $\text{Fe}^{3+}/\Sigma\text{Fe}_{\text{primary}}$ | primary $fO_2$ (1 GPa, 1350°C) | Cu$_{\text{primary}}$ (ppm) | F (TiO$_2$) |
|--------------|-----------------------------------|---------------------------------|----------------------------|--------------|
| **Sarigan**  |                                   |                                 |                            |              |
| SARI15-04-03 | 0.279                             | 1.59                            | 113                        | 0.20         |
| SARI15-04-07 | 0.275                             | 1.28                            | 109                        | 0.20         |
| SARI15-04-11 | 0.225                             | 1.33                            | 113                        | 0.19         |
| SARI15-04-15 | 0.208                             | 1.10                            | 128                        | 0.17         |
| SARI15-04-17 | 0.208                             | 1.14                            | 114                        | 0.18         |
| SARI15-04-18 | 0.276                             | 1.20                            | 115                        | 0.18         |
| SARI15-04-21 | 0.230                             | 1.42                            | 134                        | 0.16         |
| SARI15-04-22 | 0.210                             | 1.15                            | 128                        | 0.17         |
| SARI15-04-23 | 0.251                             | 1.63                            | 134                        | 0.18         |
| SARI15-04-24 | 0.276                             | 1.45                            | 114                        | 0.18         |
| SARI15-04-25 | 0.255                             | 1.73                            | 107                        | 0.18         |
| SARI15-04-27 | 0.273                             | 0.95                            | 115                        | 0.21         |
| SARI15-04-29 | 0.276                             | 1.22                            | 112                        | 0.22         |
| SARI15-04-31A| 0.273                             | 1.27                            | 105                        | 0.20         |
| SARI15-04-33 | 0.173                             | 0.68                            | 107                        | 0.18         |
| Sample   | $\text{Fe}^{3+}/\Sigma\text{Fe}_{\text{primary}}$ | primary $\delta O_2$ (1 GPa, 1350°C) | Cu$_{\text{primary}}$ (ppm) | F (TiO$_2$) |
|----------|-----------------------------------------------|-------------------------------------|---------------------------|------------|
| **Guguan** |                                               |                                     |                           |            |
| GUG11-02 | 0.242                                         | 1.55                                | -                         | 0.23       |
| **Pagan** |                                               |                                     |                           |            |
| PAGA8-2  | 0.186                                         | 0.95                                | -                         | 0.16       |
| **Alamagan** |                                         |                                     |                           |            |
| ALA-02-01 | 0.230                                         | 1.53                                | 99                        | 0.20       |
| ALA-02-03 | 0.227                                         | 1.50                                | 96                        | 0.15       |
| ALA-02-04 | 0.221                                         | 1.46                                | 155                       | 0.15       |
| ALA-02-05 | 0.235                                         | 1.41                                | 84                        | 0.23       |
| ALA-02-07 | 0.219                                         | 1.38                                | 114                       | 0.19       |
| ALA-02-08 | 0.217                                         | 1.34                                | 95                        | 0.24       |
| ALA-02-09 | 0.199                                         | 1.16                                | 95                        | 0.24       |
| ALA02-11 | 0.195                                         | 1.09                                | 97                        | 0.22       |
| ALA02-15 | 0.223                                         | 1.16                                | 89                        | 0.20       |
| ALA02-16A | 0.207                                         | 1.27                                | 182                       | 0.18       |
| ALA-03-01 | 0.199                                         | 0.92                                | 66                        | 0.18       |
| **Agrigan** |                                               |                                     |                           |            |
| AGR07-15A | 0.195                                         | 1.18                                | 141                       | 0.17       |
| AGR07-15B | 0.184                                         | 1.00                                | 148                       | 0.16       |
| AGRI04-14 | 0.188                                         | 1.04                                | 136                       | 0.17       |
Supplementary text to accompany the manuscript titled, “A review of transition row element proxies for mantle source oxygen fugacity”

LA-ICP-MS analysis

Abundances of 5 minor (Na$_2$O, Al$_2$O$_3$, P$_2$O$_5$, CaO, and TiO$_2$) and 11 trace elements (Li, Sc, V, Cr, Co, Ni, Cu, Zn, Sr, Y, and Zr) were determined in olivine hosts by laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) at the Graduate School of Oceanography, University of Rhode Island on a Thermo X-Series II quadrupole ICP-MS coupled with a New Wave UP 213 Nd-YAG laser ablation system following techniques outlined by Kelley et al. (2003) and Lytle et al. (2012), using $^{26}$Mg as the internal standard for olivine. The laser was operated at 60-65% energy output and 5 Hz, to achieve a slow drilling rate of $\sim$1 $\mu$m/s through thin samples. Laser spot sizes ranged from 20-80 $\mu$m. United States Geological Survey glass standards BCR-2g, BHVO-2g, BIR-1g, and Max Planck Institutes glass standards GOR-132-G, StHls-G, T1-G, ML3B-G and KL2-G were used to create a linear calibration curve ($R^2$>0.990) for each run (Jochum et al., 2006; Kelley et al., 2003). San Carlos olivine (Fo$_{88}$) was analyzed periodically as a check on the determination of unknown olivine compositions. Olivine grains were analyzed in single analyses. Counting statistics were examined carefully for each element and those elements that did not return strong signals for the entire length of the laser ablation period were discarded.

Inclusion/olivine host equilibrium and post-entrapment crystallization corrections
We use only olivine host-melt inclusion pairs that satisfy the screening tests of Brounce et al. (in review), which we summarize briefly here. Equilibrium host forsterite contents (Fo) were calculated for melt inclusions and compared to the measured Fo for the olivine host of each inclusion using a FeO/MgO $K_D^{\text{Olv/liq}} = 0.3$ (Roeder and Emslie, 1970). If the predicted equilibrium Fo\text{inclusion} matched the Fo\text{host}, we assumed equilibrium between inclusion and host. If the Fo\text{inclusion} was lower than the Fo\text{host}, indicative of crystallization within the inclusion after it was trapped in its olivine host, olivine of the equilibrium major element composition was added to the inclusion major element composition in 0.1% increments until the Fo\text{inclusion} and Fo\text{host} were equal. If the predicted equilibrium Fo\text{inclusion} was higher that the Fo\text{host}, no action was taken. Those inclusions that required >2% correction or whose Fo\text{host} - Fo\text{inclusion} disagreed by more than 2% were excluded. Each melt inclusion suite was compared to published whole rock and melt inclusion data for each volcano. Inclusion compositions that deviate significantly from the major element relationships defined by the available published data were excluded.
MANUSCRIPT 4: The redox budget of the Mariana subduction zone

In preparation for submission to an AGU Journal

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Abstract

Oceanic lithosphere is altered and oxidized as it spreads along the seafloor, until it subducts at convergent margins where fluids and melts from the subducting plate contribute to the composition of arc and back-arc basalts. The oxidized nature of Mariana arc magmas is likely acquired through the transfer of oxidized species from the subducting slab to the mantle wedge beneath the volcanic arc. Despite having a critical role in the relationship between material recycling at subduction zones and oxidation, it is unclear what percentage of the oxidized material is transported into the mantle wedge and output during arc or back-arc volcanism, or whether any amount of this oxidized material is transported past subduction zones and into the deep mantle. We present \( \text{Fe}^{3+}/\Sigma \text{Fe} \) ratios determined on bulk sediments and altered oceanic crust recovered from ODP Site 801 in the western Pacific in order to constrain the bulk oxidation state of the Pacific plate prior to subduction. We performed micro-colorimetric determinations of the \( \text{Fe}^{2+} \) contents of 9 sediment samples, 8 variably altered MORBs, 1 hydrothermal deposit, 2 veins, 2 hyaloclastites, and 8 mixed composite powders from the sediment and upper 500 m of altered oceanic crust at ODP Site 801, a geochemical reference site for the subduction inputs to the Mariana subduction zone. Site 801 sediments have \( \text{Fe}^{3+}/\Sigma \text{Fe} \) ratios >0.69 and the altered oceanic crust (801 Super Composite) has \( \text{Fe}^{3+}/\Sigma \text{Fe} \) of 0.51. Bulk \( \text{Fe}^{3+}/\Sigma \text{Fe} \) ratios of altered oceanic crust at Site 801 increase from 0.16 (pristine MORB glass measured previously [see Chapter 2] by XANES) to 0.78 with increasing extent of alteration. Using bulk \( \text{Fe}^{3+}/\Sigma \text{Fe} \) ratios determined here, and Fe redox information from previous chapters in this volume, we calculated a mass balance of \( \text{Fe}^{3+} \), and the associated \( \text{O}_2 \).
equivalent through the Mariana subduction zone. We subtracted the Fe$^{3+}$ of pristine oceanic crust from that of altered oceanic crust to estimate the amount of Fe$^{3+}$ taken up by oceanic crust during alteration on the seafloor. Comparing this value to the output of Fe$^{3+}$ from Mariana arc and back-arc lavas, we find that 50-70% of the O$_2$ equivalent added to the oceanic crust by alteration on the seafloor is not output by arc or back-arc magmas. If this oxygen is retained in the slab that subducts into the deep mantle, it may contribute to mantle redox heterogeneity.

1. Introduction

Oceanic crust is created at mid-ocean ridges and is progressively altered and oxidized as it spreads along the seafloor, until it comes to a convergent margin and subducts [Alt and Teagle, 2003; Lecuyer and Ricard, 1999; Rouxel et al., 2003]. Despite the clear influence that the subducting slab imparts on the trace element and isotopic composition of arc lavas, the ultimate fate of the oxidized signature within the subducting slab is unclear. The oxidized nature of arc basalts is linked to the oxidized condition of the subducting slab [Brounce et al., in revision; Kelley and Cottrell, 2009; Mungall, 2002; Parkinson and Arculus, 1999; Wood et al., 1990], but the efficiency of the transfer of oxygen or oxidized species from the slab to the mantle wedge is poorly constrained. The transfer of significant quantities of oxygen from Earth’s surface past subduction zones to the deeper mantle holds significant consequences for the long-term evolution of Earth’s interior. If 100% of the excess oxygen added to the slab by alteration and sedimentation is returned to the surface by arc and back-arc volcanism, then no surface-derived oxygen is returned to the deep mantle. On the other hand,
recycling of oxidized species may have low efficiency, in which case subduction transfers oxygen from Earth’s surface into the deep mantle over geologic time scales [Sleep et al., 2012]. A mass balance of Fe$^{3+}$ using globally averaged data from oceanic crust, oceanic sediments, arc basalts, and oceanic island basalts suggests that the Earth’s mantle has been a sink for oxidized iron through geologic time [Lecuyer and Ricard, 1999]. However, subduction zones active today vary widely in the composition and flux of sediments being recycled, the age and extent of alteration of oceanic crust being subducted, the extent of serpentinization of the underlying lithosphere, the extent to which sediments and oceanic crust are returned to the arc crust during subduction, and the composition and flux of material erupted at arc volcanoes, such that this balance of Fe$^{3+}$ cycling in the Earth has large uncertainties. Establishing links between the altered, subducting slab and the materials emplaced in the arc and back-arc crust in a single convergent margin system are necessary to determine the efficiency of redox transfer in the subduction cycle. Iron is a useful tracer of the balance of oxygen through subduction zones because it exists as Fe$^{2+}$ and Fe$^{3+}$, and their charges are balanced mostly by oxygen. Accurately determining the proportions of Fe$^{2+}$ and Fe$^{3+}$ in subduction inputs and outputs is a key step towards developing an accurate model of the transfer of oxygen through subduction cycles.

Here, we present measurements of the Fe$^{2+}$O of lithologies representative of inputs to the Mariana convergent margin, determined by whole-rock wet chemistry, in order to constrain the bulk oxidation state of material entering the subduction zone. We pair these new data with previously collected major element concentrations on the same samples [Fisk and Kelley, 2002; Kelley et al., 2003] to calculate Fe$^{3+}$/ΣFe ratios.
(i.e., $\text{Fe}^{3+}/[\text{Fe}^{2+} + \text{Fe}^{3+}]$). These data constrain the proportion of oxidized Fe in the subducting sediment and the extent to which the oxidation state of Fe has changed during alteration of oceanic crust. We demonstrate that even minimal post-eruptive alteration elevates $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios significantly in basaltic oceanic crust and that this alteration persists uniformly to 500m depth into igneous basement. We use $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios determined in this study to calculate a mass balance for $\text{Fe}^{3+}$ and the equivalent $\text{O}_2$ necessary to balance it through the Mariana subduction system, in order to determine the fate of oxygen in the subducting slab through the subduction cycle.

2. Methods

Terry Plank donated powdered samples of sediment and altered oceanic crust, as well as composite powders described by Kelley et al. [2003] and Plank et al. [2000] (Table 1). All samples were recovered from ODP Site 801 in the western Pacific during Legs 129 [Lancelot et al., 1990] and 185 [Plank et al., 2000; Fig. 1]. We followed the micro-colorimetric methods described by Wilson [1960] and Carmichael [2014]. All wet chemical procedures were carried out in the Wet Chemistry Laboratory at the National Museum of Natural History, Smithsonian Institution. Each run included 10-20 unknown samples plus three USGS rock powders (BIR-1, QLO-1, BCR-1) that are certified for $\text{Fe}^{2+}$ concentrations.

The procedure that we outline here are techniques taken from Carmichael [2014], for which we provide a detailed description of the execution of each step. Concentration units are weight of solid reagent in grams over the final solution volume in milliliters, expressed as $\% \text{w/v}$. This procedure requires solutions of an $\text{Fe}^{2+}$O
standard (0.01% w/v), beryllium sulfate (50% w/v), ammonium acetate (50% w/v),
ammonium vanadate, and 2:2’ bipyridine (0.15% w/v). This procedure makes use of
the reaction:

\[
V^{5+} + Fe^{2+} \leftrightarrow V^{4+} + Fe^{3+}
\]  

(1)

The direction in which the reaction proceeds will depend on pH, and in solutions
above pH ~5, the reaction will move from right to left, reducing Fe\(^{3+}\) to Fe\(^{2+}\). During
digestion of rock powders, V\(^{5+}\) is added to oxidize Fe\(^{2+}\) from the rock powder at pH <
5. Once the rock powder is completely in solution, the pH of the solution is increased
to ~5 and EQ 1 is reversed to regenerate Fe\(^{2+}\) in the presence of a coloring agent, 2:2’
bipyridine. The complexation of Fe\(^{2+}\) with bipyridine ligands colors the solution red,
which can be quantified using a spectrophotometer.

2.1. Solution recipes

First, we will outline the recipes for creating the solutions referenced in this
procedure. Some of the materials necessary for these solutions are hazardous. Consult
the material safety data sheets for each compound before proceeding. To make the
Fe\(^{2+}\)O standard solution, weigh 0.5458 grams of powdered ferrous ammonium sulfate
(99% purity) and empty into a 1 L acid cleaned, glass volumetric flask. Add ~100 mL
of distilled water to the flask to dissolve the ferrous ammonium sulfate. Add 110 mL
of 50% strength reagent grade sulfuric acid and mix well. Dilute the solution to 1 L
with distilled water. Mix well. This solution has shown no evidence for becoming
unstable over several months, but a new solution should be made on an annual basis.
To make the 2:2’ bipyridine solution, weigh out 0.15 grams of solid 2:2’ bipyridine
(98% purity) and empty into a 100 mL acid cleaned, glass volumetric flask. Add ~50
mL of distilled water to the flask, place a glass stopper in the flask, and place the flask on a hot plate set to ~70°C. Let sit until the 2:2’ bipyridine is in solution, swirling the flask occasionally. Let the solution cool back to room temperature and dilute to 100 mL with distilled water. Mix well. To make the beryllium sulfate solution, weigh out 50 grams of solid beryllium sulfate (99.99% purity) and empty into a 100 mL acid cleaned, glass volumetric flask. Add ~50 mL of distilled water to the flask and swirl the flask until the beryllium sulfate is in solution. Dilute the flask up to 100 mL with distilled water. Mix well. To make the ammonium acetate solution weigh out 50 grams of solid ammonium acetate (97% purity) and empty into a 100 mL acid cleaned, glass volumetric flask. Add ~50 mL distilled water to the flask and stir until the ammonium acetate is in solution. Dilute the flask up to 100 mL with distilled water. Mix well. To make the ammonium vanadate solution weigh out 0.1647 grams of solid ammonium vanadate (99.99% purity) and empty into a 100 mL acid cleaned, glass volumetric flask. Add 5.6 mL of full strength, reagent grade sulfuric acid and stir. Dilute the flask up to 100 mL with distilled water. Mix well.

2.2. Micro-colorimetry procedure

First, 2-6 milligrams of powder were weighed to a precision of ± 0.005 milligrams on an analytical microbalance into small aluminum weigh boats. The powder was carefully transferred into an acid cleaned, 15 mL Teflon vial. The weight of the weigh boat plus the powder and the weight of the weigh boat after transferring the powder into the Teflon vial were recorded to allow the calculation of the precise weight of sample powder in the Teflon vial. Once all of the powders were in Teflon vials, 1.0 mL of ammonium vanadate solution and 1.0 mL of hydrofluoric acid were
added to each vial. The ammonium vanadate solution supplies $\text{V}^{5+}$ to the solution, which at this step will oxidize $\text{Fe}^{2+}$ present in the rock powder to $\text{Fe}^{3+}$. The concentration of the solution is such that 1.0 mL of ammonium vanadate solution will suffice to oxidize 1.0 mg of $\text{Fe}^{2+}\text{O}$. The hydrofluoric acid is necessary for complete dissolution of silicates at low temperature. The vials were capped and left at room temperature until the sample powders were completely in solution (24-72 hours). Once the samples were completely dissolved (i.e., no small colored particles visible), one acid cleaned, glass 100 mL volumetric flask for each unknown and USGS standard in solution in the Teflon vials, plus five additional flasks for a blank and calibration standard solutions were assembled. To each flask, we added 5.0 mL of 2:2’ bipyridine solution and 10.0 mL of ammonium acetate solution. The bipyridine solution is the coloring agent that will complex with $\text{Fe}^{2+}$ to create solutions with variable hues of red, dependent on the $\text{Fe}^{2+}$ content in the rock powder. The ammonium acetate is used because it is a colorless solution that will buffer the pH of the solution at ~5. To make the four calibration standard solutions, we added 2, 4, 6, and 8 mL of $\text{Fe}^{2+}\text{O}$ standard solution to four flasks containing bipyridine and ammonium acetate solutions. These flasks were then diluted up to 100 mL with distilled water. To make a blank solution, we took one flask with bipyridine and ammonium acetate solution and diluted up to 100 mL with distilled water. Five mL of beryllium sulfate solution was added to the Teflon bottles containing the dissolved sample powders, to complex the fluoride ions generated by the hydrofluoric acid, which neutralizes the acid. After swirling the vials well, the contents of each Teflon vial were quantitatively washed with distilled water into a 100 mL flask (containing bipyridine and ammonium acetate solutions). To
accomplish this, the contents of each Teflon vial were emptied in the volumetric flask, then rinsed three times with distilled water, pouring each rinse into the flask as well. Each of these flasks was then diluted up to 100 mL with distilled water. A glass stopper was inserted into the top of each flask and tipped upside down to ensure a homogeneous solution.

Each solution (blank, calibration standard solutions, and sample solutions) was pipetted into 1 cm cells (~2 mL of solution, enough to fill the cell) and analyzed on a spectrophotometer at 525 nm (green visible light). Illuminating a red object with green light will cause the light to scatter, making the red object look black. The deeper the hue of red in each solution that is analyzed, the less light passes through the solution to the detector on the spectrophotometer, and the higher the absorbance value assigned to the solution. Absorption at 525 nm for the blank solution was subtracted from each calibration standard solution and sample solutions. A calibration line was constructed using the blank subtracted absorption values for the 2, 4, 6, and 8 mL FeO standard solutions (equivalent to 200, 400, 600, and 800 micrograms FeO in solution), achieving a minimum $R^2$ value of 0.9995 (Figure 2). This calibration line was then used to calculate the micrograms of $Fe^{2+}$O from the absorption values of unknown solutions and USGS standard powders. Combining this with the original weight of sample measured into the Teflon bottle for digestion, we calculated $Fe^{2+}$O concentrations for each sample. Analyses of these USGS standards never deviated from the certified $Fe^{2+}$O content by more than 0.46 wt% (absolute) for the lowest $Fe^{2+}$O standard (QLO-1, 2.97 wt%) and by 0.27 wt% (absolute) for the highest $Fe^{2+}$O standard (BCR-1, 8.8 wt%).
4. Results

Analytical results are presented in Table 1. Pristine glass chips from ODP Site 801, measured by XANES (see chapter 2, this volume), have the same Fe\(^{3+}/\Sigma\text{Fe}\) ratios as modern MORB glass [~0.16; Brounce et al., in prep], indicating that before alteration, the igneous basement here has a similar bulk redox state to modern MORB. Whole-rock basalts that were petrographically described as “minimally altered” are more oxidized (0.29 – 0.46 Fe\(^{3+}/\Sigma\text{Fe}\); Fig. 3), which demonstrates that even minor alteration can oxidize Fe in basaltic rocks. The oxidation state of Fe increases with increasing extent of alteration, (0.47-0.78 Fe\(^{3+}/\Sigma\text{Fe}\) in pervasively altered samples) and the samples that include iron oxide veins, alteration halos, and celadonite are mostly Fe\(^{3+}\) (0.69-0.95 Fe\(^{3+}/\Sigma\text{Fe}\); Fig. 3). The overlying sediments are very oxidized (0.69-0.95 Fe\(^{3+}/\Sigma\text{Fe}\)), and some of the sediment samples have low FeO\(^*\) (i.e., total Fe expressed as FeO) which when combined with their bulk oxidation state, reflect very low Fe\(^{2+}\)O concentrations which likely approach the detection limit of the wet chemical methods used here. The gray and brown bars on figure 3 show the Fe\(^{3+}/\Sigma\text{Fe}\) ratios of composite powders constructed by physically mixing individual sample powders from recovered material at ODP Site 801 (Kelley et al., 2003). The 801 Super Composite, intended to represent the bulk composition of the upper 500 m of altered oceanic crust at Site 801, has an Fe\(^{3+}/\Sigma\text{Fe}\) ratio of 0.51, broadly consistent with the range in Fe\(^{3+}/\Sigma\text{Fe}\) ratios of discrete samples. The 801 SED composite, made up of representative interflow material within the altered oceanic crust at Site 801, has slightly lower Fe\(^{3+}/\Sigma\text{Fe}\) ratio than the range observed for individual sediment materials.
in the overlying sediment package (0.67, Fig. 3). The other MORB composite powders, for specific depth intervals have a small range from 0.51-0.52 Fe\(^{3+}/\Sigma\)Fe (Table 1). This constancy demonstrates that, at a minimum, the upper 500 m of igneous basement at ODP Site 801 has been affected by alteration reactions that increase the Fe\(^{3+}/\Sigma\)Fe ratios of bulk oceanic crust over the original igneous value. Two composite powders meant to represent a massive alkali basalt flow (Top Alkali Basalt, TAB-FLO) and the highly altered interflow material associated with that flow (TAB-VCL) have Fe\(^{3+}/\Sigma\)Fe ratios of 0.40 and 0.38, respectively. This unit is younger than the MORB tholeiites (157 Ma for TAB, 165-170 Ma for MORB; Fisk and Kelley, 2002) and not thought to be representative of normal MORB oceanic crust. As a result, it may have had a different starting Fe\(^{3+}/\Sigma\)Fe ratio and potentially a different alteration history [Kelley et al., 2003; Plank et al., 2000].

There are five samples in this study that were also analyzed by Rouxel et al. [2003] for Fe\(^{3+}/\Sigma\)Fe ratios using a titration method (Table 1). The analytical procedure is not discussed in Rouxel et al. [2003], so it is difficult to directly compare the data in this study with the data that has been previously published. Two of those samples are taken from the surface pelagic clay units (801A3R2-145 and 801A5R3-145), and both have Fe\(^{2+}O\) concentrations below the detection limit of this study and previous work [Rouxel et al., 2003]. Sample 801C4R1-72 is a hydrothermal deposit that is very oxidized, and though we report a Fe\(^{3+}/\Sigma\)Fe ratio for this sample, it is very close to the detection limit of our procedure. Sample 801C5R1-95a, a pervasively altered basalt, agrees with the Fe\(^{3+}/\Sigma\)Fe ratio calculated from data from Rouxel et al. [2003] to within 0.06. Sample 801C15R7-31, also a pervasively altered basalt, has a Fe\(^{3+}/\Sigma\)Fe ratio
determined in this study of 0.33 and 0.52 as determined by Rouxel et al. [2003], which is not in good agreement. Although the powder samples that were used for analysis in this study and in Rouxel et al. [2003] are aliquots taken from the same powder made onboard the Joides Resolution during drilling operations at Site 801, it is possible that the powder for 801C15R7-31 itself is heterogeneous. The source rock for this powder is a pervasively altered basalt that is heterogeneous in nature and although great care was taken in creating all powders, it could be difficult to ensure that the powders made from these rocks are homogeneous. It may also be that, because the procedures for determining Fe$^{2+}$O$_{actual}$ in each study are different, that some analytical offset exists. This is difficult to assess from the brief description of the methods, which do not include any explicit information about the use of rock standards during analysis, provided by Rouxel et al. [2003].

5. Discussion

The Pacific plate at ODP Site 801 is clearly oxidized as the result of alteration reactions that take place on the seafloor, prior to subduction (Figure 3). In order to assess the fate of this oxidized signature, we present a mass balance calculation for Fe$^{3+}$ through the Mariana subduction system, using data presented in this work and in previous chapters in this volume. Implicit in such a mass balance is the assumption that Fe$^{3+}$ is a conserved element, i.e., there is a fixed concentration of Fe$^{3+}$ that is redistributed during subduction recycling and its valence state does not change. This is likely not the case. Iron can be multi-valent, existing at Fe$^0$, Fe$^{2+}$, and Fe$^{3+}$ in solid Earth materials depending upon the oxygen fugacity of the system. Materials in the
subducting slab, the melts and fluids that come off of the slab during subduction, the mantle wedge, and melts of the mantle wedge all likely exist in a range of \( f\text{O}_2 \) where both \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) are present and electronic exchange can take place between Fe and other multi-valent elements (e.g., S, C, V) in order to satisfy the \( f\text{O}_2 \), P, T, and compositional constraints on the system. Though \( \text{Fe}^{3+} \) is a useful tracer for oxygen uptake in altered oceanic crust, it is not necessarily mobilized from the slab to the wedge when the fluids or melts are released from the slab. It is likely that whatever is mobilized, \( \text{O}_2 \) moves in some form (another oxidized mobile species, for example \( \text{S}^{6+} \)) from the slab to the wedge. For this reason, we calculate the \( \text{O}_2 \) necessary to balance \( \text{Fe}^{3+} \) as \( \text{Fe}_2\text{O}_3 \), such that the system has no bulk electronic charge, which makes it unnecessary to know what is carrying the \( \text{O}_2 \). We include this \( \text{O}_2 \) calculation as part of the mass balance calculations.

To calculate the \( \text{Fe}^{3+} \) content of material entering the Mariana subduction zone, we take the average \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratios and \( \text{FeO}^* \) concentrations of discrete sediment samples from Site 801 (0.84, 5.88 wt% \( \text{FeO}^* \)) and 801 Super Composite (0.51, 12.34 wt% \( \text{FeO}^* \)) to represent the \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratios of bulk sediment and the upper 470 m of bulk altered oceanic crust in the Pacific plate prior to subduction. For the \( \sim 6.5 \) km of dike and gabbro units that likely underlie this, we assume that the dike and gabbro units have a \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratio that sums to the \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratio of primary mid-ocean ridge melts (0.135), the average of compiled \( \text{FeO}^* \) contents of gabbros reported by Lecuyer and Ricard [1999], and an average \( \text{FeO}^* \) content for MORB glass. Using these assumptions, we calculate a \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratio of 0.16 and \( \text{FeO}^* \) equal to 10.43 wt% for the dike units and 0.13 and 5.8 wt% for the gabbro units [Cottrell and Kelley, 2011;
The total input flux of Fe$^{3+}$ to the Mariana trench from the subducting sediments and altered oceanic crust can be calculated following the methods outlined by Kelley et al. [2005] and Lecuyer and Ricard [1999]. The input flux for Fe$^{3+}$ can be calculated using the equation:

$$F_{in} = \sum z_i \times \rho_i \times v_i \times [Fe^{3+}]_i$$  \hspace{1cm} (2)

where $z_i$ is the thickness of layer i, $\rho_i$ is the density of layer i, $v_i$ is the convergence rate [Kato et al., 1998], and $[Fe^{3+}]_i$ is the concentration of Fe$^{3+}$ calculated from Fe$^{3+}$/ΣFe ratios determined here for layer i. Summing over each layer yields a total input flux for Fe$^{3+}$ of 131.3 kg/yr/cm arc length, or 56.4 kg/yr/cm arc length O$_2$ (Table 2, Fig. 4). A significant portion of this comes as the result of oxidation on the seafloor, so we also calculate the Fe$^{3+}$ content of pristine MORB to estimate how much of this input flux was generated at the mid-ocean ridge and how much is the result of alteration. We use the same constraints for the dike and gabbro units as above, except that we extend the pristine basalt layer thickness to be 2000 m thick, essentially treating the altered igneous basement layer from ODP Site 801 as an unaltered basalt unit with Fe$^{3+}$/ΣFe = 0.16. Assuming a crustal production rate at mid-ocean ridges equal to the rate of subduction, we estimate that pristine MORB has an output flux of 92.6 Fe$^{3+}$ or 39.8 O$_2$ (kg/yr/cm arc length, Fig. 4). The difference in the fluxes for altered Pacific plate and pristine MORB (41.1 Fe$^{3+}$, or 17.6 O$_2$ kg/yr/cm arc length) represents the oxidation of Fe$^{2+}$ to Fe$^{3+}$ (or the uptake of O$_2$) into the Pacific plate during alteration reactions on the seafloor between the time the crust was created and the time that the slab will be subducted (Fig. 4).
To calculate the output flux of Fe$^{3+}$ to the Mariana subduction system, we consider the magmatic output along the arc and back-arc. For the volcanic arc, we use an average primary melt Fe$^{3+}/\Sigma Fe$ ratio of 0.244 and FeO* of 9.1 wt% from Mariana arc basaltic melt inclusions and submarine glasses [Brounce et al., in review]. For the back-arc, we use an average primary melt Fe$^{3+}/\Sigma Fe$ ratio of 0.172 and FeO* of 8.13 wt% from Mariana trough submarine glass [Brounce et al., in review; Kelley and Cottrell, 2009]. The output flux can be calculated then using the equation,

$$F_{out} = \sum P_j \rho_j [Fe^{3+}]_j$$

where $P_j$ is the production rate of crust in setting $j$ [Dimalanta, 2002; Reymer and Schubert, 1984], $\rho_j$ is the density of crust in setting $j$, and $[Fe^{3+}]_j$ is the Fe$^{3+}$ concentration calculated for each setting. This yields a range of permissible output fluxes for Fe$^{3+}$ between 14.0 and 18.8 kg/yr/cm arc length for the volcanic arc and 25.1 – 54.2 kg/yr/cm arc length for the back-arc spreading center. For both the arc and the back arc, these output flux ranges represent Fe$^{3+}$ or O$_2$ contributions from the subducted slab as well as from the pristine mantle wedge (i.e., the mantle material prior to the addition of slab fluids). For considering the fate of oxidized signatures in slabs through the subduction system, quantifying the contribution solely from the subducted slab is key. To do this, we assume that, outside of the mantle wedge that is influenced by subduction, the oceanic upper mantle is homogeneous with respect to $fO_2$ and that primary melts of this mantle have an Fe$^{3+}/\Sigma Fe$ ratio = 0.14 independent of the extent of melting [Cottrell and Kelley, 2011]. We also assume that pressure of melting is the dominant control on the FeO* content of a primary mantle melt [Gale et al., 2013; Langmuir et al., 1992], so we assign arc and back-arc primary melts the
same FeO* contents as those calculated above for arc (9.1 wt%) and back-arc (8.13 wt%) primary melts. Note that we do not consider Fe\(^{3+}\) a conserved element, nor do these calculations necessitate that Fe itself is mobile during subduction. Rather, we are taking advantage of the observation that Fe speciation will respond to the transport of any multi-valent elements that may be mobile in slab-derived fluids or melts (e.g., S, C, V) and may thus trace the transport of oxidized slab materials in the subduction system. The mantle contribution for arc magmas then is between 3-4 O\(_2\) (kg/yr/cm arc length) and between 8-10 Fe\(^{3+}\) (kg/yr/cm arc length), and between 8-18 O\(_2\) (kg/yr/cm arc length) and 20-44 Fe\(^{3+}\) (kg/yr/cm arc length) for the back-arc, which when combined, represent a significant proportion (~72%) of the total output flux in the Mariana subduction system (Fig. 4). Independent of the mantle contribution, the output flux for arc and back-arc magmatism combined is 4.5-7.8 O\(_2\) (kg/yr/cm). This represents the proportion of the oxidized signature from the altered Pacific slab that contributes to magmatism in the Mariana subduction system. When combined with our estimate of the oxygen acquired by the Pacific plate during alteration on the seafloor, we balance the flux of O\(_2\) through the Mariana subduction system, yielding an excess of 9-12 O\(_2\) kg/yr/cm that is taken up during sedimentation and alteration of the oceanic crust and enters the subduction zone, but is not output from the arc or back-arc.

The calculated Fe\(^{3+}\) or O\(_2\) that is not accounted for in the outputs or the Mariana subduction system represents 50-70% of the total O\(_2\) taken up by the Pacific plate over the duration of its ~170 million years at the surface of Earth. There are several possibilities for the fate of this oxidized material. First, the output flux
calculation here does not include any output of oxidized fluids to the forearc, which is expressed along much of the Mariana margin through serpentine mud volcanism [Parkinson and Pearce, 1998] and fluid seeps [O'Hara et al., 2012]. Constraining the mass flux in this area is difficult because of the heterogeneity of materials coming out (fluids, mud, serpentinized xenolith blocks), the lack of redox information for most of these samples, and the uncertainty in how pervasive this activity may be in the forearc, with both depth in the trench and along strike. These uncertainties make it very difficult at this time to constrain an output flux for the forearc.

Second, it is possible that some or all of the excess Fe$^{3+}$ or O$_2$ is transferred from the slab to the mantle wedge and remains there, for example, by serpentinizing mantle wedge peridotite. This is similarly difficult to assess because of the lack of a comprehensive understanding of the mechanisms for material transfer from the slab to the volcanic arc. However, serpentine minerals become unstable at $\sim$600°C [Ulmer and Trommsdorff, 1995] and the wedge can reach temperatures $>1300^\circ$C [England and Katz, 2010], so it is unlikely that a significant portion of the wedge remains serpentinized.

Third, it is possible that some or all of the excess is retained in the subducting slab when it is subducted past the Mariana subduction system and into the deep mantle. In this case, the excess oxidized signature would suffer the same fate(s) of deep subducted slabs, of which there are many possibilities. They may be subducted to the transition zone and/or the core mantle boundary, where they potentially contribute to the sources for mantle plumes. In this scenario, we would predict that EM-I, EM-II, or HIMU style plumes may have some portion of the return flux of the excess oxidized
signatures from subducting slabs, because the isotopic signatures of these endmembers are hypothesized to be derived from ancient subducted slabs [e.g., Kelley et al., 2005; Zindler and Hart, 1986].

6. Conclusions

We present the Fe$^{3+}/\Sigma$Fe ratios of sediments and variably altered oceanic crust recovered from ODP Site 801 in Jurassic aged Pacific plate in order to constrain the bulk oxidation state of materials entering the Mariana subduction system. The overlying sediments are very oxidized, ranging from 0.69 to >0.96 Fe$^{3+}/\Sigma$Fe, with three samples exceeding the detection limit of our analytical procedure. In the basaltic crust, minimally altered basalt ranges from 0.29 to 0.46 Fe$^{3+}/\Sigma$Fe, demonstrating that even small amounts of alteration lead to significantly increased Fe$^{3+}/\Sigma$Fe ratios in igneous materials. Pervasively altered basalts are even more oxidized, with Fe$^{3+}/\Sigma$Fe ratios from 0.47 to 0.78. The iron oxide veins, celadonite veins, and alteration halos included in these very altered basalts range from 0.52 to 0.95 Fe$^{3+}/\Sigma$Fe ratio. Composite powders meant to be representative of the bulk composition of the basement at ODP Site 801 are consistent with the Fe$^{3+}/\Sigma$Fe ratios measured on discrete samples. In particular, the 801 Super Composite has Fe$^{3+}/\Sigma$Fe equal to 0.51, broadly consistent with the oxidation state of Fe in various levels of altered basalts. These data are used to calculate a mass balance of Fe$^{3+}$ and associated O$_2$ through the Mariana subduction system. We show that the flux of oxidized material into the subduction system is much greater than the flux out of the subduction system along the volcanic arc and back-arc. Of the oxidation that takes place in the Pacific crust as the result of
alteration reactions on the seafloor prior to subduction, 50-70% is not output along the arc or back-arc and may be subducted into the deep mantle where it might contribute to the source of mantle plumes.

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Figure 4.1 Location map for samples used in this study. Blue circles mark the position of arc volcanoes, from which the Fe$^{3+}$/$\Sigma$Fe ratios of both melt inclusions and submarine glasses were used to constrain the flux of Fe$^{3+}$ out of the volcanic arc. The dark gray circles mark the position of submarine glass samples that were used to constrain the flux of Fe$^{3+}$ out of the back-arc. The position of ODP Site 801 is marked with the white star. The basemap was created using GeoMapApp [Ryan et al., 2009].
Figure 4.2 Plot of FeO content of calibration solutions versus the absorbance of laser light at 525 nm, and the calibration lines used to calculate the FeO content of unknown solutions in this study. The equations of the lines and $R^2$ values for each session are shown on the plot.
Figure 4.3 The Fe$^{3+}$/ΣFe ratios of materials in this study (brown, green, orange, and blue circles) versus their position in the drill core. The x symbols represent the Fe$^{3+}$/ΣFe ratios determined on materials from the same core by Rouxel et al. [2003], for comparison. The white diamonds show the Fe$^{3+}$/ΣFe ratios of two pristine MORB glass chips, determined via Fe-XANES [Brounce et al., in prep]. A simplified schematic of materials recovered during drilling at Site 801 during legs 129 and 185 is shown to the right.
Figure 4.4 A diagram outlining the Fe$^{3+}$ inventory calculations presented here. All values are shown per cm arc length.
Table 4.1. Fe redox analyses for ODP Site 801 discrete samples and composite powders

| Sample    | meters below seafloor | Unit description         | Fe$^{2+}$/O (wt%) | FeO* (wt%)$^1$ | Fe$^{3+}$/ΣFe | Fe$^{3+}$/ΣFe (Rouxel et al., 2003) |
|-----------|------------------------|--------------------------|-------------------|----------------|--------------|----------------------------------|
| Discrete 801 powders                             |                        |                          |                  |               |                          |                                   |
| 801A3R2-145| 15                     | Pelagic Clay             | below detection     | 6.60           | >0.99        |                                   |
| 801A5R3-145| 36                     | Pelagic Clay             | below detection     | 5.43           | >0.99        |                                   |
| 801A8R1-1 | 60.6                   | Chert                    | below detection     | 0.27           |              |                                   |
| 801A17R1-28| 147.5                  | Porcellanite             | 0.99               | 3.24           | 0.69         |                                   |
| 801A19R1-65| 167                    | Volcanic turbidite       | 1.13               | 5.78           | 0.80         |                                   |
| 801B5R2-0 | 225                    | Volcanic turbidite       | 2.19               | 8.91           | 0.75         |                                   |
| 801B25R1-49| 397.7                  | radiolarite              | 0.18               | 1.98           | 0.91         |                                   |
| 801B33R1-143| 436                   | radiolarite              | 0.64               | 6.54           | 0.90         |                                   |
| 801B35R3-19| 455.5                  | radiolarite + claystone  | 0.34               | 8.82           | 0.96         |                                   |
| 801B37R1-36| 461.9                  | uppermost basalt,        | 0.76               | 3.52           | 0.78         |                                   |
| 801B41R1-26| 483.3                  | pervasively altered      | 6.10               | 9.59           | 0.36         |                                   |
| 801B43R1-132| 493.5                 | minimally altered basalt| 6.13               | 11.25          | 0.45         |                                   |
| 801B43R3-111| 496.1                 | minimally altered basalt | 3.90               | 7.21           | 0.46         |                                   |
Table 4.1. continued

| Sample     | meters below seafloor | Unit description                        | Fe²⁺O (wt%) | FeO⁺ (wt%)¹ | Fe³⁺/ΣFe (Rouxel et al., 2003) |
|------------|------------------------|------------------------------------------|-------------|-------------|-------------------------------|
| 801C4R1-72 | 522.4                  | hydrothermal deposit                      | 0.53        | 11.50       | 0.95                          | >0.99                        |
| 801C5R1-95a| 532.2                  | pervasively altered basalt with celadonite| 0.97        | 5.35        | 0.82                          | 0.88                         |
| 801C15R7-31| 621.7                  | bleached basalt                           | 2.44        | 5.05        | 0.52                          | 0.33                         |
| 801C19R2-24a| 653.4                 | hyaloclastite                             | 2.16        | 11.33       | 0.81                          |                              |
| 801C24R1-46| 691.8                  | pervasively altered basalt                | 7.20        | 13.59       | 0.47                          |                              |
| 801C30R1-111a| 748.4                | minimally altered basalt                 | 9.21        | 13.83       | 0.33                          |                              |
| 801C31R4-43| 761.0                  | minimally altered basalt                 | 9.72        | 13.67       | 0.29                          |                              |
| 801C34R1-93a| 786.2                 | iron oxide vein, alteration halo          | 6.81        | 14.11       | 0.52                          |                              |
| 801C38R3-53a| 826.3                 | hyaloclastite and pillow margin           | 4.74        | 15.42       | 0.69                          |                              |
| 801C52MI47a| 933.3                  | minimally altered basalt                 | 7.44        | 12.29       | 0.39                          |                              |
| 801SED     |                        | interflow sediments in igneous basement   | 2.91        | 8.75        | 0.67                          |                              |
| 801SUPER   |                        | bulk composition of altered igneous crust | 6.01        | 12.34       | 0.51                          |                              |

Composites, Kelley et al 2003
| Sample            | meters below seafloor | Unit description                      | Fe$^{2+}$/O (wt%) | FeO* (wt%)$^1$ | Fe$^{3+}$/ΣFe | Fe$^{3+}$/ΣFe (Rouxel et al., 2003) |
|-------------------|-----------------------|---------------------------------------|------------------|---------------|--------------|----------------------------------|
| 801TAB-VCL        | alkali basalt volcanioclastic sediments |                             | 3.97             | 6.43          | 0.38         |                                  |
| 801TAB-FLO        | alkali basalt flow    |                             | 5.36             | 8.95          | 0.40         |                                  |
| 801TAB0-50        | bulk composition of top 50m of alkali basalt |                             | 4.92             | 8.35          | 0.41         |                                  |
| 801MORB0-110      | 110 m of MORB bulk composition of |                             | 5.56             | 11.45         | 0.51         |                                  |
| 801MORB110-220    | MORB 110-220 m bulk composition of |                             | 6.02             | 12.35         | 0.51         |                                  |
| 801MORB220-440    | MORB 220-440 m bulk composition of |                             | 6.24             | 13.10         | 0.52         |                                  |

$^1$total Fe expressed as FeO*, from Kelley et al. [2003]
|                                   | Fe$^{3+}$/ΣFe | FeO* (wt%) | Fe$^{3+}$ (wt%) | layer thickness (m) | density (g/cm$^3$) | convergence rate | Fe$^{3+}$ (kg/yr/cm) | O$_2$ equivalent (kg/yr/cm) |
|-----------------------------------|--------------|-----------|----------------|---------------------|---------------------|-------------------|----------------------|----------------------------|
| **Input to Mariana convergent margin** |              |           |                |                     |                     |                   |                      |                            |
| Sediment                          | 0.84         | 5.88      | 3.84           | 455                 | 1.82                | 5.475             | 13.2                 | 5.7                        |
| Altered oceanic crust              | 0.51         | 12.34     | 4.91           | 470                 | 2.8                 | 35.4              | 15.2                 |                            |
| Dike unit                          | 0.16         | 10.43     | 1.29           | 1500                | 2.8                 | 29.8              | 12.8                 |                            |
| Gabbro unit                        | 0.13         | 5.80      | 0.58           | 5000                | 3.3                 | 52.9              | 22.7                 |                            |
| **Total input**                    |              |           |                |                     |                     |                   |                      |                            |
| **Pristine oceanic crust**         |              |           |                |                     |                     |                   |                      |                            |
| Basalt                            | 0.16         | 10.43     | 1.29           | 2000                | 2.8                 | 5.475             | 39.7                 | 17                         |
| Gabbro                            | 0.13         | 5.8       | 0.58           | 5000                | 3.3                 | 52.9              | 22.7                 |                            |
| **Total pristine MORB**            |              |           |                |                     |                     |                   |                      |                            |

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Table 4.2. continued

|                  | Fe$_{3+}$/ΣFe | FeO* (wt%) | Fe$_{3+}$ (wt%) | layer thickness (m) | density (g/cm$^3$) | convergence rate (kg/yr/cm) | O$_2$ equivalent (kg/yr/cm) |
|------------------|---------------|------------|-----------------|---------------------|---------------------|-----------------------------|----------------------------|
| **Output to Mariana convergent margin** |               |            |                 |                     |                     | arc crust production rate (cm$^3$/yr/cm) |                           |
| Volcanic arc (min) | 0.24          | 9.10       | 1.72            | 2.8                 |                     | 29                          | 14.0                       |
| Volcanic arc (max) |               |            |                 |                     |                     | 39                          | 18.8                       |
| Mantle contribution | 0.14          | 9.10       | 0.98            |                     |                     | 8.0 - 10.8                   | 3.5 - 4.6                  |
| Back-arc (min)    | 0.17          | 8.13       | 1.08            | 5500                | 2.8                 | 1.500                       | 25.1                       |
| Back-arc (max)    |               |            |                 |                     |                     | 3.240                       | 54.2                       |
| Mantle contribution | 0.14          | 8.13       | 0.88            |                     |                     | 20.4 - 44.1                 | 8.7 - 18.9                |
| **Total output (min)** |               |            |                 |                     |                     | 10.6                        | 4.6                        |
| **Total output (max)** |               |            |                 |                     |                     | 18.1                        | 7.8                        |

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Table 4.3: $\text{Fe}^{2+}O$ for USGS standard powders

| Standard | Fe$^{2+}$O$_{\text{actual}}$ (wt%, measured) | Fe$^{2+}$O$_{\text{actual}}$ (wt%, published) |
|----------|---------------------------------------------|---------------------------------------------|
| QLO-1    | 3.26                                        | 2.97                                        |
| $l\sigma$| 0.18                                        |                                             |
| n        | 6                                           |                                             |
| BCR-1    | 8.87                                        | 8.80                                        |
| $l\sigma$| 0.20                                        |                                             |
| n        | 5                                           |                                             |
| BIR-1    | 8.72                                        | 8.34                                        |
| $l\sigma$| 0.10                                        |                                             |
| n        | 7                                           |                                             |
APPENDIX 1: A guide to Fe-XANES on natural glasses at BNL NSLS X26a

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Brookhaven National Laboratory
www.bnl.gov

National Synchrotron Light Source
www.nsls.bnl.gov

X26A
http://www.bnl.gov/x26a/
Section A: Contact Information for X26a

Beamline phone: 631-344-5626

Tony Lanzirotti
University of Chicago
lanzirotti@bnl.gov
630-252-0433

Sue Wirick
University of Chicago
swirick@bnl.gov
631-553-9301 (cell)

Bill Rao
University of Kentucky
rao@bnl.gov

Section B: Beam set up

Fe XANES:

Fe foil: 7112.0 eV

<311> monochromator @ 7200 eV

Shaping time: 1 µs for all detectors

Detector: 30 mm distance, 4ME plus 2 Si drift

Background subtraction: -1 (none)

No beryllium window

Fe XANES sv file:

| Region | Start (eV) | End (eV) | Step (eV) | Dwell |
|--------|------------|----------|-----------|-------|
| 0      | 7020.00    | 7105.00  | 10.0      | 1.0   |
| 1      | 7106.00    | 7118.00  | 0.1       | 5.0   |
| 2      | 7118.20    | 7140.00  | 1.0       | 2.0   |
| 3      | 7141.00    | 7220.00  | 4.0       | 2.0   |
**Fe EXAFS sv file:**

| Region | Start (eV) | End (eV) | Step (eV) | Dwell |
|--------|------------|----------|-----------|-------|
| 0      | 6900.00    | 7105.00  | 1.0       | 1.0   |
| 1      | 7106.00    | 7118.00  | 0.1       | 5.0   |
| 2      | 7118.20    | 7140.00  | 1.0       | 2.0   |
| 3      | 7141.00    | 7800.00  | 4.0       | 2.0   |

**Section C: IDL prompts**

*IDL prompts for important widgets:*

a. stage_widget

b. x26a_flyscan

c. xanes_scan

*Stage widget instructions*

1. Move to desired position using the Motor XYZ window.

2. Enter desired sample name in “Save position as” field in the stage_widget window.
   a. Example drift point sample name: “LW_0_D0”
   b. Example standard mount sample name: “AII_25a” or “LW_-30b”
   c. Example unknown sample name: “Sari15-04-01a” or “Ala02-02b”

3. Hit enter.

4. At the bottom of the stage_widget window, a line of dialogue should indicate that the position has been saved.

*Building a points list*
1. Open a text editor (e.g. WordPad) from the start menu.

2. Be sure that there are no carriage returns or spaces in the new document.

3. Follow the “Stage widget instructions” outline above for saving sample positions.

4. For each sample position saved, copy the saved position name into the text editor. Every new saved position should be entered in its own line.

5. Follow the saved sample position name immediately (no spaces) with a comma (,).

6. Immediately after the comma (no spaces), specify the file name that the saved position should be saved as. The file name for unknown samples and standard glasses should always end with *.001 (where * is the name of the file). For drift points, they should increase numerically through the entire session (e.g., *.001, *.002, *.003…)

7. There should be no spaces under any condition and only carriage returns where a new saved position is entered. Check that there are no carriage returns in the text editor before the first line or after the last line in the points list.

8. The first 4 – 5 samples should be bracketed on both sides with a drift point taken on LW_0 if the points list is started soon after the beam becomes available. This allows for the changes in the energy of the beam at X26A to be modeled in a linear fashion.

**Example points list:

LW_0_D0,LW_0.001
9. When the points list is complete, print a copy and have several people read it over carefully for errors. In particular,
   a. all saved position names must match those names that were saved using the stage widget
   b. no space, but one comma separates the saved position name from the chosen file name
   c. the chosen file name to be written follows intuitively from the name of the saved position
   d. all chosen file names end with *.001, where * is the chosen file name.
   e. all chosen file names are unique and can be paired with a unique saved position name
   f. all drift points follow in numerical order
   g. all drift points are saved on the appropriate mounts (upper or lower)
   h. there are no extraneous spaces or carriage returns
10. When all present parties approve the points list, copy the entire points list to the clipboard. In XANES Scan, choose File > Edit Points List.

11. A new window will open. Paste the points list here.

12. Check that there are no carriage returns or spaces before the first line or after the last line of the points list. NOTE: carriage returns are often included at the end of the points list after pasting. Always remove these.

13. Go to File > Save Points List.

14. Then File > Done with Points List.

15. In XANES Scan, go to the bottom of the window and check the box labeled “Use Points List”.

16. If it is certain that no errors with the points list exist and the points list was copied and saved properly, “Start Scan” will enable the points list. It is recommended to stay at the beam long enough to see the motor move (verify that the position is correct) and the scan begin to collect data.

Concentration mapping (melt inclusions)

*Note: this technique produces easy to read element concentration maps for olivine or plagioclase hosted melt inclusions. Maps collected on other natural glasses and experimental glasses are more difficult to impossible to read.

1. Open x26a_flyscan in IDL.

2. In x26a_xmap 12 Detector Control, change Collection Mode to “MCA mapping” (If x26a_xmap 12 Detector Control is not open, go to: x26a.adl > beamline curve > MCA electronics > xmap)
3. In x26a_flyscan, go to Root Directory > Data > select beam session folder > OK.

4. Activate every field, hit enter.

5. ALWAYS start in lower left hand corner and end in the upper right hand corner of map. Move to desired map “starting” location in stage control, focus the z direction and enter the motor X and Y positions in x26a_flyscan. Move to desired stop location, enter X and Y positions in x26a_flyscan. Make note of these positions in the beam notebook for every sample.

6. Choose a file name, type it in the “File Name” field in x26a_flyscan and hit UPDATE. The predicted map time will be shown at the bottom of the x26a flyscan window. If you wish to shorten or lengthen this time, change the value in the “Pixel Size” field and hit enter. This value will be copied to “Step Size” directly underneath the “Pixel Size” field. Do not edit the 2nd step size window. Although this may vary, the target map collection time is 1-3.5 minutes.

7. When you are ready to map, hit “SCAN”.

Every row creates its own file in your directory, every row should be the same file size. All rows for one sample name will be compiled into one folder within the current beam directory, labeled with the sample name that you chose to enter in x26a_flyscan.

When are you finished mapping and ready to continue with XANES analyses, go to x26a_xmap 12 Detector Control window and change Collection Mode to “MCA spectra”.

To view concentration maps:
1. Open xMap Plotter on the center work station from the icon on the desktop.

2. Select First File > navigate to the current beam directory > select the folder for the sample of interest

3. Highlight the first file within the sample folder and take note of how many total files were written for the sample. Click “Open”.

4. In xMap Plotter window, enter the number of files that are contained within the sample map folder in “Last file #” field. Hit “Enter”.

5. In “Pixel Size” field, enter the pixel size chosen in x26a_flyscan for the sample mapping.

6. Be sure that the element of interest is marked as Fe.

7. Click “Process”. This should take ~1 minute.

8. It is important to note that the origin of the map coordinates are centered at [0, 0, z], motor position relative to the starting [x, y, z] of the absolute motor position registered as “Starting Motor Position” in x26a_flyscan.

9. Any lines drawn on the map are directional (draw lines from left to right) and the “origin” (x, y = 0) of the line profile selected are not necessarily hinged to the origin [0, 0, z] of the concentration map. Measure carefully and be sure that chosen points along the line profile are accurately translated into absolute motor position.

10. Choose three points by checking Fe concentration maps (Fe minimum for olv hosted inclusions; Fe maximum for plag hosted inclusions) in both the x and y directions. Make note of the relative motor positions in both x and y directions for these points in the beam notebook.
11. Calculate absolute motor positions for each of the three chosen points by adding the relative x and relative y motor positions of each point to the absolute x and y starting motor position for the concentration map.

12. Move to these absolute motor positions by manually entering the motor positions into the motor widget. Save each point as you move to it by using stage_widget in the normal fashion.

When are you finished mapping and ready to continue with XANES analyses, go to x26a_xmap 12 Detector Control window and change Collection Mode to “MCA spectra”.

Section D: Trouble shooting

The x-ray beam dumps regularly at 0700 and 1900 EST. You may request to delay the beam dump by up to 5 minutes by calling the control room and asking for more time very politely.

The x-ray beam may also dump unexpectedly at any time of day without warning. This frequently happens during electrical storms, very windy days, or during winter storm conditions (although it has also happened on beautiful sunny days in May). It may take minutes to days to resolve the problem. Refer to Beam TV for updated information. It is rarely a good idea to call the control room for information during these times.
As with any complicated experimental technique, both software and hardware malfunctions may take place and these may put both manual and automated data collection in jeopardy. In most cases, it is very obvious when a problem has occurred.

Common problems:

- **one or more IDL sessions may be “frozen”**
  1. It is likely that this IDL session must be killed and restarted. If this occurs for widgets that are hardware associated (e.g. Motor control XYZ) it may only be necessary to kill that particular session and restart, without concern over altering *.sv file information. If this occurs for stage_widget, be sure to check if previously saved positions are still saved when stage_widget is rebooted. If this occurs for the xanes_scan window, take caution when re-loading *.sv file info. Remember to always hit enter in every field and check all scan parameters for accuracy.

- **beam may be available, but no scan activity occurs**
  1. This commonly results in a wide variety of consequences. All IDL sessions may have to be killed and restarted.

- **data quality over one or more detectors may be poor**
1. This may be due to a focus error (human). Move to the point and check the z position of the motor. It is recommended to recheck the z position for all remaining saved positions before continuing.

2. This may be due to a focus error (motor). Move to the point and check the z position. Recheck all saved motor positions for accuracy in x, y and z. Monitor sample list progress to be sure the error does not propagate. If the error continues, there may be a serious stage motor malfunction and no saved sample positions should be trusted. Call beam technicians for assistance.

3. This may be due to poor positioning of saved points. This is a risk when points are saved near cracks or edges. Move the data point 5 – 10 microns further from the crack or edge and re-collect the spectra.

4. This may be due to detector error (all detectors). Detector errors appear to be random and affect 1-10 data points per 12 hour session. There has been no satisfactory solution proposed for this. It is advised to check all data as it is collected to be sure all samples have three acceptable spectra collected for it.

5. This may be due to detector error (less than 11 detectors). This appears to be random as well but occurs
rarely. In mu_beta_plot it is possible to select which detectors to use when stacking spectra. Unselect the detector(s) that are have collected poor quality data.

- **collected spectra may be of acceptable quality, but is clearly not the expected “glass-like” shape**

  1. This may be due to poor positioning of saved points. If this occurs for a glass chip, be sure that the correct photos are being used to choose points. Check the z position of the motor carefully. Move the position 5-10 microns from the original spot and re-collect the spectra. If this occurs for a melt inclusion, re-map the inclusion and check the line spectra carefully. If the problem persists, the inclusion must be thinned to allow the beam to pass through the glassy part of the inclusion without interacting with the phenocryst host. If the problem continues to persist, the inclusion is too small to be analyzed by XANES.

  2. This may be due to a motor position error. Re-check the saved motor positions. If the problem persists, there may be a serious motor malfunction. Call a beam technician for assistance.

- the stage motor may be moving in abnormally small increments or abnormally slowly
1. This happens occasionally when switching from MCA mapping to MCA spectra.

2. Go to X26A_SampleXYZ. Click “More details”.

3. In the affected dimension (X or Y, whichever is not working properly) click “More Details” > all.

4. Under “Dynamics”, Maximum speed should be set to 1.00. Speed should also be set to 1.00. If they do not read thus, change them. If they do read thus, click in the field and hit enter. Close the window and test for the correction.

**Abort Scan instructions (easy)**

1. Go to x26a XMAP 12 Detector Control window and click “Abort”.

2. Wait. IDL may take up to 1 minute to register this command.

3. Scan functions will stop. Address the issue that necessitated the abort and restart.
   
   a. If you were scanning on a points list:
      
      i. This abort command will only abort the current point on the list. The scan will automatically move to the next point and begin writing data.
      
      ii. If this is undesired, you must either abort each point manually OR proceed to kill IDL sessions (instructions below).
   
   b. This frequently will not work if the x-ray storage ring has been “dumped” unexpectedly. The loss of beam should automatically prompt IDL to abort the current scan. When the beam becomes available again,
IDL will restart scanning where it last stopped. This abort scan procedure does not work very consistently in this case as well.

Kill IDL

*Note: you should ALWAYS try the “Abort Scan” instructions above before attempting this procedure. This will exit all beam control windows and requires careful attention to detail.

1. Exit the IDL session window for xanes_scan by clicking on the “x” in the upper right hand corner.
2. Exit all other IDL session windows in the same manner.

Restart IDL

*Note: Be very careful to follow all steps in the order that they are listed here.

1. Start xmapswin32 by double clicking on the desktop icon on the beam control workstation.
2. Open the first IDL session by double clicking on the IDL desktop icon on the beam control workstation. At the prompt, type med_12 to open the med_12 window. In the med_12 window, choose our beam session folder.
3. Open the second IDL session by double clicking on the IDL desktop icon on the beam control workstation. At the prompt, type stage_widget to open the stage_widget window.
4. Open the third IDL session by double clicking on the IDL desktop icon on the beam control workstation. At the prompt, type x26a_flyscan to open the x26a_flyscan window.
5. In x26a Detector Control window, choose ROI/SCA 0-15.

6. Choose 0 (zero) to pull up a new window.

7. In this window, under navg column, change all 0 (zeros) to -1 and hit enter in every field.

8. Close this window by hitting the “x” in the upper right hand corner.

9. In x26a Detector Control window, be sure that MCA spectra is chosen.

10. In MED control, choose “erase” and then “start”.

11. In x26a Beamline control, go to motors > monochrometer > mono energy > type 7200 and hit enter. Close this window by clicking on the “x” in the upper right hand corner.

12. Open the fourth IDL session by double clicking on the IDL desktop icon on the beam control workstation. At the prompt, type xanes_scan to open the xanes_scan window.

13. In the xanes_scan window, load the saved scan parameters from the current beam session directory (will be a *.sv file).

14. In the xanes_scan window, choose plot > cps

15. In the xanes_scan window, choose ME4-2SD

16. In the xanes_scan window, be sure the current beam session directory is chosen as the root directory.

16. In the xanes_scan window, activate every field and hit enter while checking all values to be sure that they are the correct *.sv file information (see Section B).
APPENDIX 2: A guide for FTIR (SI/URI): Introduction to Omnic/Atlus software and guidelines for performing analyses on hydrous basaltic glasses

Maryjo Brounce

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Section I. The instrument

A. Department of Mineral Sciences, Smithsonian Institution

The instrument is located in room E-424, near the freight elevator and Exhibit Hall exit. The Nicolet 6700 is the newer instrument that sits on the right hand bench. The Excalibur is the older instrument and sits along the back wall. These instructions pertain exclusively to the Nicolet 6700.

Allen wrenches, stage holders, calibration equipment, and spare bulbs are housed in the wooden case next to the instrument or in the drawers of the desk that the instrument sits on.

The instrument is usually kept “on”. If there are no green lights on the display panel of the instrument, there may have been some unusual service. Contact Tim Rose before proceeding.

B. Kelley Laboratory, University of Rhode Island

The instrument is located in CACS101. The FTIR is the instrument that sits on the table top to the right hand side of the room.

Allen wrenches, stage holders, calibration equipment, and spare bulbs are housed in drawers of the desk that the computer for this instrument sits on.
The instrument is usually kept “on”. If there are no blue lights on the display panel of the instrument, there may have been some unusual event that requires service. Contact Katie Kelley.

*The main bench (SI/URI):*

The main bench is the large box on the right of the microscope. There are two blue lights, one that will blink while the IR source is on and one that displays that the instrument itself is on. There is an on/off switch to the left of this that will power on/power down the instrument. On the right hand side of the bench on the URI instrument, there is a large knob – this is the ATR crystal where reflection bench work can be done (solids, liquids). There are two doors on the front that can be lifted – inside is the sample compartment for the main bench.

*The microscope (SI/URI):*

The microscope is attached to the left hand side of the instrument. It has motorized stage movement that can be controlled by using the joystick on the desk. The focus knob is also motorized. Rotating the mechanical stop will change the z-position of the stage rapidly, rotating the knob in small degree increments will change the z-position of the stage slowly. Rotating away from your body will move the stage up, rotating towards your body will move the stage down. The SI microscope has both a 15x and 32x objective. These objectives can be changed by simply rotating the objective mount (do NOT grab the objective to rotate, grab the neck that the objectives are mounted to). Be sure that the sub-stage condenser is the appropriate condenser for the objective
chosen (e.g. the 15x condenser should be used with the 15x objective). The URI microscope has a visible 10x and two 15x IR objectives. They are all fit to the nosepiece at any given time. One of the 15x IR objectives has a metal fitting on the bottom for the ATR crystal. The other does not. Either can be used in during normal transmission microscope work. Only the objective with the ATR crystal fitting can be used for reflectance FTIR work. If using the heating stage, you must use the 15x IR objective that does not have the ATR crystal attached. These objectives can be changed by simply rotating the objective mount (do NOT grab the objective to rotate, grab the neck that the objectives are mounted to). When changing out the IR objectives, be sure to lower the sub-stage condenser all the way down before moving the stage all the way down.

The extra condenser should be in the room, likely in a nondescript cardboard box. To change the condenser, move the stage as high as is safe to do so. On the right hand side of the condenser, there is a small set screw. Loosen this screw and the condenser should become removable. Replace the condenser, tighten the set screw, and return the stage to its normal position.

To focus the condenser, there is a knob to the right and below the stage. With the aperture light on, turn this knob to focus the light cone to z-position of the stage.

There is both reflected and transmitted light options on the microscope. On the left hand side, at the base of the microscope, there are two knobs. The front-most knob
turns on and controls the intensity of transmitted light; the second knob turns on and controls the intensity of reflected light. The third knob turns on and controls the light passing through the aperture of the instrument. Note: any analysis performed on the instrument is independent of your control of the knob for these light sources (i.e. there is no configuration that you must return the light sources to in order to successfully collect high quality data).

There is an upper and lower polarizer on both the SI and URI microscopes for viewing in cross-polarized light. The upper polarizer is removable and is located just under the oculars, pointing at your body. The lower polarizer is rotatable and also removable – located on the left hand side of the lower base of the microscope towards the back of the instrument.

The camera that provides the live video feed to the OMNIC/Atlus software is on the top of the microscope-viewing column. If the video feed is out of focus, on the right hand side of the camera there are two allen bolts, one marked “Focus” and one marked “Lock”. First loosen the bolt marked “Lock” and then turn the “Focus” bolt until the image on the live video feed is in focus again.

The two buttons at the base of the microscope pointing towards your body control the sampling mode (transmission or reflectance) and which detector (position 1 or position 2) is to be used for the experiment. There is also a means to control this through the OMNIC/Atlus software.
On the right hand base of the microscope there are 3 small knobs in addition to the large knob that controls the aperture window size and rotation angle. There is also a means to control this through the OMNIC/Atlus software. This choice is at the user’s discretion, however it is recommended that the user choose the software option.

Purge gas (SI):

On the wall behind the instrument, there are three gas flow meters that turn on/off/control the supply of building supplied gases to the equipment in the room. The two left most meters control gas flow into the older instrument in the room. The meter on the right hand side controls gas flow to the Nicolet 6700.

Purge gas (URI):

To the left of the table that the FTIR sits on there is a purge gas generator. A large on/off switch is located on the front of the instrument. A column with indicator paper is also located on the front of the instrument, which will indicate when the instrument (and the air it is exhausting) is dry. The generator should typically run for ~1 hour before connecting the air exhaust to the FTIR microscope/bench. There is a water vent in the back of the generator with a small length of tube that will drip water (sometimes violently) that is condensed from the air inside of the generator. The small tube should always sit inside of a container, the level of water in the container should be checked regularly. A black tube comes out of “outlet” connector and has a 3 way split. Two
tubes come out of this and connect (1) to the “purge in” port on the microscope and (2) to the back of the main bench.

Section 2. Starting a run

For the SI instrument, use the calendar on top of the bookshelf to schedule yourself for a day in the lab to be sure to avoid any conflicts. To resolve any conflicts, seek Tim Rose. For the URI instrument, use the google calendar to schedule yourself for a day in the lab. For an invitation to use the calendar and to resolved any conflicts, seek Katie Kelley. The evening before you are scheduled to use the instrument, put your samples in the desiccator on the computer desk.

Liquid Nitrogen should be poured into the proper detector compartment that you plan to use for the day. The detector compartments are located at the top of the microscope unit, marked with scotch tape on the instrument. For both URI and SI instruments, position 2 houses the MCT A detector. Position 1 houses the MCT A* high-resolution detector. Use the small dewar or green thermos (do NOT use any type of threaded or sealed lid while LN is in any container), fill it with LN from the EPMA or SEM lab at SI, and from the R. Robinson lab supply in the basement of CACS at URI. A small funnel should be located on top of the FTIR. Insert this funnel into the appropriate compartment and fill slowly with LN until it appears to overflow. Let the instrument rest for ~30 minutes.
Prepare a slide with your samples, making sure that all samples lay perfectly flat on the sample mount. Leave one blank spot through which the IR beam can pass without hitting sample/copper/plastic. Place your sample mount in the locking mechanism on the stage and lower the plastic cache around your sample. Go to the gas flow knobs on the wall to the left and turn the right most flow meter all the way open (bead should float to >25 units on the flow meter). Let the gas flux purge the cache chamber for at least 15 minutes.

Open Omnic software by double clicking the icon on the computer desktop. The software has a menu bar that is typical of Windows software that reads File, Edit, Collect, View, Process, Analyze, Report, Atlus, Window and Help across the top. Underneath of this bar there is a drop down menu that says Experiment: Default – Transmission (default.exp). The next row contains several “quick buttons” that are shortcuts to software navigation options that can also be found in the top menu bar.

Section 3. Experiment Set up (SI/URI)

Click the “Expt Set” quick button, or choose Collect > Experiment Setup from the top menu bar to set the experiment parameters.

The Experiment Set up window houses all of the software controls for the FTIR instrument such as whether your sample will be in the bench or on the microscope stage, which detector you wish to use, ect…
The first tab is labeled “Collect”. Here, you can set the number of scans to stack for each spectra, wavenumber resolution, the available formats for saving data, and how/when to collect background and which background file to apply to the next sample spectra. The following figure shows a typical experimental set up for analyzing hydrous basaltic glasses.
The second tab is labelled “Bench”. The total interferogram, summed from the interferograms of each wavelength of IR light, as measured by the detector is shown here. If the condenser is focused properly, the Peak-to-Peak value for the interferogram should read ~10-12 V for a ~20x20 aperture through air. In this tab you must also indicate whether you will be using the bench or the microscope detector (the top position in the list is “Position 2” on instrument), beamsplitter (KBr), source (IR or turbo-IR; turbo-IR will increase sensitivity by increasing the intensity of IR light), region of interest, etc… The following figure shows a typical experimental set up for analyzing hydrous basaltic glasses.
The third and fourth tabs, Quality and Advanced do not contain any routinely useful information. The fourth tab, “Diagnostic” looks like:

![Experiment Setup](image)

By clicking “Align”, the moving mirrors inside of the bench will be re-aligned. This takes about 2 minutes and should be done periodically.

**Section 4. Performing an experiment (SI/URI)**
Typically, one sample should be analyzed at three distinct locations within the sample. A background spectra is taken and subtracted from each sample spectra in order to subtract out any spectral contributions from the fluxing gas in the instrument or within the cache.

After the experiment is set up appropriately, navigate to the first sample and focus on the surface in reflected light. Choose an appropriate aperture size either by using the knobs at the base of the microscope on the right hand side or by using the OMNIC/Atlus software. To do this, in the top menu bar choose Atlus > Apertures Dimensions. A window will appear that allows you to set the X and Y dimensions as well as the rotation angle. Always check the microscope and re-focus the condenser every time the aperture dimensions change or the stage position has changed. If there appears to be an offset between what the software is registering and the actual microscope image, you can re-initialize the aperture by going to Atlus > system configuration. Under Microscope, there is a button called “Aperture”. Click this. After about 60 seconds, the problem should be fixed.

Without changing the stage focus or aperture dimensions, move the blank space on the sample mount. Refocus the condenser. In Experiment Setup, under the Collect tab, in the section called “Background Handling”, click the radio knob for “Collect background before every sample”. Click OK.
To collect background spectra, use the quick button “Collect Bkg”. The software may/may not prompt you to prepare to collect a background spectrum. If it does, just hit OK. The background will begin to collect. You may stop data collection at any time by clicking “Pause”, located in the lower left hand corner. Close the window and choose “No” to the dialogue box asking if you’d like to add the spectra to a window. During collection, there will be a drop down bar across the top of your actively collecting spectra window, with options of adding the spectra that you are collecting to certain windows. If there are no windows currently open, the only choice will be to “add to a new window”. If there are other windows open, you will be given the option to add it to any of those windows. You have the entire length of the data collection to choose which window to add the spectra to but you must choose before collection ends.

When collection ends, a box will appear, confirming that you wish to add this spectra to whichever window you chose during collection from the drop down menu. If you hit “Yes”, the spectra will appear in the window that you indicated. If you hit “No”, the spectra go away and the data are lost. If this happens, you must recollect the spectra. The addition of these spectra to any window has no implications for the format or way in which the data can be ultimately saved. Even if the window chosen is not your ideal window, it is best to just choose “Yes” so that your data does not disappear.
Save the background spectra by choosing File > Save As > navigate to your folder under C:/My Documents, choose a file name and save as a *.spa. If you have several spectra open in the same window, the drop down menu above the chart will allow you to select the spectra that you wish to save. As a general rule, the spectra currently plotted in the color red is the currently active spectra upon which any action will be taken.

To apply this background file to the subsequent sample spectra, go to Experiment Setup, under the Collect tab, in the section called “Background Handling”, click the radio knob for “Use specified background file”. The “Browse” button will become active. Click this and navigate to the background *.spa file that you just saved. Click OK in Experiment Setup.

Navigate back to your sample, choose your spot and be sure that the stage and condenser focus as well as the aperture dimensions are all still appropriate. If any of these things are changed at this time, you must recollect a background file. To collect a single point sample spectra, click the quick button “Col Smp” or go Collect > Collect Sample. Hit OK to the title of the spectra (this has no bearing on the name of the file that you will write the data to). The software may or may not prompt you to prepare to begin to collect sample spectra. If it does, hit OK. As with the background collection, a drop down menu will be available for you to choose a window in which to add the spectra that you are currently collecting. When the collection is over, go to
File > Save as > navigate to your folder and save two copies of your sample spectra, one as a *.spa and one as a *.csv.

Section 5. Introduction to Atlus software (SI/URI)

To access the Atlus imaging tools, choose Atlus > Show Atlus window from the top menu bar. If nothing happens, Atlus is probably already open. Minimize the experiment window within the larger Omnic window and look around:
The Atlus screen will look like this:
The left hand image can house a static image or image mosaic that you create. The right hand image is the live video feed. See Section 1 for details on how to adjust the live video feed focus.

In Atlus, you may create a static image by drawing a box in the left hand image and choosing Atlus > capture mosaic. Be aware that large mosaic images take a long time to make. The best approach is to click on the “Full Range View” quick button at the bottom of the Atlus window and to navigate at the microscope to the sample mount. When you know that you are in the general area, you can click on the square quick button (third button from the left) and draw and small square on the order of the size of the red cross hairs that mark your location. A map of this size will take ~2 minutes to collect. When you are finished with this composite image, go to Atlus > clear.
mosaic. You may save or print this mosaic by going to Atlus > save mosaic and Atlus > print mosaic:

Once the map is made, you may readjust the X and Y scales of the left hand image by clicking on the “Zoom to points” button (located in the bottom row of quick buttons):
You may navigate around the stage by clicking on the “Stage movement tool” quick button and clicking on the right or left hand image. On the right hand image, you may navigate by clicking on the red aperture and dropping it in a new location (with the arrow quick button chosen).

If you manually choose points and analyze in a one-by-one fashion, you may lay markers down on the left hand image by clicking on the flag button and dropping the marker where you would like a marker to appear. This image can be saved by choosing: Edit > Copy Video Image and pasting into the Paint application.

On the right hand image, you may drop individual data points:
a line transect:

or a 2D map:
Be careful with point placement and focus – if your sample does not lay flat or is not wafered evenly, automation may not be the best idea.

Any of these geometries will allow you to collect spectra on a point-by-point basis in an automated way. You may adjust these patterns with respect to the number of points, the motor step size, or the length of time that you wish the points/lines/map to collect in by clicking on Expt Setup, under the “Mapping” tab:
After changing any numbers in the text fields, hit “Update” and time estimation will appear. **ONE PIXEL IN THE MAP OR TRANSECT WILL ALWAYS BE THE SAME SIZE AS YOUR APERTURE WINDOW.** For instance, a map was made of a glass inclusion ~70 ums in diameter with a 20x20 um aperture and 5x5 um stage motor steps. In the map, clicking on the center pixel retrieves a baseline corrected spectra that yields a total intensity of the 3530 cm\(^{-1}\) peak of 1.501. Then, a single point with a 20x20 um aperture was manually centered on the inclusion and one spectra collected. This baseline corrected spectra yields a total intensity of the 3530 cm\(^{-1}\) peak of 1.507. **Whether a mathematical construct can be performed within the Atlus or Omnic software to yield higher resolution has yet to be determined.**
Collect and set a single background point as instructed above. When all is ready for data collection, go to Collect > Collect Map. Follow the prompts for providing a sample name.

Common issues:

1. Video feed image appears distorted – dropped data points or maps do not hold in a constant location when you navigate around in Atlus.
   a. First try to close Omnic and restart the computer. Reopen Omnic and see if the problem persists.
   b. If the problem persists, Go to Atlus > system configuration. Under Video, there is a “Video Calibration” button. Choose this and place the calibration slide (looks like a ruler printed on glass). Choose the objective size that is currently installed and hit edit. Follow the instructions.
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