

Variations in $\text{Fe}^{3+}/\sum\text{Fe}$ of Mariana Arc Basalts and Mantle Wedge $f\text{O}_2$

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RECEIVED JANUARY 22, 2014; ACCEPTED NOVEMBER 6, 2014

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 $\text{Fe}^{3+}/\sum\text{Fe}$ ratios determined in olivine-hosted glass inclusions and submarine glasses from five Mariana arc volcanoes and two regions of the Mariana Trough. For single eruptions, $\text{Fe}^{3+}/\sum\text{Fe}$ ratios vary along liquid lines of descent that are either slightly oxidizing (olivine + clinopyroxene + plagioclase fractionation, $\text{CO}_2 \pm \text{H}_2\text{O}$ degassing) or reducing (olivine + clinopyroxene + plagioclase \pm magnetite fractionation, $\text{CO}_2 + \text{H}_2\text{O} + \text{S}$ degassing). Mariana samples are consistent with a global relationship between calc-alkaline affinity and both magmatic H_2O 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 $\text{Fe}^{3+}/\sum\text{Fe}$ 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 relative to mid-ocean ridge basalts ($\sim\text{QFM}$, where QFM is quartz–fayalite–magnetite buffer), ranging from QFM + 1.0 to QFM + 1.6 for Mariana arc basalts, whereas back-arc related samples record primary oxygen fugacities that range from QFM + 0.1 to QFM + 0.5. This Mariana arc sample suite includes a diversity of subduction influences, from lesser influence of a

homogeneous H_2O -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 relative to 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 ($f\text{O}_2$) 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 multivalent 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,

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however, the fO_2 of the upper mantle and whether it varies spatially and over geological time is widely debated (e.g. Christie *et al.*, 1986; Bryndzia & Wood, 1990; Wood *et al.*, 1990; Carmichael, 1991; Ballhaus, 1993; Parkinson & Arculus, 1999; Bezos & Humler, 2005; Lee *et al.*, 2005, 2010, 2012; Kelley & Cottrell, 2009, 2012; Rowe *et al.*, 2009; Cottrell & Kelley, 2011, 2013; Trail *et al.*, 2011).

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 downgoing slab contributes chemically to the mantle source of arc magmas (e.g. Plank & Langmuir, 1993; Elliott *et al.*, 1997; Lecuyer & Ricard, 1999; Alt & Teagle, 2003). Arc basalts have a higher proportion of oxidized (Fe^{3+}) relative to reduced (Fe^{2+}) iron, expressed as the $Fe^{3+}/\sum Fe$ ratio [i.e. $Fe^{3+}/(Fe^{2+} + Fe^{3+})$], than do mid-ocean ridge basalts (MORBs) (Carmichael, 1991). There is disagreement as to whether this arises owing to differentiation processes (e.g. crystal fractionation, crustal assimilation, degassing) in the arc crust or to differences in the fO_2 of the mantle source. Experimentally calibrated trace element proxies for mantle fO_2 , which are potentially more immune to differentiation processes in the arc crust, suggest that the fO_2 of arc mantle is similar to that of MORB primary magmas (Lee *et al.*, 2005, 2010, 2012). 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.

A global study of basaltic glasses shows that those magmas most heavily influenced by subduction have higher $Fe^{3+}/\sum Fe$ ratios than MORB (Kelley & Cottrell, 2009). 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 $Fe^{3+}/\sum Fe$ ratios, and the $Fe^{3+}/\sum Fe$ ratios of reconstructed primary melts correspond to a source mantle that is oxidized 1–1.6 orders of magnitude relative to the MORB source (Kelley & Cottrell, 2012). In addition, a paired study of whole-rock $Fe^{3+}/\sum Fe$ ratios determined by wet chemical methods and fO_2 calculated from magnetite–ilmenite mineral pairs demonstrates that andesites from the Mexican volcanic belt experienced no net change in bulk $Fe^{3+}/\sum Fe$ 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 $Fe^{3+}/\sum Fe$ ratios recorded by arc magmas reflect a mantle source that has higher fO_2 than MORB-source mantle.

Outside 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). However, magmatic H_2O and $Fe^{3+}/\sum Fe$ ratios are strongly correlated (Kelley & Cottrell, 2009), and high magmatic fO_2 also enhances the appearance of oxides relative to silicates on the basalt liquidus (Osborn, 1959; Botcharnikov *et al.*, 2008). The effects of fO_2 and H_2O on magmatic differentiation may thus be difficult to segregate. Magnetite fractionation in a system closed to oxygen is also expected to reduce magmatic $Fe^{3+}/\sum Fe$ 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 $Fe^{3+}/\sum Fe$ ratios in olivine-hosted melt inclusions from single eruptive events at five subaerial 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.*, 2011, 2014) 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.

GEOLOGICAL SETTING

The Mariana subduction system is a well-studied ocean–ocean convergent margin with an active subaerial and submarine arc made up of ~40 volcanic centers and the Mariana Trough, an actively extending back-arc basin (Fig. 1; Stern, 1979; Hickey-Vargas & Reagan, 1987; Bloomer *et al.*, 1989; Woodhead, 1989; Fryer, 1996; Tollstrup

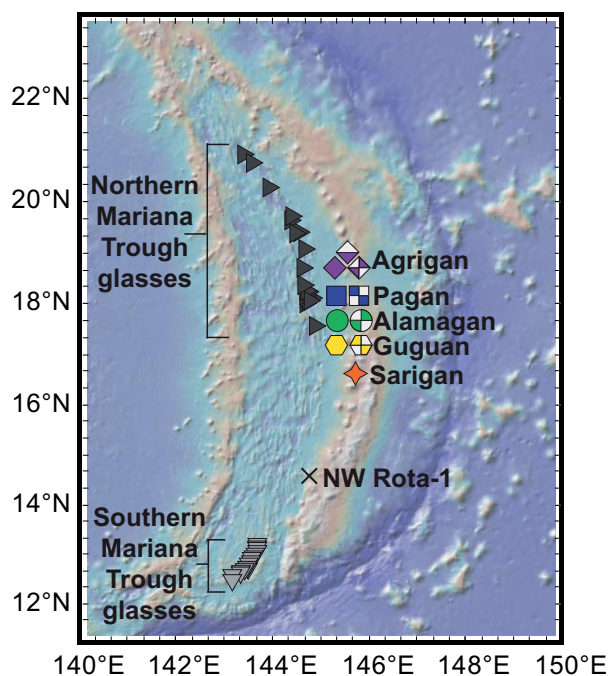


Fig. 1. Location map for samples used in this study. All colored symbols for Agrigan, Alamagan, Guguan, and Sarigan volcanoes, as well as the solid blue square for Pagan volcano represent olivine-hosted melt inclusions. Checkered square for Pagan volcano, cross for NW Rota-1 volcano, and light grey inverted triangles along the Mariana Trough represent submarine glasses. Dark grey triangles in the Northern Mariana Trough are seafloor glasses from Newman *et al.* (2000) and Kelley & Cottrell (2009). The basemap was created using GeoMapApp (<http://www.geomapp.org>; Ryan *et al.*, 2009).

& Gill, 2005). 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 compositions of erupted products along these arc volcanic centers are well studied and are primarily basaltic (Meijer & Reagan, 1981; Bloomer *et al.*, 1989; Pearce *et al.*, 2005; Wade *et al.*, 2005; Shaw *et al.*, 2008; Kelley *et al.*, 2010; Martindale *et al.*, 2013). 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 $\sim 13^\circ\text{N}$. 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 (Syracuse & Abers, 2006; Ribeiro *et al.*, 2013). 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 $f\text{O}_2$ and shallow crustal processes on the $\text{Fe}^{3+}/\Sigma\text{Fe}$ 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 with 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>; Fig. 1). Each tephra sample was washed in de-ionized water and sieved, taking care to avoid any samples with clasts larger than 2 cm 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 polytungstate 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 $>50\ \mu\text{m}$ 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 Fig. 2. Photomicrographs of every inclusion are shown in Supplementary Data Appendix K (supplementary data are available for downloading at <http://www.petrology.oxfordjournals.org>).

Submarine glass samples

Glassy pillow lavas from the southernmost Mariana Trough (Malaguana–Gadao ridge) were dredged from

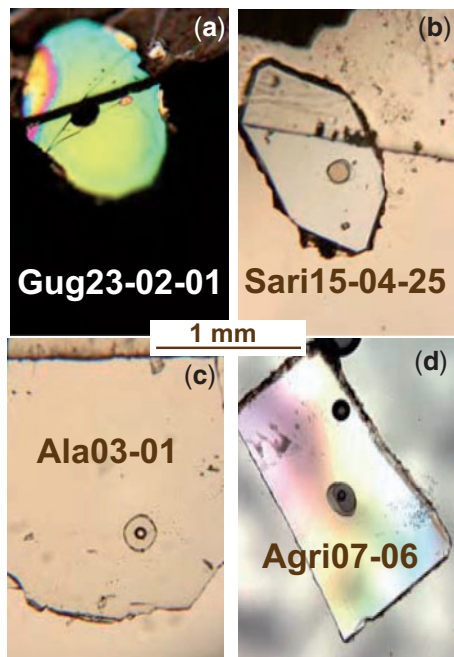


Fig. 2. Representative photomicrographs of melt inclusions in this study. (a) Melt inclusion Gug23-02-01 was doubly polished and the photomicrograph was taken in cross-polarized light. Melt inclusions Sari15-04-25 (b), Ala03-01 (c) and Agri07-06 (d) were doubly exposed and photomicrographs were taken in transmitted light.

the seafloor between 12.5 and 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.*, 2011, 2014). 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; Stolper & Newman, 1994; Gribble *et al.*, 1996, 1998; Newman *et al.*, 2000; Pearce *et al.*, 2005; Kelley & Cottrell, 2009; Fig. 1).

Analytical methods

Electron microprobe analysis

Submarine glass chips and glass inclusions were exposed on a single side and polished for electron microprobe analysis (EMPA) using a JEOL-8900 five-spectrometer microprobe at the Smithsonian Institution. During major element analysis the beam was operated at 10 nA, an accelerating voltage of 15 kV and 10 μm beam diameter. Sodium and potassium were measured first with 20 s peak count times to minimize alkali loss. Subsequently, Si, Ti, Al, Fe*, Mn, Ca and P were measured with 30–40 s 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, and 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 Supplementary Data Appendix E are average values of all 3–6 analysis spots on each olivine.

FTIR analysis

After EMPA of melt inclusions, all sample pits were polished away, being careful to account for possible beam 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 and 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 \times 12 μm to as large as 60 μm \times 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_2O absorption (1630, 5200 cm^{-1}) bands were summed to calculate total H_2O concentrations. In samples where the 3530 cm^{-1} band was not saturated, total H_2O 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 ($\sigma \pm 1 \mu\text{m}$). 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 $\text{Fe}^{3+}/\sum\text{Fe}$ ratios via micro X-ray absorption near edge structure spectroscopy (μ -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 an Si [311] monochromator and a nominal beam size of $9 \mu\text{m} \times 5 \mu\text{m}$. A beryllium window over the detector was used to attenuate high count rates above the main Fe $\text{K}\alpha$ fluorescence peak. Reference glass LW-0 was monitored continuously during each experimental session to correct for instrument drift. Further details related to this correction have been given by Cottrell *et al.* (2009).

Spectra were scrutinized for any influence from host olivines, phenocrysts, or microphenocrysts 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 Supplementary Data Appendix A (Fig. A1). Determination of $\text{Fe}^{3+}/\sum\text{Fe}$ ratios in basaltic glasses following the methods of Cottrell *et al.* (2009) has an associated precision of ± 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 system 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}Ca as the internal standard. The laser energy was 0.20–0.30 mJ at the sample surface for a reference spot (60 μm , 10 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 $\sim 1 \mu\text{m s}^{-1}$ through thin samples. Spot sizes ranged from 20 to 80 μm . United States Geological Survey glass standards BCR-2g, BHVO-2g and 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.*, 2000; 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 Fe^{2+}/Mg $K_D^{\text{oliv/liq}} = 0.3$ (Roeder & Emslie, 1970), and compared with the measured forsterite contents [Fo ; $\text{Mg}/(\text{Fe}^{2+} + \text{Mg})$] of the olivine host of each inclusion. If the predicted equilibrium $\text{Fo}_{\text{inclusion}}$ matched the measured Fo_{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 Fo_{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 Fo_{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 Supplementary Data Appendix B. Furthermore, for each melt inclusion suite, the inclusion compositions were compared with published whole-rock and melt inclusion data for each volcano, with particular

attention to variation in FeO* vs MgO (Supplementary Data Appendix A; Danyushevsky *et al.*, 2000). Inclusion compositions that fell outside 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 fO_2 . 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

To constrain the effects of fractional crystallization and volcanic degassing on $Fe^{3+}/\sum Fe$ 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 geographical location and is compared with published natural sample compositions and data from this study in Supplementary Data Appendix A. Each model follows the general pattern of olivine \pm clinopyroxene \pm plagioclase \pm magnetite fractionation. The model parameters, including mineral–melt models and pressure conditions that were chosen to generate each liquid line of descent (LLD), can be found in Appendix A. Volatile element behavior was investigated for each LLD by examining the behavior of volatile species (e.g. H₂O, CO₂, S) relative to other volatiles (e.g. CO₂ vs H₂O). For all samples, we also compare major and volatile element variations with previously published melt inclusion data from the same island (Fig. 4 and Supplementary Data Appendix A). Here, we outline the magmatic processes that are captured by these samples and the magnitude and variations of their $Fe^{3+}/\sum Fe$ 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 and Supplementary Data Appendix A, Fig. A2). The two inclusions with the highest H₂O concentrations in this study are from samples Agri07 and Agri04. The inclusion from Agri07 has a low CO₂ concentration that is inconsistent with closed-system degassing behavior, where high-pressure CO₂ volatilization and lower pressure H₂O volatilization should produce a near-vertical relationship between CO₂ and H₂O in Fig. 4a for an ascending, degassing magma (Dixon *et al.*,

1995). There is also no correlation between S and H₂O (Fig. 4b). Taken together, neither H₂O–CO₂ nor H₂O–S variations are consistent with simple degassing processes, suggesting that the volatile contents of these inclusions represent complex degassing behaviors.

Agrigan melt inclusions have $Fe^{3+}/\sum Fe$ ratios that range from 0.217 to 0.344. The highest MgO sample in this suite (MgO = 5.82 wt %) has $Fe^{3+}/\sum Fe = 0.242$, which is more oxidized than the most oxidized MORB glass at a comparable MgO content ($Fe^{3+}/\sum Fe = 0.178$ at 6.18 wt % MgO) from Cottrell & Kelley (2011; Fig. 5). There is no correlation between H₂O concentrations and $Fe^{3+}/\sum Fe$ ratios among these inclusions, despite >4 wt % difference in the highest and lowest H₂O 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 to 7.17 wt % (Fig. 3a–d). The single glass inclusion produced interference fringes in the FTIR spectra such that dissolved CO₂ 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 $Fe^{3+}/\sum Fe$ ratio of 0.222 at MgO = 5.44 wt %. Submarine Pagan glasses have $Fe^{3+}/\sum Fe$ 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 $Fe^{3+}/\sum Fe$ ratios do not vary systematically with MgO concentrations. It is important to note that the composition and $Fe^{3+}/\sum Fe$ 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 $Fe^{3+}/\sum Fe$ ratio to submarine glasses from Pagan, demonstrating that melt inclusions have the potential to record similar compositional and redox information to 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 ranges 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 to 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

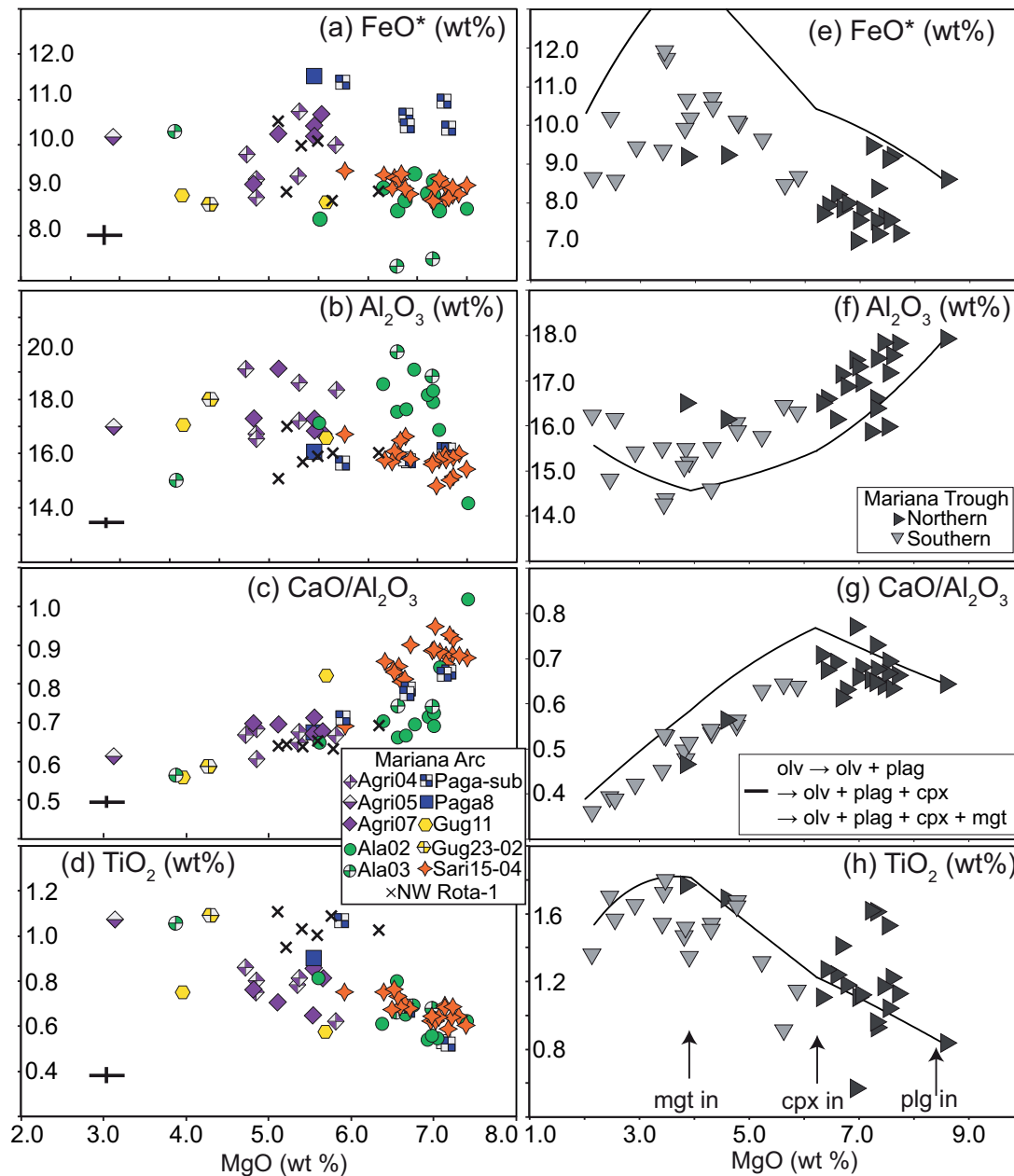


Fig. 3. Major element variations for Mariana arc melt inclusions and submarine glasses (a–d) and back-arc submarine glasses (e–h). All symbols are as in Fig. 1. Black line in (e)–(h) shows the trajectory of $\text{olv} \pm \text{plag} \pm \text{cpx} \pm \text{mgt}$ fractionation, generated using Petrolog3 (Danyushevsky & Plechov, 2011) fractionating the composition of 80-1-3 (VG10498) at 15 kbar, using mineral–melt models of Roeder & Emslie (1970), Ariskin & Barmina (1999) and Danyushevsky (2001) 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 (a)–(d).

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 and b, and Supplementary Data Appendix A, Fig. A4).

Alamagan inclusions have $\text{Fe}^{3+}/\sum\text{Fe}$ ratios that range from 0.207 to 0.267, with $\text{Fe}^{3+}/\sum\text{Fe} = 0.244$ 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 ($\text{Fe}^{3+}/\sum\text{Fe} = 0.16$; Cottrell & Kelley, 2011). The $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of these inclusions generally decrease with MgO (Fig. 5). There is no systematic variation in $\text{Fe}^{3+}/\sum\text{Fe}$ ratios with variable H_2O concentrations (Fig. 4c).

Guguan volcano. Two Guguan glass inclusions are basaltic in composition and have MgO concentrations of 3.96

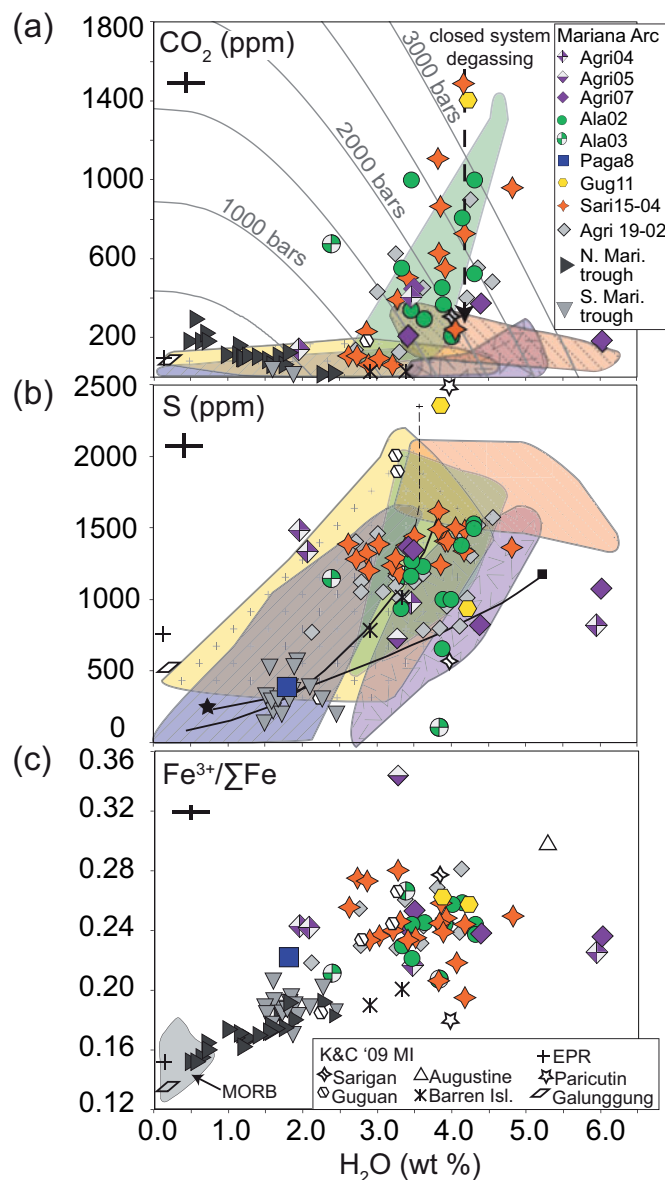


Fig. 4. Volatile element variations for Mariana arc melt inclusions and back-arc submarine glasses. Shaded regions [Q6] in (a) and (b) are melt inclusion data from Shaw *et al.* (2008) and Kelley *et al.* (2010), and are shown for comparison (blue - Pagan, yellow - Guguan, green - Alamagan, purple - Agrigan, orange - Sarigan). (a) H_2O vs CO_2 variation. Isobars and closed-system degassing curve were calculated for a basalt at $1200^\circ C$ using VolatileCalc (Newman & Lowenstern, 2002). Errors associated with H_2O concentrations are ~ 0.25 wt % and ~ 75 ppm for CO_2 concentrations. (b) S vs H_2O . Model curves for concomitant S and H_2O degassing are semi-empirical and taken from Sisson & Layne (1993, black square) and Wade *et al.* (2006, small cross). Dashed line represents the extension of the degassing trajectory to high sulfur concentrations. Black star represents an approximately degassed magma. (c) $Fe^{3+}/\Sigma Fe$ vs H_2O for Mariana arc melt inclusions from this study and from Kelley & Cottrell (2012, light grey diamonds), and back-arc submarine glasses. Grey MORB field is from Cottrell & Kelley (2011). Additional melt inclusion data are from Kelley & Cottrell (2009), plotted for comparison. Error bars are shown in the upper left-hand corner of each plot.

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 (Supplementary Data Appendix A, Fig. A5). We thus consider their compositional differences within the context of the literature data. One inclusion yielded a

resolvable CO_2 concentration, recording an $H_2O + CO_2$ pressure of entrapment of 4.3 kbar (Fig. 4a; Newman & Lowenstern, 2002). Sulfur and H_2O concentrations in these inclusions are consistent with sulfur degassing (Fig. 4b). These inclusions have $Fe^{3+}/\Sigma Fe = 0.257$ and 0.263, both more oxidized than the most oxidized MORB glasses (Fig. 5; Cottrell & Kelley, 2011).

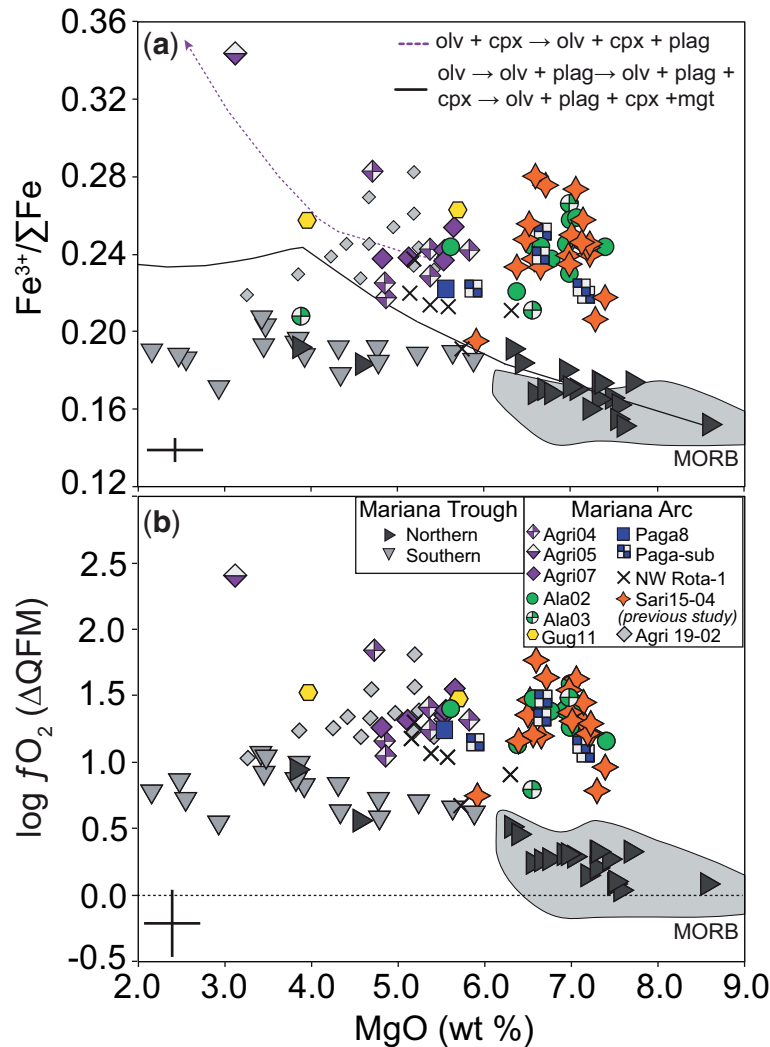


Fig. 5. (a) $\text{Fe}^{3+}/\Sigma\text{Fe}$ vs MgO for Mariana arc melt inclusions from this study and from Kelley & Cottrell (2012, light grey diamonds), submarine glasses from Pagan and NW Rota-1 volcanoes, and submarine glasses from the Mariana Trough. Grey field represents global MORB glass data from Cottrell & Kelley (2011). Black line is the trajectory of $\text{olv} \pm \text{plag} \pm \text{cpx} \pm \text{mgt}$ fractionation, as in Fig. 2. Dotted purple line is the trajectory of isobaric $\text{olv} \pm \text{cpx} \pm \text{plag}$ fractionation from a starting composition similar to the composition of melt inclusion Agri04-05, generated using Petrolog3 (Danyushevsky & Plechov, 2011) at 1 kbar, using the mineral–melt models of Roeder & Emslie (1970) and Danyushevsky (2001) in a system closed to oxygen. (b) Magmatic $f\text{O}_2$, plotted relative to the QFM buffer vs MgO for the same samples. Oxygen fugacities and the position of the QFM buffer (Frost, 1991) are calculated at the pressures and temperatures of melt inclusion entrapment using the algorithm of Kress & Carmichael (1991). Pressures for each melt inclusion suite are taken as the average pressure of entrapment recorded by the CO_2 – H_2O 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.

Although these melt inclusions are sourced from a different tephra layer, their compositions and oxidation states are consistent with Guguan melt inclusions from Kelley & Cottrell (2009).

Sarigan volcano. Sarigan melt inclusions are basaltic and have a narrow range of MgO, from 5.20 to 6.96 wt %. They record pressures of entrapment between 0.87 and 3.4 kbar and demonstrate closed-system H_2O – CO_2 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 $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from 0.195 to 0.280, all of which are more oxidized than average MORB glasses with similar MgO concentrations (Cottrell & Kelley, 2011). There are no systematic variations in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios with indices of crystal fractionation, sulfur or H_2O concentrations (Figs 5, 6 and 4c, respectively).

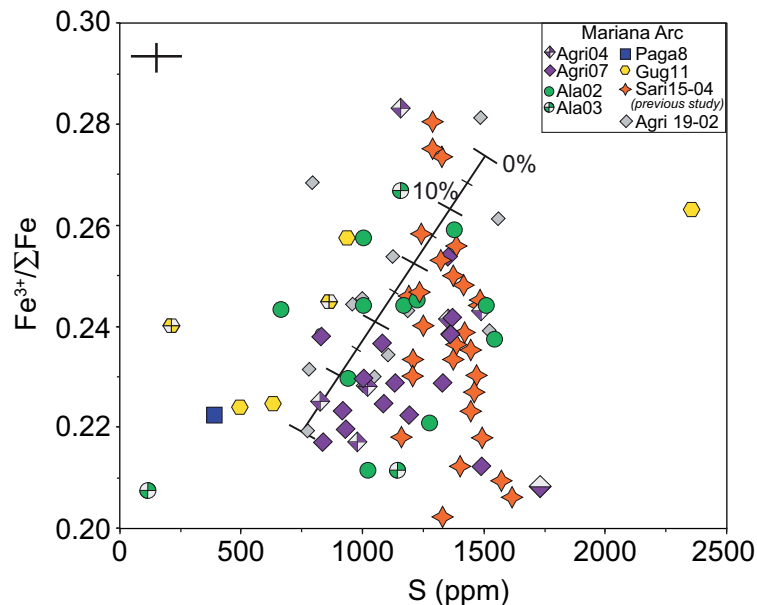


Fig. 6. $\text{Fe}^{3+}/\Sigma\text{Fe}$ vs S for melt inclusions from Agrigan, Pagan, Guguan, Sarigan, and Alamagan volcanoes, and melt inclusions from Agrigan volcano from Kelley & Cottrell (2012, light grey diamonds). The black line with tick marks is a model for S degassing and associated Fe reduction, from Kelley & Cottrell (2012). Error bar is shown in the upper left-hand corner.

NW Rota-1 volcano. Submarine glasses from NW Rota-1 submarine volcano are basaltic and have $\text{MgO} = 5.15\text{--}6.29$ wt %. These glasses have $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios between 0.190 and 0.237, all more oxidized than MORB glasses with the same MgO concentrations (Cottrell & Kelley, 2011). Like the submarine Pagan glasses, $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios do not 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 Stolper & Newman (1994), Newman *et al.* (2000) and Pearce *et al.* (2005). They are basaltic in composition and range in MgO from 3.87 to 7.72 wt %. Dissolved H_2O and CO_2 concentrations are consistent with the pressure of the water column at an eruption depth of ~ 4 km. Stolper & Newman (1994) and Newman *et al.* (2000) have shown that these glasses are the result of magmas that were variably saturated with an $\text{H}_2\text{O}\text{--CO}_2$ -rich fluid upon eruption. The range in H_2O contents of these samples results from the variable influence of the subducting slab in the genesis of Northern Mariana Trough magmas (Stolper & Newman, 1994).

$\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for these glasses were reported by Kelley & Cottrell (2009) and are examined here in the context of the Mariana subduction system. $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios range from 0.150 to 0.182, overlapping the MORB array in samples with <1.0 wt % H_2O , but vertically

offset to $\sim 1\%$ higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for samples with >1.0 wt % H_2O . There is a strong positive correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and H_2O 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 SiO_2 ranging from 51.90 to 59.83 wt % and MgO ranging from 2.15 to 5.87 wt %. Although separated geographically from Northern Mariana Trough samples by >700 km, major element variations for Southern Mariana Trough glasses are similar to those of the Northern Mariana 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 select trace element contents (V, Cr; Fig. A9). This is also supported by the modeled LLD (black line in Fig. 3e–h).

Only two of these samples have resolvable CO_2 concentrations, but these yield saturation pressures that are consistent with their depths of collection (Fig. 4a; Newman & Lowenstern, 2002). Sulfur concentrations vary from 157 to 583 ppm, increasing with decreasing H_2O concentrations until $\text{H}_2\text{O} \sim 2$ wt %, at which point sulfur concentrations begin to decrease with decreasing H_2O concentrations. Samples from the southern portion of the Mariana Trough display a range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from 0.171 to 0.207, although, in contrast to the Northern Mariana Trough glasses, these ratios do not correlate strongly with MgO, H_2O or S concentrations (Figs 5a, 4c and 6, respectively).

DISCUSSION

Relationships of $\text{Fe}^{3+}/\sum\text{Fe}$ to magmatic differentiation processes

Fractional crystallization

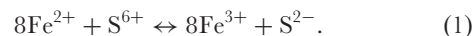
If Fe^{3+} behaves simply as an incompatible element and magmatic $f\text{O}_2$ is not buffered, low-pressure fractionation of olivine, clinopyroxene, and plagioclase from basaltic magmas should lead to an increase in the $\text{Fe}^{3+}/\sum\text{Fe}$ ratio of the magma. Data for MORB are consistent 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, Fe^{2+} partitions into olivine and clinopyroxene, whereas Fe^{3+} 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 the magmatic $\text{Fe}^{3+}/\sum\text{Fe}$ ratio. Each modeled LLD for the Mariana arc demonstrates these principles of crystal fractionation-induced oxidation (Fig. 5; Supplementary Data Appendix A).

Major element variations of melt inclusion and submarine glass suites from the Mariana arc are consistent with a general pattern of olivine \pm clinopyroxene \pm plagioclase fractionation. In all cases, the $\text{Fe}^{3+}/\sum\text{Fe}$ ratios in both arc melt inclusions and submarine glasses are more oxidized than the most oxidized MORB glasses from Cottrell & 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 $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of any arc melt inclusion or submarine glass in this study cannot be re-created 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 $\text{Fe}^{3+}/\sum\text{Fe}$ ratios in most of the Mariana arc samples. The exceptions to this are two inclusions from Agrigan volcano, where an increase in $\text{Fe}^{3+}/\sum\text{Fe}$ 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 $\sim 2\%$ of the total proportion of fractionating phases (ol $\sim 64\%$, cpx $\sim 34\%$) before this increase in magmatic $\text{Fe}^{3+}/\sum\text{Fe}$ ratios. At melt MgO = 4.1 wt %, the modal proportion of plagioclase increases to $\sim 10\%$ (ol $\sim 55\%$, cpx $\sim 35\%$), and continues to rise as fractionation continues. At the same time, the modal proportion of olivine decreases. The associated increase in $\text{Fe}^{3+}/\sum\text{Fe}$ 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 $\text{Fe}^{3+}/\sum\text{Fe}$ ratios. Our data are consistent with this model prediction (Fig. 5a) and these two samples suggest that this increase in $\text{Fe}^{3+}/\sum\text{Fe}$ ratios may be as great as ~ 0.1 (absolute).

Spinel may fractionate at high pressure in magmas. There is no evidence that these magmas were ever in equilibrium with a spinel phase, but if they were and $D_{\text{Fe}^{3+}}^{\text{sp}/\text{liq}} > 1$, in a system closed to oxygen the impact of spinel fractionation from the magma will reduce $\text{Fe}^{3+}/\sum\text{Fe}$ ratios in the magma. In this case, the $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of the highest MgO melt inclusions in this study are minima. Magnetite ($\text{Fe}^{3+}_2\text{Fe}^{2+}\text{O}_4$) is the next solid phase with $D^{\text{Fe}^{3+}} > 1$ 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 \pm clinopyroxene \pm plagioclase such that the net effect is to maintain roughly constant magmatic $\text{Fe}^{3+}/\sum\text{Fe}$ ratios after magnetite-in (Fig. 5; Supplementary Data Appendix A). The $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of Mariana back-arc samples are consistent with the predicted magmatic oxidation from the modeled LLD until ~ 5.5 wt % MgO (Fig. 5a), although at lower MgO concentrations the $\text{Fe}^{3+}/\sum\text{Fe}$ 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 ~ 4 wt % MgO, much lower MgO than the point at which the natural data fall away from the modeled LLD (Fig. 3e–h; Supplementary Data Appendix A, Fig. A9). Other processes, such as sulfide fractionation or sulfur degassing, may influence magmatic redox conditions for these samples.

Sulfide fractionation may affect magmatic $\text{Fe}^{3+}/\sum\text{Fe}$ ratios via the Fe–S redox couple



For example, equation (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 the melt, provided the magnetite has a higher $\text{Fe}^{3+}/\sum\text{Fe}$ ratio than the melt. If the concentrations of both Fe^{2+} and Fe^{3+} are controlled only by crystal fractionation, when magnetite

begins fractionating, equation (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 equation (1) will also produce a new equilibrium proportion of Fe^{3+} . If equation (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_2O (Fig. 4b). Experimentally constrained estimates for the sulfur content at sulfide saturation (SCSS) for relevant pressures, temperatures, compositions, and $f\text{O}_2$ range from 950 ppm to >2000 ppm for all Mariana Trough glasses (Liu *et al.*, 2007; Jenner *et al.*, 2010; Jugo *et al.*, 2010). 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_2S 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 $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of these samples because of the evidence for simultaneous magnetite fractionation. The relative constancy of $\text{Fe}^{3+}/\sum\text{Fe}$ ratios in Mariana Trough samples with $\text{MgO} < 5.5$ wt % suggests that the redox equilibria illustrated by equation (1) may have played an important role in controlling $\text{Fe}^{3+}/\sum\text{Fe}$ 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 $\text{Fe}^{3+}/\sum\text{Fe}$ ratios during magmatic processes.

The effect of $f\text{O}_2$ on tholeiitic index

Magmatic differentiation may influence the $\text{Fe}^{3+}/\sum\text{Fe}$ ratio, as discussed above, but magmatic $f\text{O}_2$ 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 (Spulber & Rutherford, 1983; Sisson & Grove, 1993; Botcharnikov *et al.*, 2008). 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 $\text{MgO} = 4.0 \pm 1.0$ wt % divided by the $[\text{FeO}^*]$ at $\text{MgO} = 8.0 \pm 1.0$ wt % ($\text{FeO}_{4.0}^*/\text{FeO}_{8.0}^*$), such that a tholeiitic magma has a $\text{THI} > 1.0$, and a calc-alkaline magma has a $\text{THI} < 1.0$ (Zimmer *et al.*, 2010). Samples from both the Mariana arc and trough from this study are consistent with observations by 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 ($\text{THI} > 1.2$) and has lower pre-eruptive water contents (Fig. 7). Globally, the THI is also well correlated with magmatic $f\text{O}_2$, where arc samples are more oxidized than back-arc basalt 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 $f\text{O}_2$ 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 $f\text{O}_2$. For example, magmas erupted from Augustine volcano have a THI of 0.65, lower than any of the predicted THI values 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 $f\text{O}_2$ of $\sim\text{QFM} + 2.0$ 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, $f\text{O}_2$ may play a role in generating calc-alkaline differentiation trends in arc magmas. Additionally, it may be difficult to isolate the specific effects of H_2O and $f\text{O}_2$ 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 ~ 2 wt % H_2O degassing, but show no corresponding variations in $\text{Fe}^{3+}/\sum\text{Fe}$ ratios (Fig. 4). This demonstrates that H_2O degassing is not an oxidizing process in basaltic magmas, rather it is redox neutral (Carmichael, 1991; Frost & Ballhaus, 1998; Cottrell & Kelley, 2011; Crabtree & Lange, 2011). Water concentrations correlate strongly with $\text{Fe}^{3+}/\sum\text{Fe}$ 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 (Stolper & Newman, 1994; Newman *et al.*, 2000). Using H_2O as a proxy for slab-derived influence on the arc and back-arc mantle sources, subduction influence has also been linked to

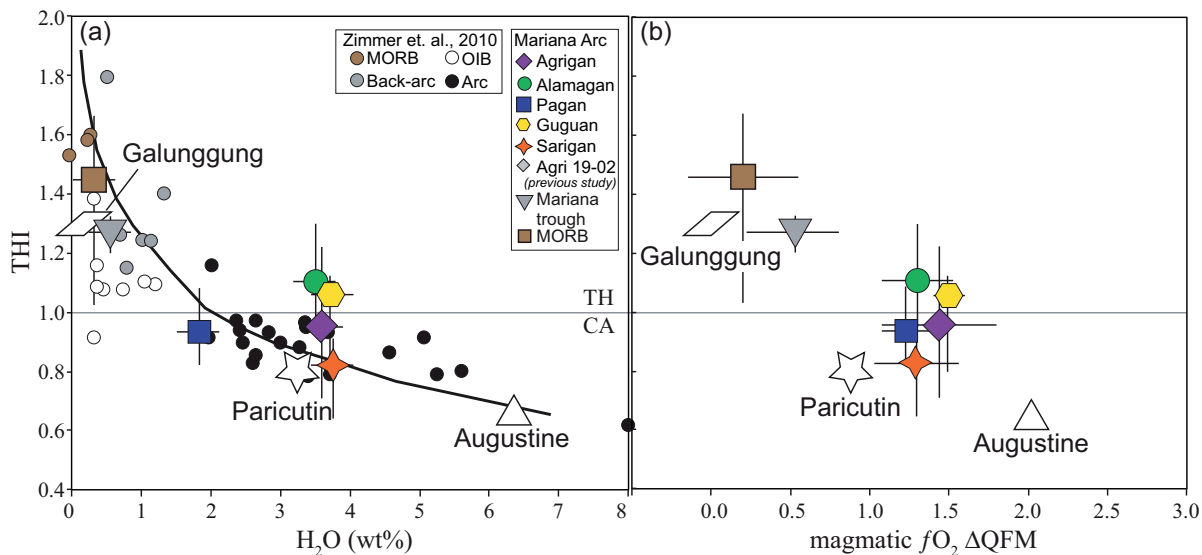


Fig. 7. Tholeiitic index (THI) vs (a) pre-eruptive H_2O content and (b) magmatic $f\text{O}_2$ relative to the QFM buffer. THI calculations, small circles in (a) and the black curve are from Zimmer *et al.* (2010). The grey line marks the boundary between tholeiitic and calc-alkaline differentiation trends, as defined by Zimmer *et al.* (2010). Magmatic $f\text{O}_2$ values are calculated as in Fig. 5. Brown square represents the average of MORB data from Cottrell & Kelley (2011). Grey triangle represents both Northern and Southern Mariana Trough samples from this study. Error bars for H_2O and magmatic $f\text{O}_2$ 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.

magmatic and mantle source oxidation (e.g. Fig. 4d; Kelley & Cottrell, 2009). It is important to note that H_2O 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_2O concentrations as well as their oxidized condition on the mantle source beneath the Mariana arc and trough (see below).

Kelley & Cottrell (2012) suggested that sulfur degassing played a dominant role in controlling $\text{Fe}^{3+}/\sum\text{Fe}$ 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 6 moles of electrons are transferred to $\text{Fe}^*_{(\text{melt})}$ for every 1 mole of $\text{S}^{2-}_{(\text{melt})}$ that is degassed as $\text{S}^{4+}_{(\text{vapor})}$ (black line, Fig. 6) as a possible explanation for magmatic reduction and associated S loss. Figure 6 shows the relationship between sulfur concentrations and $\text{Fe}^{3+}/\sum\text{Fe}$ ratios, as observed in melt inclusion suites from Sarigan, Alamagan, Agrigan, and Guguan volcanoes. Sulfur degassing is probably recorded by Alamagan, Agrigan, and Guguan melt inclusions. Agrigan inclusions show a slight reduction in $\text{Fe}^{3+}/\sum\text{Fe}$ ratios with decreasing sulfur concentration that is consistent with the melt inclusion suite studied by Kelley & Cottrell (2012). In contrast, the two Guguan inclusions are different in their sulfur concentrations by >1000 ppm but do not vary significantly in their $\text{Fe}^{3+}/\sum\text{Fe}$ ratios, and there is no correlation between the sulfur concentrations and $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of Alamagan melt 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 $\text{Fe}^{3+}/\sum\text{Fe}$ 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 affect the $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of melt inclusions in this study. The $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of hydrous melt inclusions have been postulated to be affected by hydrogen diffusion into 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) and Bucholz *et al.* (2013), however, have shown that $\text{Fe}^{3+}/\sum\text{Fe}$ ratios in melt inclusions that have been dehydrated or hydrated are rapidly re-equilibrated with the $\text{Fe}^{3+}/\sum\text{Fe}$ ratios of the external melt. Those researchers hypothesized 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 to 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 fO_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, Fig. 4 demonstrates coherent trends with respect to H_2O degassing for Sarigan melt inclusions, diminishing the likelihood that this 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), allowing 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 diffusively re-equilibrated (see Supplementary Data Appendix A, Fig. A11). Finally, the trace element heterogeneity recorded in melt inclusion populations from Sarigan and Alamagan volcanoes shows strong evidence of retaining magmatic trace element variability (see Appendix A, Fig. A10), supporting the notion that the heterogeneity recorded in melt inclusion suites in this study reflects true magmatic heterogeneity rather than post-entrapment melt inclusion processes (Cottrell *et al.*, 2002).

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 $Fe^{3+}/\sum Fe$ ratios in arc basalts, although these effects are minor, and neither can explain the oxidation of Fe in arc basalts relative to MORB. This suggests a fundamental difference between the $Fe^{3+}/\sum Fe$ 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 & 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 geographical 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 fitted to the most incompatible major elements (e.g. P_2O_5) and the slope of a line defined by the natural data was used for the calculation instead (Supplementary Data Appendix E). For Fe, $Fe_{(actual)}$ and $Fe_2O_{3(actual)}$ concentrations were plotted versus MgO concentration and projected back along the slopes of lines defined by the natural data for each sample suite. The 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, owing 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 Fo_{90} olivine (Supplementary Data Appendices A and 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 back clinopyroxene and olivine simultaneously until achieving equilibrium with Fo_{90} olivine. When applied to a suite of 20 melt inclusions from Sarigan volcano, this method returned nearly identical average primary melt $Fe^{3+}/\sum Fe$ ratios to 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 $fO_2 \sim 0.28$ 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, back-arc basin basalts, and arc samples). An important conclusion drawn from this test is that the choice of correction method does not significantly affect 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 and 2). Primary fO_2 was calculated using the algorithm of Kress & Carmichael (1991; Tables 1 and 2) relative to the QFM

Table 1: Maximum $Fe^{3+}/\sum Fe$ ratios and average calculated primary melt compositions and fO_2 for the Mariana arc and Southern Mariana Trough

	Agrigan	Pagan	Alamagan	Guguan	Sarigan	NW Rota-1	Southern Mariana Trough
MgO_{max}^1	5.66	7.17	7.40	5.70	7.23	6.33	5.93
$Fe^{3+}/\sum Fe (MgO_{max})^2$	0.254	0.219	0.244	0.263	0.240	0.211	0.185
Pressure ³	0.2	0.3	0.2	0.2	0.2	0.1	0.1
Temperature ⁴	1164	1100 ¹²	1196	1100	1203	1100 ¹²	1200 ¹²
1 σ	29	n.d.	30	n.d.	9	n.d.	n.d.
Magmatic log fO_2	-7.03	-8.07	-6.91	-7.88	-6.71	-8.44	-7.46
1 σ	0.52	0.15	0.51	0.03	0.54	0.22	0.16
Magmatic log fO_2^5	1.44	1.23	1.30	1.50	1.30	1.02	0.76
1 σ	0.36	0.15	0.22	0.03	0.27	0.22	0.16
Pre-eruptive H ₂ O (wt %) ⁶	3.78	1.81	3.70	4.05	3.96	n.d.	0.50
THI ⁷	0.950	0.933	1.108	1.058	0.824	n.d.	1.276
$Fe^{3+}/\sum Fe_{prim}^8$	0.182	0.192	0.219	0.242	0.216	0.163	0.167
1 σ	0.01	0.01	0.02	0.00	0.02	0.01	0.01
Pressure ⁹	1.8	1.58	1.3	1.1	1.1	0.8	0.64
1 σ	0.2	0.2	0.2	0.1	0.1	0.1	0.08
Temperature ¹⁰	1384	1361	1256	1234	1256	1303	1263
1 σ	46	22	26	6	13	30	21
Primary log fO_2	-4.12	-4.15	-5.39	-5.53	-5.62	-6.03	-6.66
1 σ	0.3	0.2	0.4	0.1	0.2	0.4	0.25
Primary log fO_2^{11}	1.09	1.09	1.34	1.62	1.29	0.59	0.48
1 σ	0.1	0.2	0.2	0.1	0.2	0.2	0.02
Ba/La	19.5	40.8	34.9	48.0	46.4	17.3	15.9
1 σ	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
1 σ	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
1 σ	0.05	0.37	0.52	—	0.39	0.29	0.74

—, trace element concentrations were measured on a single sample. 1 σ values represent the standard deviation of the sample population from the average values reported. n.d., insufficient data were available to perform the calculation.

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

² $Fe^{3+}/\sum Fe$ 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 fO_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 & Carmichael (1991).

⁶Pre-eruptive water content determined by averaging the H₂O contents of inclusions that form vertical paths on a CO₂-H₂O diagram (Fig. 4b). For Guguan, this is the H₂O 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 $Fe^{3+}/\sum Fe$ ratio calculated for a primary magma at a given geographical 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 fO_2 relative to the quartz-fayalite-magnetite oxygen buffer (ΔQFM) at pressure and temperature of melt generation. Calculated using the algorithm of Kress & Carmichael (1991).

¹²Estimated from melt inclusion data from other suites in this study.

Table 2: Primary melt $Fe^{3+}/\sum Fe$, fO_2 and trace element compositions for Northern Mariana Trough lavas

Sample	$Fe^{3+}/\sum Fe_{prim}^1$	P^2	T^3	$\log fO_2$	$\log fO_2^4$	Ba/La	Th/La	Zr/Y
73-2-1	0.151	0.9	1262	-6.69	0.25	6.97	0.083	3.76
71-1-14	0.173	0.8	1232	-6.87	0.52	9.91	0.123	3.79
82-1-1	0.164	0.8	1249	-6.70	0.45	7.34	0.080	3.19
76-1-1	0.133	1.3	1356	-5.68	0.08	5.04	0.066	3.26
75-1-2	0.145	1.1	1301	-6.29	0.18	5.87	0.077	3.91
80-1-3	0.139	1.3	1322	-5.96	0.17	8.31	0.073	2.21
46-1-6	0.151	0.9	1267	-6.64	0.26	11.3	0.081	2.86
74-1-1	0.165	0.8	1241	-6.84	0.40	7.11	0.101	3.52
47-1-5	0.160	0.8	1246	-6.84	0.34	12.7	0.107	2.64

¹Calculated primary $Fe^{3+}/\sum Fe$ ratio.

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

³Temperature of melt generation ($^{\circ}C$), calculated using the Si-thermobarometer of Lee *et al.* (2009).

⁴Log fO_2 relative to the quartz-fayalite-magnetite oxygen buffer (ΔQFM) at pressure and temperature of melt generation.

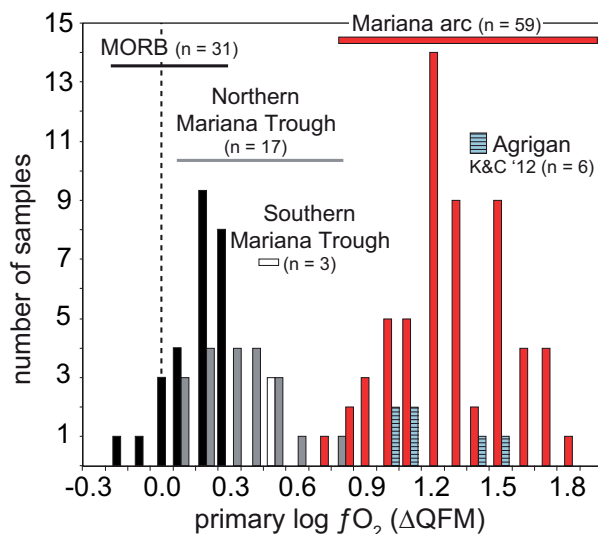


Fig. 8. Histogram showing calculated primary fO_2 (ΔQFM) for several tectonic regimes. MORB data were calculated by adding equilibrium olivine compositions in 0.1% increments to the compositions of MORB glasses with $MgO > 7$ wt %; data from Cottrell & Kelley (2011). Pressures and temperatures of melt generation were calculated using the Si-thermobarometer of Lee *et al.* (2009). Oxygen fugacities were calculated from $Fe^{3+}/\sum Fe$ ratios after Kress & Carmichael (1991). Gray bars with horizontal-line shading represent primary fO_2 values for Agrigan volcano from Kelley & Cottrell (2012). The dashed line marks the position of QFM, which is equal to the approximate primary fO_2 for MORB-source mantle (Cottrell & Kelley, 2011).

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 ($\sim QFM + 0.1$ 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 $QFM + 0.2$ and $QFM + 1.8$, which is 0.4–1.5 orders of magnitude more oxidized than the most oxidized MORB 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 owing 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 $\sim QFM + 1$, 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 $Fe^{3+}/\sum Fe$ ratios owing to the effects of crystallization or degassing (< 0.05 , absolute). Similarly, the mantle wedge under the Mariana Trough generates melts with fO_2 values 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 $Fe^{3+}/\sum Fe$ ratios despite evidence for sulfur degassing and magnetite fractionation. Mariana Trough basalts erupt with $Fe^{3+}/\sum Fe$ 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, 2010, 2012). 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 convergent margins (e.g. Plank & Langmuir, 1993; Elliott *et al.*, 1997; Plank, 2005). 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 MORB. 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 (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 \sim 15, Plank & Langmuir, 1998), and thus sediment melts that move from the slab into the mantle wedge probably 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 & Langmuir, 1998; Plank, 2005).

Arc and back-arc samples from the Marianas fall on a mixing line between mantle with Sm/La \sim 1.35 and Th/La \sim 0.02 and the bulk composition of sediments recovered from Ocean Drilling Program (ODP) Site 801, \sim 1100 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 currently 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 Fig. 9b towards a fluid with a high Ba/La ratio,

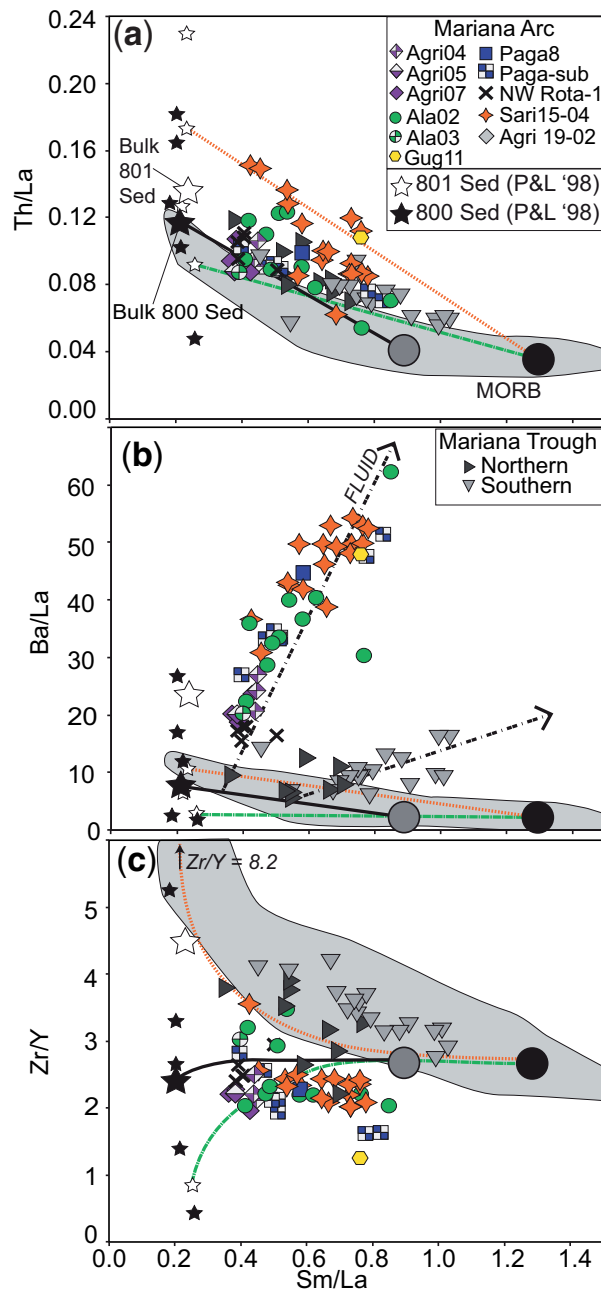


Fig. 9. (a) Th/La, (b) Ba/La, and (c) Zr/Y vs Sm/La for melt inclusions, submarine glasses from Pagan and NW Rota-1 volcanoes, and Mariana Trough submarine glasses. The grey field is Pacific MORB data from Niu & Batiza (1997), shown for comparison. Data for discrete sedimentary materials from the Pacific plate 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 are 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 continuous 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 800. Dot-dash black lines in (b) show approximate mixing trajectories with fluids of unconstrained composition.

though a lower Ba/La ratio than that of the fluid influencing the arc samples (Stolper & Newman, 1994; Pearce *et al.*, 2005). Mariana arc samples display a large range in Ba/La ratios that reflects 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 those of Southern Mariana Trough samples. This is an interesting observation considering its position relative to the trench, where it sits ~50 km 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 the 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 are inherent to the mantle (Langmuir *et al.*, 2006) or generated by prior melt extraction (e.g. McCulloch & Gamble, 1991; Woodhead *et al.*, 1993; Kincaid & Hall, 2003). 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 as a result of melt extraction at the back-arc (Woodhead *et al.*, 1993; Pearce *et al.*, 2005). 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 source (Fig. 9c; Tables 1 and 2; Langmuir *et al.*, 2006). The Zr/Y ratios of Mariana arc basalts are significantly lower, however, reflecting the more depleted sub-arc mantle source, consistent with the predicted effects of back-arc spreading in mantle circulation and prior geochemical studies of the

Mariana arc (McCulloch & Gamble, 1991; Pearce *et al.*, 2005; Kelley *et al.*, 2010). 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 the observed heterogeneity in trace element compositions discussed here, we emphasize that major element compositions are relatively restricted and uncorrelated with trace element ratios such as La/Yb, which is greater than can be expected from simple fractionation of La from Yb during differentiation (Supplementary Data Fig. A13). This suggests that although 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 (Supplementary Data Appendix A).

Variations in fO_2 with mantle source-related variables. To assess the source of elevated fO_2 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 fO_2 . There are no systematic relationships between primary fO_2 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 (1) that the Mariana Trough taps an enriched mantle source (Langmuir *et al.*, 2006), and (2) 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 melt extraction increases the activity of Fe^{3+} in spinel, then large-degree melting and/or previous melt extraction 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 values 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, MORB encompasses 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

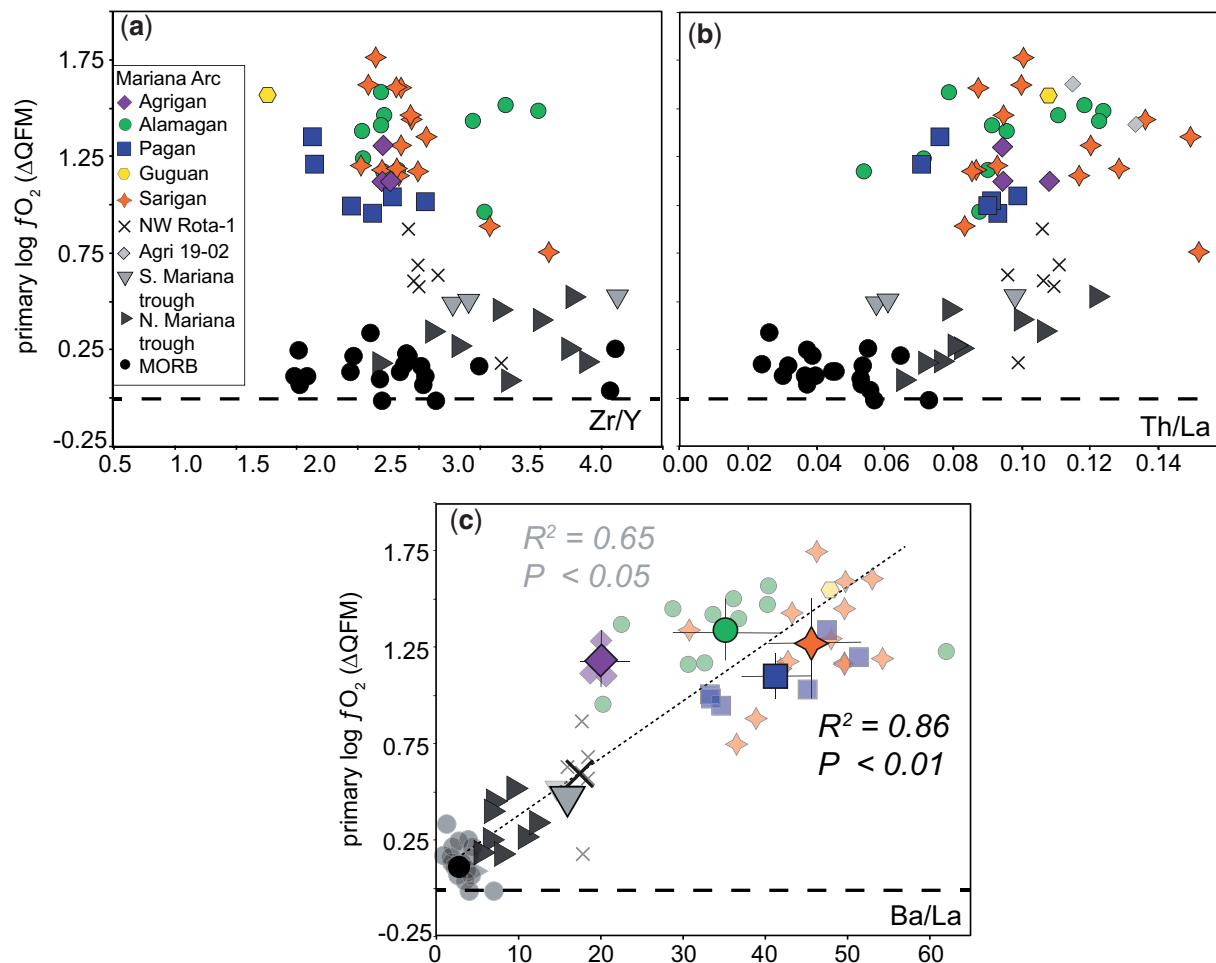


Fig. 10. Primary fO_2 (ΔQFM) vs (a) Zr/Y, (b) Th/La, and (c) Ba/La for MORB, Northern Mariana Trough, Southern Mariana Trough, NW Rota-1 submarine volcano, and Agrigan, Alamagan, Pagan, Sarigan and Guguan volcanoes. MORB data are from Cottrell & Kelley (2013). In (c), large colour-saturated symbols represent the average calculated primary fO_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 linear regression statistics for these average values are shown in black ($R^2=0.86$, $P<0.01$). The linear regression statistics for the entire dataset are shown in gray ($R^2=0.65$, $P<0.05$). The bold dashed line marks the position of QFM, which is equal to the approximate primary fO_2 for MORB-source mantle (Cottrell & Kelley, 2011). Single primary melt compositions for each location are shown as small symbols. The dotted black line is a standard linear regression through the average fO_2 and Ba/La data for MORB, all of the Northern Mariana Trough data, and the average fO_2 and Ba/La for the Southern Mariana Trough and each of the volcanic centers.

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 subducted sediments at this arc either (1) are not significantly oxidized relative to MOR source mantle, and/or (2) make up too small a proportion of the total primary melt to affect mantle fO_2 . The Northern Mariana Trough samples range from having no detectable subduction component to showing moderate influence from the subducting slab. Those samples from the Northern

Mariana Trough with higher Th/La ratios also have higher Ba/La ratios, 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 from that of the subduction components that reach the volcanic arc and may be neither a ‘sediment melt’ nor 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 a 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 a primary fO_2 that is slightly more oxidized than the Northern Mariana Trough (QFM + 0.5), with evidence for greater slab fluid influence (Ba/La ~ 16). Primary melts from NW Rota-1 have $fO_2 \sim$ QFM + 0.6, which is only slightly elevated relative to the Southern Mariana Trough primary fO_2 . NW Rota-1 also is 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 fO_2 from NW Rota-1 to Guguan (Ba/La ~ 48 , QFM + 1.6). A positive relationship between Ba/La ratio and fO_2 is also observed within single calculated primary melts at Pagan volcano ($R^2=0.77$), although their fO_2 values 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 fO_2 in the mantle wedge up to five times that of MOR primary fO_2 . Elevated slab fluid additions under the volcanic arc increase primary fO_2 up to \sim QFM + 1.6. These conclusions have several important implications for potential buffering assemblages in the mantle wedge and the fO_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 serpentinized prior to subduction (Ranero *et al.*, 2003; Ivandic *et al.*, 2008; Van Avendonk *et al.*, 2011; Savage, 2012) 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 (Schmidt & Poli, 1998; Hacker, 2008; 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_2O 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 $\sim 600^\circ C$ 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 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 fO_2 of primary melts under the back-arc, where subduction influence is lower than in 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 fO_2 for arc basalts, although the relationship between slab fluid influence (Ba/La) and primary fO_2 in Fig. 10c indicates that there are no buffering species present in the mantle wedge in this range of fO_2 . Sulfur speciation is shown to be highly sensitive to changes in fO_2 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 fO_2 until either the sulfur phase is exhausted or another, more oxidized phase is added (e.g. Fe_2O_3 ; Mungall, 2002). The complete conversion of S^{2-} to S^{6+} does not occur until QFM + 2 (Jugo *et al.*, 2010), about five times more

oxidized than the most oxidized primary melts calculated in this study. 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 fO_2 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 \pm clinopyroxene \pm plagioclase crystallization with simultaneous $CO_2 \pm H_2O \pm S$ 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 re-created by simple fractional crystallization of an 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 \pm plagioclase \pm clinopyroxene \pm magnetite crystallization with simultaneous $CO_2 + H_2O \pm S$ 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 fO_2 correlate between MORB, Mariana Trough, and arc samples, suggesting that fO_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 fO_2 values at both back-arc and arc volcanoes are elevated over the 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 MORB. Primary fO_2 correlates with slab fluid indices (Ba/La) from the back-arc to the arc, as well as between arc volcanic centers and between 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 owing 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 are necessary to test this hypothesis.

ACKNOWLEDGEMENTS

We are very grateful for thorough and thoughtful reviews from Carl Spandler, Ian Parkinson, Cyn-Ty Lee, and John MacLennan, which improved this paper significantly. Terry Plank and Yoshi Tamura generously shared sample material used in this study. Tony Lanzirotti and Sue Wirick assisted in all aspects of beamline operations and analysis related to the collection of μ -XANES data. Marion Lytle and Tim Rose shared their expertise in LA-ICP-MS and EPMA, respectively. We would like to thank the captain and crew of the R.V. *Thomas G. Thompson* for their efforts during the TN273 cruise. We are also very grateful to Robert Stern and Fernando Martinez for continued guidance and kindness, and for never hesitating to share their expertise.

FUNDING

Access to the National Synchrotron Light Source, Brookhaven National Laboratory was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. We acknowledge support from Smithsonian's Scholarly Studies Program (E.C.), NSF MARGINS-EAR-0841108 (K.A.K.), NSF OCE-0961559 (K.A.K.), and NSF MARGINS-EAR-0841006 (E.C.). NSF OCE-1258771 provides curatorial support for geological samples at the University of Rhode Island.

SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal of Petrology* online.

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