# Temporal evolution of mantle wedge oxygen fugacity during subduction initiation

Maryjo Brounce[1,2]*, Katherine A. Kelley[1], Elizabeth Cottrell[2], and Mark K. Reagan[3]
[1]Graduate School of Oceanography, University of Rhode Island, Narragansett Bay Campus, Narragansett, Rhode Island 02882, USA
[2]Department of Mineral Sciences, Smithsonian Institution, National Museum of Natural History, Washington, D.C. 20560, USA
[3]Department of Earth and Environmental Sciences, University of Iowa, Iowa City, Iowa 52242, USA

## ABSTRACT

**Arc basalts have a higher proportion of Fe in an oxidized state ($Fe^{3+}$) relative to $Fe^{2+}$ compared to mid-oceanic ridge basalts (MORBs), likely because slab-derived fluids oxidize the mantle wedge where subduction zone magmas originate. Yet, the time scales over which oxygen fugacity of the mantle wedge changes during subduction initiation and margin evolution are unknown. Fe speciation ratios show that magmas produced during the early stages of subduction in the Mariana arc record oxygen fugacities ~2× more oxidized than MORB. Mantle wedge oxygen fugacity rises by ~1.3 orders of magnitude as slab fluids become more involved in melt generation processes, reaching conditions essentially equivalent to the modern arc in just 2–4 m.y. These results constrain existing models for the geochemical evolution of the mantle wedge and suggest that oxidation commences upon subduction initiation and matures rapidly in the portions of the mantle wedge that produce melts. This further implies that sulfide or other reduced phases are not present in the mantle wedge in high enough abundance to prevent oxidation of the magmas that form upon subduction initiation. The arc mantle source is oxidized for the majority of a subduction zone's lifetime, influencing the mobility of multivalent elements during recycling, the degassing of oxidized volcanic volatiles, and the mechanisms for generating continental crust from the immediate onset of subduction.**

## INTRODUCTION

Oxygen fugacity ($f_{O_2}$) is an intrinsic thermodynamic property that records the chemical activity of oxygen and controls the speciation of multivalent elements in the solid Earth (e.g., Canil, 1997; Christie et al., 1986; Jugo et al., 2010; Kress and Carmichael, 1991; Wood et al., 1990). The ratios of oxidized to total Fe [$Fe^{3+}/(Fe^{3+} + Fe^{2+})$, expressed as $Fe^{3+}/\Sigma Fe$] in arc basalts are elevated relative to those in mid-oceanic ridge basalts (MORBs); this could arise due to shallow-level differentiation processes in the arc crust or to a difference in the $f_{O_2}$ of the mantle source (e.g., Lee et al., 2005, 2010, 2012; Kelley and Cottrell, 2009). Recent measurements of elevated $Fe^{3+}/\Sigma Fe$ ratios in unaltered basaltic samples from the modern Mariana arc suggest that oxidation during differentiation is negligible and that oxidized basalts reflect a mantle wedge $f_{O_2}$ that is elevated by up to 1.8 orders of magnitude relative to MORBs (Brounce et al., 2014; Cottrell and Kelley, 2011; Kelley and Cottrell, 2012), which is linked to the influence of aqueous fluids released from the oxidized subducting oceanic lithosphere on the mantle beneath arc volcanoes (Brounce et al., 2014; Kelley and Cottrell, 2009, 2012; Mungall, 2002; Parkinson and Arculus, 1999; Wood et al., 1990; Ballhaus, 1993; Frost and Ballhaus, 1998). The time scales and material flux required to oxidize the wedge have been modeled (Evans, 2012; Evans and Tomkins, 2011) but lack observational constraints, and thus the results of these models have large uncertainties. Here, we present the $Fe^{3+}/\Sigma Fe$ ratios of fresh submarine glasses that record the earliest stages of subduction along the Izu-Bonin-Mariana convergent margin. We compare these data to published $Fe^{3+}/\Sigma Fe$ ratios of submarine glasses and olivine-hosted melt inclusions from the modern Mariana arc and back-arc (Brounce et al., 2014) to determine time scales over which the Mariana mantle wedge became more oxidized than the MORB source. We also report $Fe^{3+}/\Sigma Fe$ ratios of fresh Pacific MORB glasses recovered from Ocean Drilling Program (ODP) Site 801 (ca. 170 Ma; Fig. 1A; Fisk and Kelley, 2002) as a reference showing the uniformity of MORB-source $f_{O_2}$ since the Jurassic.

## GEOLOGIC BACKGROUND AND METHODS

Mafic pillow lavas from the Izu-Bonin-Mariana forearc south of Guam, from Deep Sea Drilling Project (DSDP) Site 458 (central Mariana forearc), and from along the Bonin Ridge (Fig. 1A) record the initiation of subduction of the Pacific plate at 52–51 Ma and the subsequent temporal evolution of Izu-Bonin-Mariana arc volcanism (Ishizuka et al., 2011; Reagan et al., 2010, 2013). The volcanic section, from oldest to youngest, comprises forearc basalt pillow lavas (FABs; 49–52 Ma), early transitional boninite pillow lavas (49 Ma; Cosca et al., 1998), late transitional boninite pillow lavas (44 Ma), and "normal" arc lavas that overlap in age with boninites and extend to the present day (younger than 45 Ma; Fig. 1B). The FABs reflect decompression melting that occurred as mantle rose to accommodate the sinking of the Pacific plate at the immediate onset of subduction (Reagan et al., 2010). The lavas recovered from DSDP Site 458 have compositions from weakly subduction influenced and FAB-like at depth to strongly influenced by subduction further upsection (Reagan et al., 2010). The transitional boninites from the upper cores have compositions approaching those of the boninites from the Bonin Islands (48–46 Ma; Ishizuka et al., 2006).

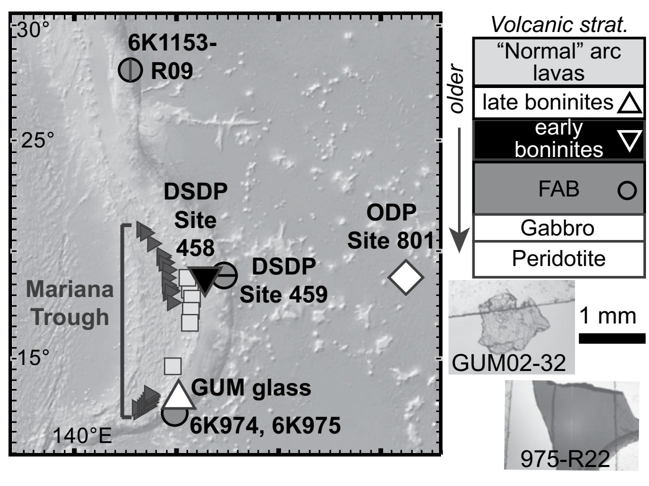


**Figure 1. A: Map of samples from this study. Individual symbols along Mariana arc (squares) and trough (triangles) show sample locations for modern (zero-age) samples. White circle is location of Ocean Drilling Program (ODP) Site 801, where pristine Jurassic-aged mid-oceanic ridge basalt (MORB) glass was recovered. Base map was created using GeoMapApp (www.geomapapp.org; Ryan et al., 2009). B: Schematic representation of forearc stratigraphy in Izu-Bonin-Mariana system. Photos are of typical samples, GUM02-32 (late boninite) and 975-R22 (FAB). DSDP—Deep Sea Drilling Project; GUM—Guam; strat.—stratigraphy; FAB—forearc basalt.**

*Current address: Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA

GEOLOGY, September 2015; v. 43; no. 9; p. 775–778 | Data Repository item 2015266 | doi:10.1130/G36742.1 | Published online 28 July 2015

Younger boninitic lavas, such as the ca. 44 Ma late transitional boninites from Guam, record the transition to normal arc lavas. Lavas with trace element compositions typical of the modern arc first erupted at ca. 45 Ma (Reagan et al., 2010). All samples included in this study were erupted in the submarine environment and have fresh glass along quench margins (Fig. 1B). We measured $Fe^{3+}/\Sigma Fe$ ratios (1σ of ±0.005) of five FAB, three boninite, and two ODP Site 801 MORB pillow glasses by micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy (see the GSA Data Repository[1]; Cottrell et al., 2009). Four early transitional boninite pillow glasses from DSDP Site 458 were too microcrystalline to obtain μ-XANES spectra free from crystal interference. For these samples, $Fe^{2+}O$ determinations were done using micro-colorimetric procedures and combined with bulk glass FeO* concentrations to calculate $Fe^{3+}/\Sigma Fe$ ratios (1σ of ±0.02; see the Data Repository; Carmichael, 2014; Wilson, 1960).

## Fe REDOX IN SAMPLES

MORB glasses from ODP Site 801 (ca. 170 Ma) have $Fe^{3+}/\Sigma Fe$ ratios of 0.167–0.168 and fall within the modern MORB field in major element composition (Fisk and Kelley, 2002) and Fe redox (Fig. 2). The FAB glasses have $Fe^{3+}/\Sigma Fe$ ratios that range from 0.165 (overlapping with MORB) to 0.195 (more oxidized than the observed range for MORB) and span a range in compositions from 7.56 to 2.75 wt% MgO (Fig. 2). Early transitional boninite glasses are more oxidized, with $Fe^{3+}/\Sigma Fe$ ratios that range from 0.249 to 0.202 at 7.56–4.56 wt% MgO, which overlap entirely with modern Mariana arc basalts and are up to 9% (absolute) more oxidized than MORB or Mariana trough glasses (Fig. 2). Late transitional boninite glasses have slightly lower $Fe^{3+}/\Sigma Fe$ ratios (0.210–0.220), consistent with the early transitional boninite glass with the lowest MgO content. From the MORB and Mariana trough fields shown in Figure 2, and the compositions of FAB glasses themselves, it is clear that typical amounts of low-pressure crystal fractionation in MORB can raise $Fe^{3+}/\Sigma Fe$ ratios by a few percent (absolute) at most (Brounce et al., 2014; Cottrell and Kelley, 2011). The elevated $Fe^{3+}/\Sigma Fe$ ratios of early and late transitional boninite glasses relative to FAB with similar MgO contents indicate that the $Fe^{3+}/\Sigma Fe$ ratios of the former cannot be generated by fractionation from the latter. We conclude that there were fundamental differences in the $f_{O_2}$ of the mantle sources that produced FAB and early and late transitional boninite magmas.

## DISCUSSION AND CONCLUSIONS

For all samples in this study, correcting for changes in magmatic $f_{O_2}$ due to crystal fractionation comes with large uncertainty because there are few glasses that remain pristine >40 m.y. after the time of eruption to define coherent liquid lines of descent. Magmatic differentiation may either reduce or oxidize magmas (Brounce et al., 2014; Cottrell and Kelley, 2011; Kelley and Cottrell, 2012) although comparisons between magmatic and primary magma $f_{O_2}$ for modern Mariana back-arc and arc samples differ by less than half of one order of magnitude (Brounce et al., 2014). We do not correct magmatic $f_{O_2}$ for differentiation, but provide an example correction in the Data Repository that demonstrates that this correction does not change our main conclusions. We use measured $Fe^{3+}/\Sigma Fe$ ratios and major element compositions to calculate magmatic $f_{O_2}$ relative to the quartz-fayalite-magnetite (QFM) buffer at pressures and temperatures used by Frost (1991), using the algorithm of Kress and Carmichael (1991; 1σ of ±0.5 log units), for all samples with MgO >4.5 wt% (see Table DR1 in the Data Repository). We pair magmatic $f_{O_2}$ (at 1200 °C, 1 atm) with measured Ba/La ratio in each sample to assess the influence that aqueous, slab-derived fluids have on wedge $f_{O_2}$ through time. Barium is mobilized in aqueous fluids preferentially over melt-mobile La, such that the ratio of Ba to La in erupted subduction-related lavas reflects the influence of slab-derived fluids in the mantle wedge in the Marianas (Brounce et al., 2014). During subduction initiation, the increasingly important role of slab-derived fluids in melt generation processes is recorded by an increase in Ba/La ratios from FAB to early and late transitional boninite lavas from the Mariana forearc.

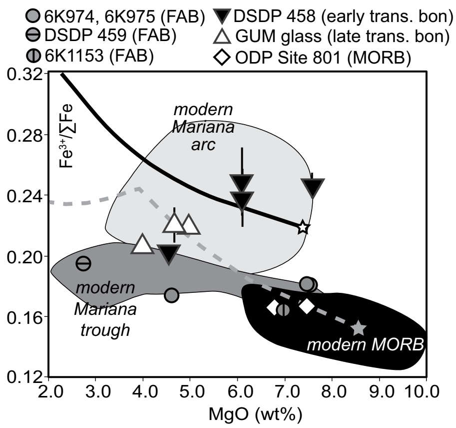


**Figure 2. Plot of $Fe^{3+}/\Sigma Fe$ ($\Sigma Fe = Fe^{3+} + Fe^{2+}$) ratios versus MgO for samples in this study. Black field represents global set of fresh mid-oceanic ridge basalt (MORB) glass (Cottrell and Kelley, 2011). Dark and light gray fields represent modern Mariana trough and arc (respectively) samples (Brounce et al., 2014). Black and gray lines are modeled liquid lines of descent (see the Data Repository [see footnote 1]) that demonstrate expected variation in Fe redox during crystal fractionation in a system closed to oxygen. Error bars represent standard deviation of replicate analyses, which are visible for some micro-colorimetric determinations. Error bars for X-ray absorption near-edge structure (XANES) measurements are smaller than symbol size (see the Data Repository [see footnote 1]). FAB—forearc basalt; DSDP—Deep Sea Drilling Project; GUM—Guam; ODP—Ocean Drilling Program; trans. bon—transitional boninite.**

MORBs from ODP Site 801 (ca. 170 Ma) have Ba/La ratios that range from 3.8 to 4.5 and $f_{O_2}$ of ~QFM + 0.3, similar to modern MORB. This indicates that there has been no change in the $f_{O_2}$ of MORB source from the Jurassic to the present day (Fig. 3A). FAB glasses have Ba/La ratios that range from 4.3 to 10.3 and $f_{O_2}$ from QFM + 0.3 to QFM + 0.6, values that overlap MORB at the low end but extend to slightly higher Ba/La ratios and $f_{O_2}$. This suggests that FAB melts are generated mainly by decompression melting, but that there are also small additions from the subducted slab at the immediate onset of subduction in the Marianas (Figs. 3A and 3B). Early transitional boninites have high Ba/La ratios (24–39) and $f_{O_2}$ (QFM + 1.0 to QFM + 1.5) that demonstrate that within 1–4 m.y. of FAB eruption, slab fluids play a significant role in melt generation processes and are capable of producing melts with $f_{O_2}$ of QFM + ~1.3, which are as oxidized as lavas erupted at the modern Mariana arc. Late transitional boninites have Ba/La ratios and $f_{O_2}$ (19–26, ~QFM + 1.0) that are consistent with those of early transitional boninite melts. The same relationship that exists in the modern Mariana system between slab fluids and oxidation is observed within 2–3 m.y. of subduction initiation, specifically that melts reflecting greater additions of slab fluids to the region of melt generation are more oxidized than those with small, or no, evidence for slab fluids (Fig. 3A).

A positive correlation between Ba/La ratio and magmatic $f_{O_2}$ from the modern Mariana back-arc to the arc (dark and light gray fields in Fig. 3A) links oxidation of back-arc and arc basalts to slab-fluid influence (Brounce et al., 2014; Kelley and Cottrell, 2009). The new observations presented here suggest that the oxidized nature of subduction zone magmas is linked intimately with subduction itself, requiring that slab fluids play an important role in oxidizing the portion of the mantle wedge that produces arc magmas from the very onset of subduction. We speculate that slab fluids have some oxidizing capacity and that the relationship between melt oxidation and slab-fluid proxies reflects the mass of fluid implicated in generating melts from mantle that, prior to infiltration by slab fluids, has $f_{O_2}$ similar to ambient upper mantle (~QFM). Late transitional boninites have lower magmatic $f_{O_2}$ than early transitional boninites and also have lower Ba/La ratios. This suggests that, in between the time of eruption of the early and the late transitional boninites, there was a change in (1) the composition of the slab fluid, (2) the ratio of fluid to mantle involved in melt

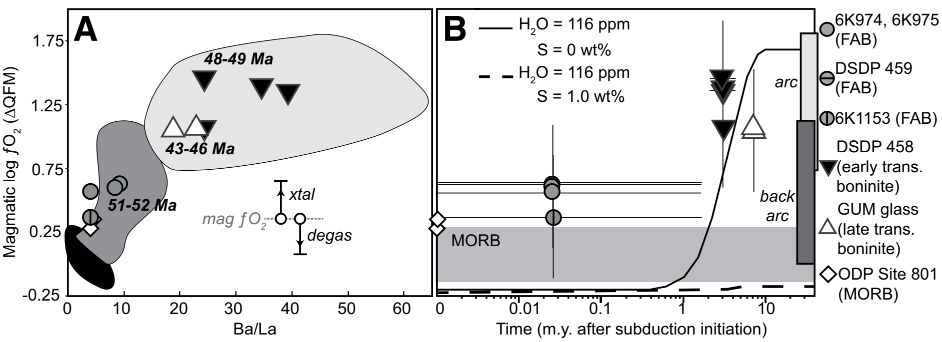


**Figure 3. Magmatic oxygen fugacity ($f_{O_2}$) relative to quartz-fayalite-magnetite (QFM) oxygen buffer versus Ba/La ratio (A) and time (millions of years) since subduction initiation (B). Data fields are magmatic $f_{O_2}$ calculated from measured glass compositions of mid-oceanic ridge basalt (MORB; black), Mariana trough (dark gray), and Mariana arc (light gray) volcanic glasses. White circles with error bars in A demonstrate approximate magnitude of uncertainty that accompanies minor effects of crystallization ("xtal") and degassing ("degas") (mag—magmatic; see the Data Repository [see footnote 1]). Horizontal error bars on individual symbols in B represent uncertainties in sample age (note log scale). Vertical error bars represent uncertainty in calibration for calculating $f_{O_2}$. Heavy solid and dashed black lines in B are redox budget models for Phanerozoic mantle (Evans and Tomkins, 2011). FAB—forearc basalt; DSDP—Deep Sea Drilling Project; GUM—Guam; ODP—Ocean Drilling Program; trans.—transitional.**

generation, or (3) both, leading to variably enriched Ba/La ratios in magmas. Therefore, Ba/La ratios need not necessarily increase through time, beyond the first-order transition from decompression-dominated melt generation (FAB) and fluid-induced melt generation (early and late transitional boninites, modern arc). Oxidation also need not increase through time (i.e., $f_{O_2}$ of FAB < early boninites < late boninites < modern arc), because mantle with $f_{O_2}$ ~QFM is continually flowing into the mantle wedge in response to subducting plate motions, and this replenishment may eventually balance oxidation from fluid addition as the system reaches a steady state between wedge and fluid flow.

Recent studies have calculated "redox budgets", or fluxes for multivalent elements in subduction systems, by comparing the average oxidation state and rate of input of downgoing materials (altered oceanic lithosphere + sediments) to the bulk oxidation state and rate of output of erupted arc lavas (Evans, 2012; Evans and Tomkins, 2011). For example, in Phanerozoic mantle, these models predict a range of outcomes, from a mantle wedge that does not oxidize on 10 m.y. time scales, to a three-orders-of -magnitude increase in $f_{O_2}$ over QFM (the $f_{O_2}$ of MORB source mantle; Cottrell and Kelley, 2011) on 10,000 yr time scales (Evans, 2012; Evans and Tomkins, 2011). A key variable that controls the rate of mantle wedge oxidation in these models is the sulfide content of the wedge, with the assumption that sulfide must be oxidized to sulfate before the wedge can produce magmas with $f_{O_2}$ greater than sulfide stability (~QFM, in Evans and Tomkins, 2011). Our study demonstrates that oxidation of the mantle wedge occurs early in the lifetime of a subduction system and that either the volume of the wedge that produces slab-influenced magmas does not have enough sulfide to delay the production of oxidized magmas, or model assumptions are incorrect.

The short time scales of slab material transfer and subsequent oxidation of the zone of melt generation in the mantle wedge that we have constrained here (14× increase in $f_{O_2}$ in 2–4 m.y.) have implications for the lifetime of redox-sensitive volcanic processes during subduction. The $^{238}U$-$^{230}Th$ systematics (Elliott et al., 1997) and $^{226}Ra$-$^{230}Th$ disequilibrium (Turner et al., 2001) in Mariana arc lavas show that fluids move rapidly from the slab surface, with <8,000–30,000 yr between the eruption of an arc magma and the slab dehydration that fueled its formation in the wedge. We further show that the arrival of slab-derived fluids in the wedge, and the melting that accompanies it, coincide with the production of oxidized magmas. Using estimated convergence rates just after subduction initiation of 2–3 cm $yr^{-1}$ (Hall et al., 2003), in the 1–4 m.y. between the eruption of FAB and early transitional boninites, the slab subducted an additional 12–70 km depth in the mantle, assuming a slab dip of 30°. The deep end of this range approaches pressure-temperature conditions that are analogous to those of the slab in the modern Mariana subduction system (even without considering that the slab surface must have already submerged to some depth in the mantle during the eruption of FAB), enabling the transfer of slab fluids broadly similar in composition into the mantle wedge. This may signal the start of true down-dip subduction, such that the next magmas to erupt, the late transitional boninites, show a similar relationship between slab-fluid influence (e.g., Ba/La) and oxidation as the modern subduction system.

The very rapid evolution to oxidized conditions in the Mariana subduction system suggests that subduction zone processes that depend upon oxidized mantle and magmas are likely to be active for the entire lifetime of a subduction zone. If $f_{O_2}$ plays a role in producing calc-alkaline differentiation trends (Osborn, 1959; Brounce et al., 2014), then these results suggest that the production of Fe-depleted continental crust is possible soon after the start of subduction. Elevated magmatic $f_{O_2}$ also leads to the release of oxidized volcanic gases to the atmosphere (e.g., $H_2O$, $CO_2$, $SO_2$; Heald et al., 1963), linking plate-tectonic cycling to the evolution of Earth's atmospheric composition through time.


## ACKNOWLEDGMENTS

We thank C.T.A. Lee, F. Gaillard, and one anonymous reviewer for their constructive reviews of this manuscript. We are grateful for guidance from R. Lange during wet chemical procedures. We thank A. Lanzirotti, S. Wirick, and W. Rao for assistance in beamline operations at the National Synchrotron Light Source (NSLS, Brookhaven National Laboratory, Upton, New York, USA). M. Lytle, S. Grocke, F. Davis, T. Rose, and T. Gooding provided valuable assistance and expertise. Access to NSLS was supported by the U.S. Department of Energy under contract DE-AC02-98CH10886. We acknowledge support from the Smithsonian Institution's Scholarly Studies Program (Cottrell), National Science Foundation (NSF) grant MARGINS-EAR-0841108 (Kelley), NSF grant MARGINS-EAR-0841006 (Cottrell), and grant NSF MARGINS-EAR-0840862 (Reagan). NSF grant OCE-0644625 provides curatorial support for marine geological samples at the University of Rhode Island, USA.


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Manuscript received 21 February 2015
Revised manuscript received 14 June 2015
Manuscript accepted 15 June 2015

Printed in USA