Water and the Oxidation State of Subduction Zone Magmas

Katherine A. Kelley and Elizabeth Cottrell

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Hydrated oxidized oceanic crust is returned to the mantle at subduction zone

- Many evidence point to oxidizing conditions in arc peridotites and magmas, but a quantitative link between oxidation state and the subduction process has not been established
- The ratio of oxidized iron to total iron (Fe^{3+}/ΣFe) in primary, mantle-derived basaltic melts reflects mantle oxygen fugacity.
- Interpretation of bulk measurements of Fe^{3+}/ΣFe rations in lavas (wet chemistry or Mossbauer spectroscopy) can be complicated because many rock samples, even at small scales, are mixture of crystals and glass that may not represent true magmatic liquids

In this study,

- The authors use a high-spatial resolution method (Fe K-edge μ-XANES spectroscopy) to determine iron oxidation states of glasses from a suite of valcanic rocks.
- in order to determine the current oxidation condition of the mantle as a function of tectonic regime.

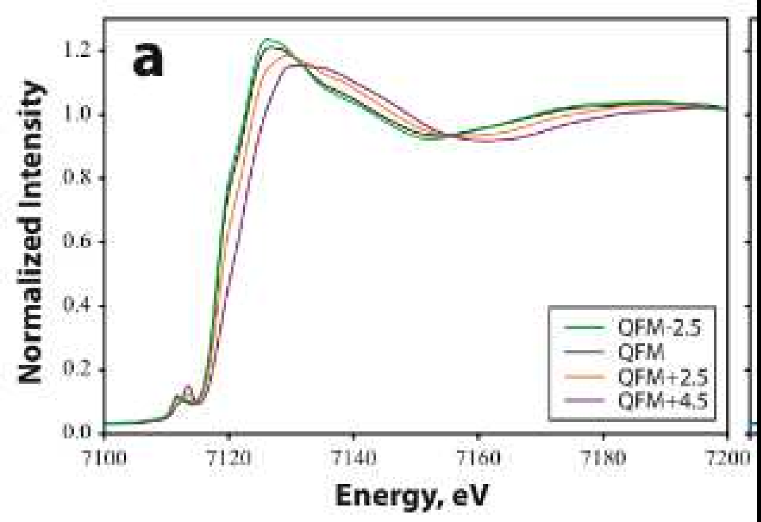
XANES spectroscopy

- X-ray Absorption Spectroscopy (XAS)
- XAS is based on the absorption of X-ray by substances present in a sample and subsequent promotion of electrons from one energy level to another in that substance.
- Absorption edge occurs when the energy of the incident photons is just sufficient to cause excitation of a core electron of the absorbing atom to a continuum state.
- The spectral region near a core excitation (near-edge region) is usually called XANES (X-ray Absorption Near-Edge Structure).
- Fe K-edge XANES (spectroscopy)
  - is sensitive to the oxidation state and coordination geometry.
  - has micrometre spatial resolution
  - is non-destructive
  - requires no sample preparation other than a polished surface
  - can be applicable to oxidation state determination of small size of melt inclusion ($< 50\ \mu$m)
- Oxidation state in glasses can be determined with great accuracy and precision, by preparing a series of standards as a function of oxygen fugacity.

Preparation of glass standards

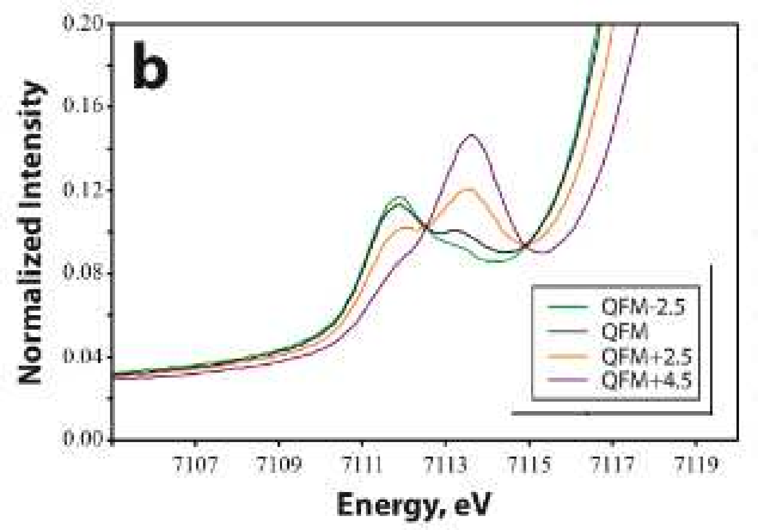
- Preparing a series of standards as a function of oxygen fugacity allows $Fe^{3+}/\Sigma Fe$ to be systematically varied.
  - $Fe^{3+}/\Sigma Fe = Fe^{3+}/(Fe^{2+}+Fe^{3+})$
  - Oxidised; $Fe^{3+}/\Sigma Fe \rightarrow 1$, Reduced; $Fe^{3+}/\Sigma Fe \rightarrow 0$
- Synthetic glass standards were prepared by equilibrating natural basalt powders at 1 atm over a range of oxygen fugacities, between -3.5 and +4.5 log units relative to the quartz-fayalite-magnetite (QFM) buffer.
- The $Fe^{3+}/\Sigma Fe$ ratio of each glass is determined by Mossbauer spectroscopy.

XANES spectra for reference glasses



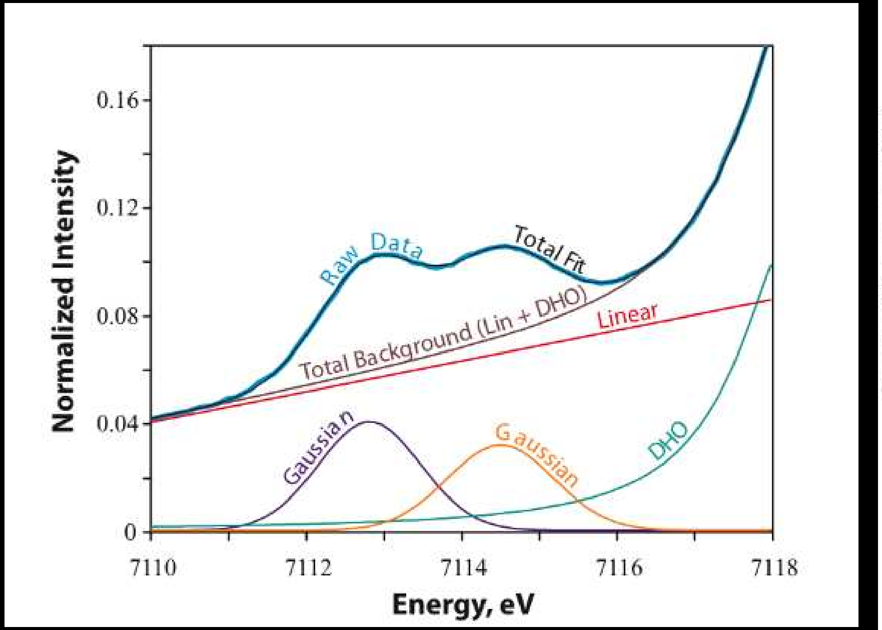
- The spectra comprises an absorption edge and a pre-edge feature.
- The absorption edge is due to the electron excitation from the core level (K shell) to a continuum state, i.e. to produce a photoelectron.
- The features in the pre-edge region are due to the electron transitions from the core level (1s) to the higher unfilled or half-filled orbitals (3d).
- This feature comprises transitions to the crystal field levels of Fe^{2+} and Fe^{3+} in the various coordination environments present in glass.

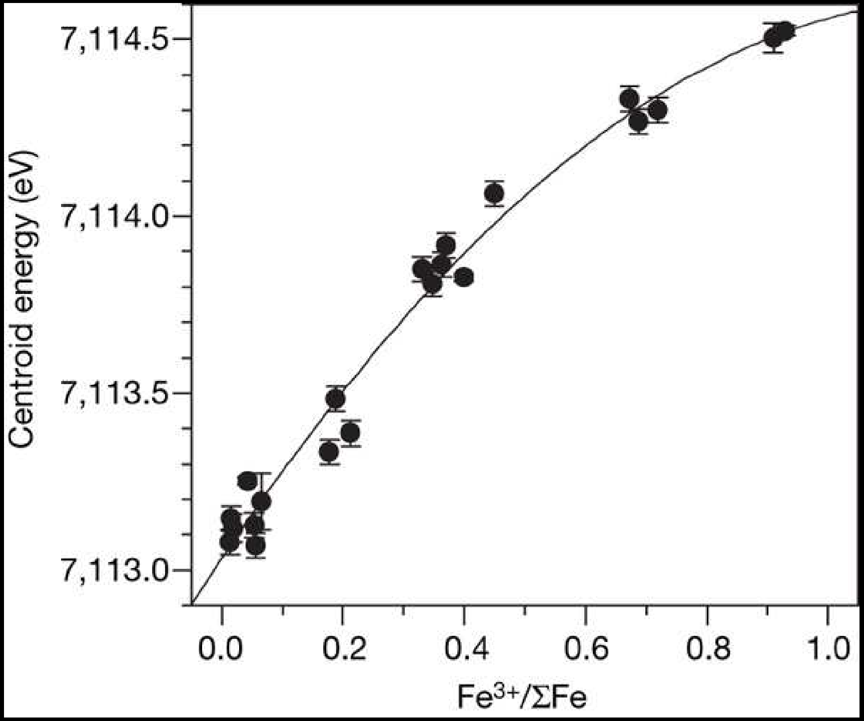
Pre-edge region of Fe K-edge XANES spectra



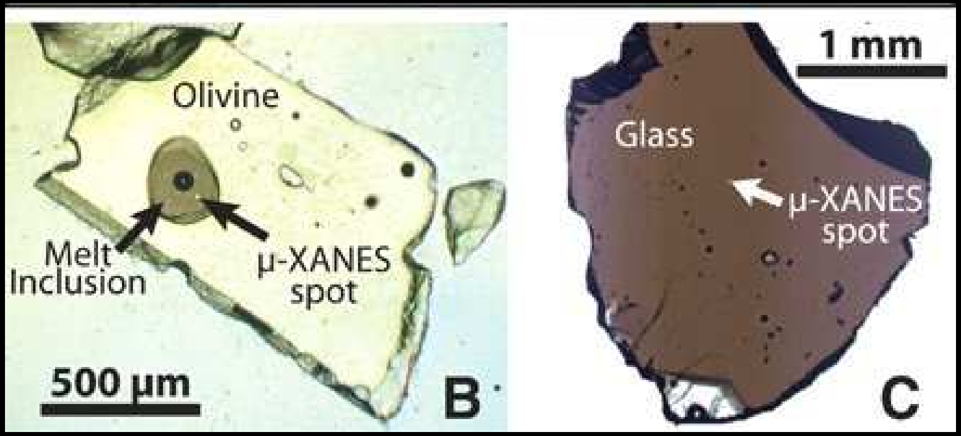
- The pre-edges show a structure consisting of two overlapping peaks separated by ca. 2 eV.
- The peak around 7114 eV increse with increasing oxygen fugacity (Fe^{3+}/ΣFe)
- The peak around 7112 eV decrease with increasing oxygen fugacity (Fe^{3+}/ΣFe)
- The pre-edge centroid position depends strongly on the Fe oxidation state.
- This allows to construct an emprical calibration curve of “pre-edge peak energy” vs. “Fe^{3+}/ΣFe”.

Example fit of pre-edge region





Analysed samples represent melts from a range of tectonic settings

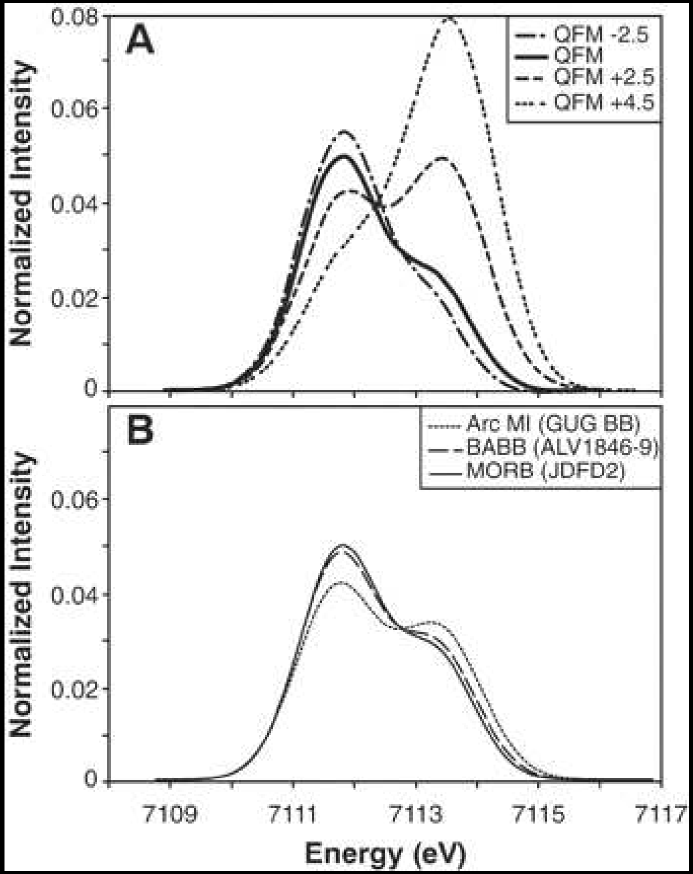


- Melts may be oxidized by crustal assimilation, crystallization, or degassing during ascent.
- Lavas erupted on land also extensively degas, which alters their primary $Fe^{3+}/\Sigma Fe$ ratios.
- Submarine pillow rim glasses and melt inclusions can preserve primitive, minimally degassed magmatic liquids.

In this study, the authors use

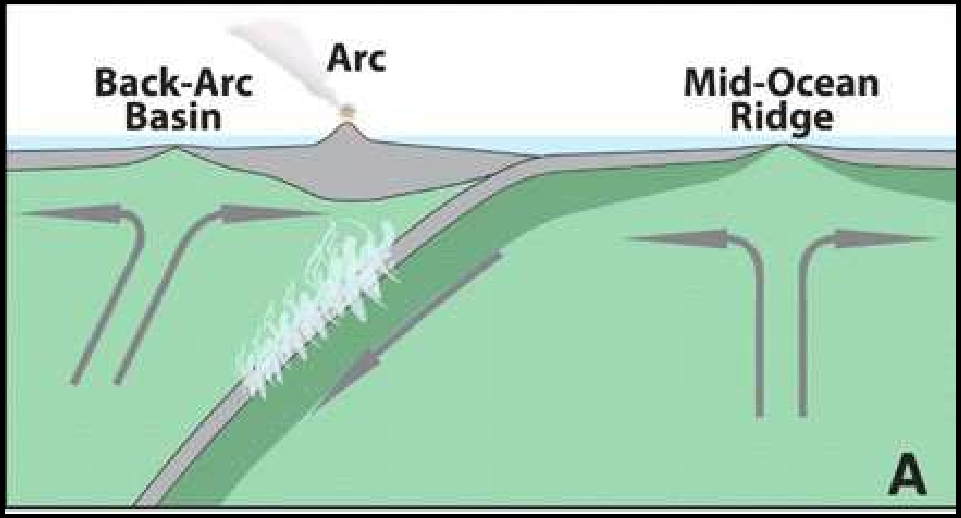
- global submarine pillow-rim glasses from primitive mid-ocean ridge basalts (MORBs) and Mariana Trough back-arc basin basalts (BABBs)
- basaltic olivine-hosted melt inclusions from one MORB and a global suite of arc volcanoes

Baseline-subtracted μ-XANES spectra



- (A) Spectra for reference glasses, equilibrated at QFM-2.5, QFM, QFM+2.5, and QFM+4.5.
- (B) Spectra for natural samples, including a MORB glass, a BABB glass, and an arc melt inclusion.

Result of XANES spectral analysis



- Based on μ-XANES spectral analysis, the Fe^{3+}/ΣFe ratio increases from the MORB (0.13 to 0.17) to BABB (0.15 to 0.19) to arc samples (0.18 to 0.32)
- This means that arc magmas are more oxidized than MORBs and BABBs

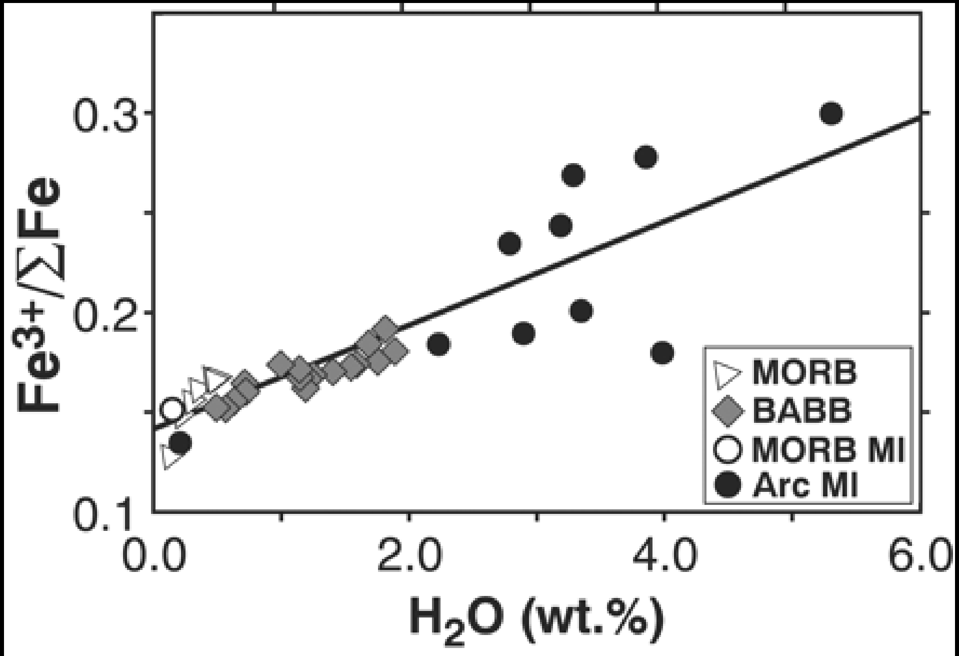
H_2O content

Pre-eruptive magmatic concentration of volatiles (such as H_2O) are also known to vary with tectonic setting, and specifically to increase at subduction zones.

- New measurements of the dissolved H_2O, CO_2, and S concentrations of basaltic glasses were also conducted, either
  - by ion microprobe
  - by FTIR spectroscopy and electron microprobe

These results show that magmatic H_2O content increases from MORBs (0.14 to 0.49 wt%) to BABBs (0.57 to 1.89 wt%) to arcs (2.23 to 5.39 wt%).

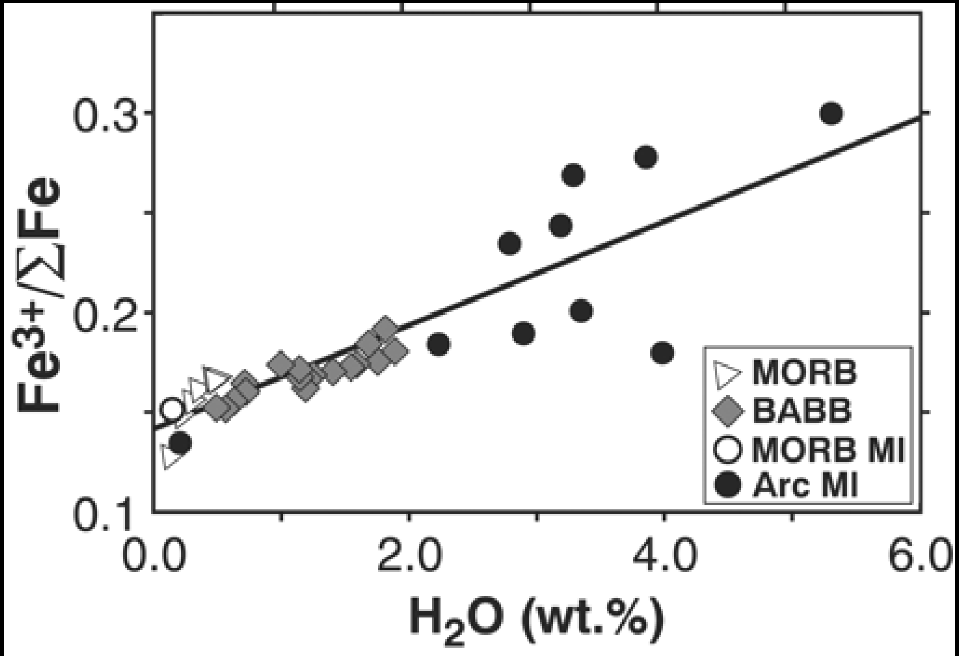
Plot of measured H_2O contents versus $Fe^{3+}/\Sigma Fe$



The oxidation state of Fe in the basaltic melts increases linearly with magmatic H_2O contents

- Shallow magmatic processes could cause linear correlations between $Fe^{3+}/\Sigma Fe$ ratios and H_2O concentrations that are unrelated to the properties of the mantle source

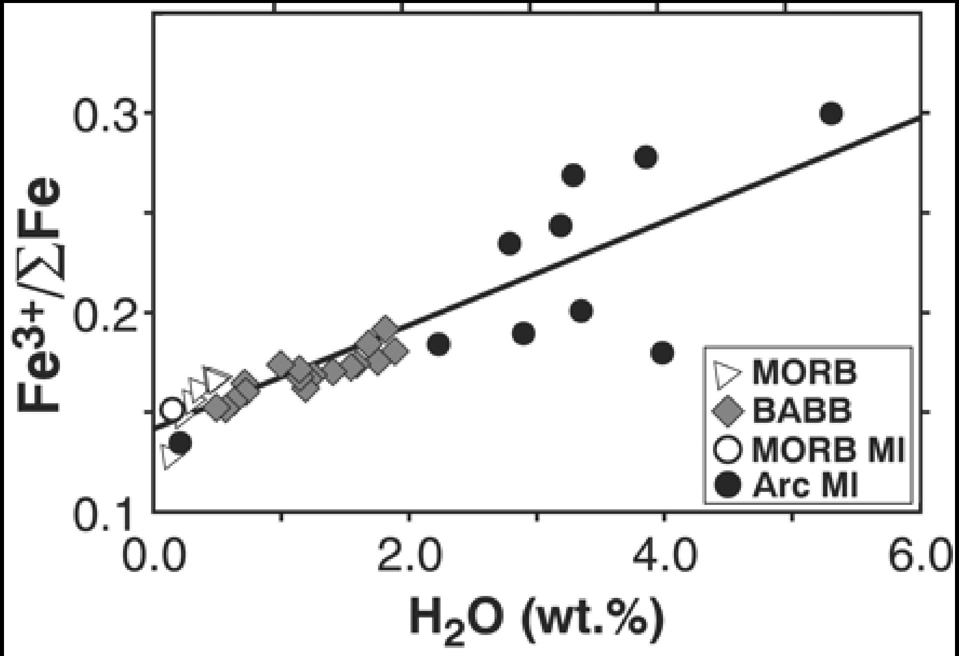
Influence of shallow magmatic processes: Degassing



Melt oxidation could occur through losses of some S species (such as H_2S) and H_2 driven by degassing or diffusion

- But this would create an inverse relation between volatile content and Fe^{3+}/ΣFe ratio
- Also glasses showing evidence of H_2O degassing are excluded

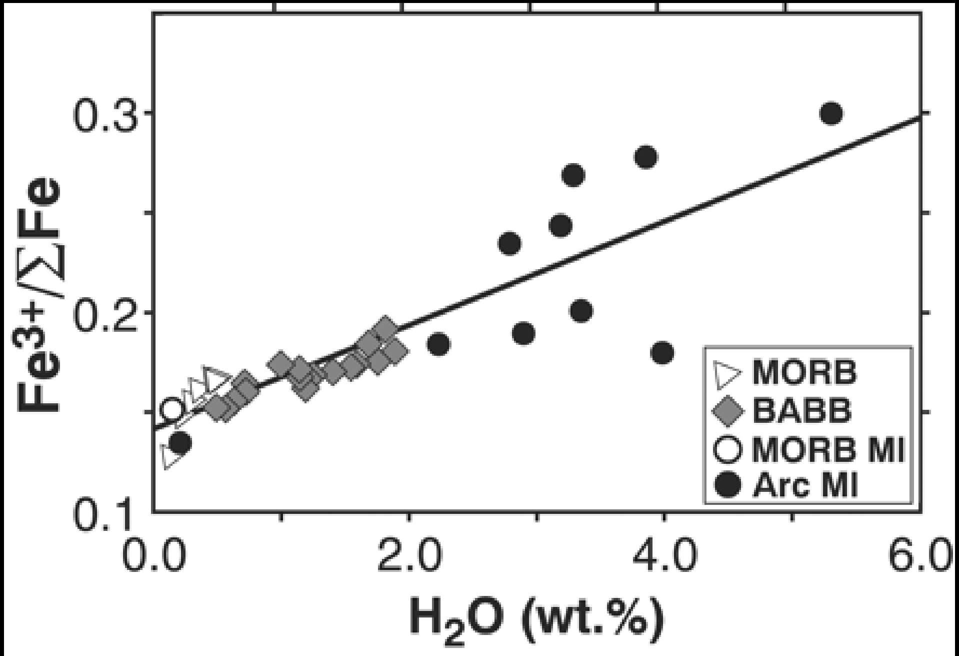
Influence of shallow magmatic processes: Fractional crystallization



Small increase in $Fe^{3+}/\Sigma Fe$ ratios and H_2O contents are expected because Fe^{3+} and H_2O are incompatible in early-crystallizing olivine, whereas Fe^{2+} is compatible

- The trajectories of $Fe^{3+}/\Sigma Fe$ and H_2O content relative to MgO content indicate that olivine fractional crystallization cannot explain the observed relation between Fe oxidation state and H2O in BABBs and arc glasses.

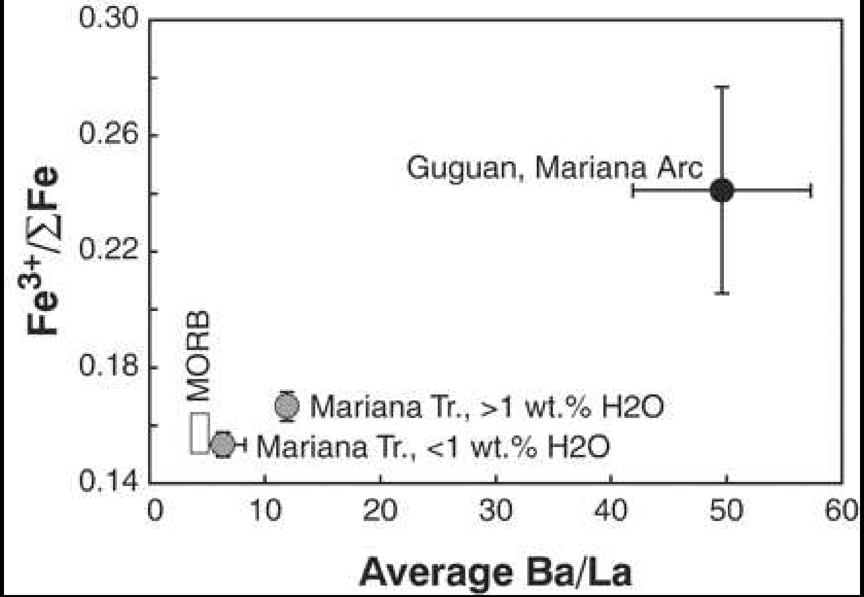
Influence of melt inclusion-specific process



The melt inclusion samples could have been modified by post-entrapment crystallization of olivine or diffusive loss of Fe^{2+}.

- Both of these processes can be detected, and the compositions can be corrected through analysis of melt compositions relative to their olivine hosts.
- On average, post-entrapment corrections resulted in $<$8% change in Fe^{3+}/ΣFe.
- The processes specific to melt inclusion are not the primary cause of the trend

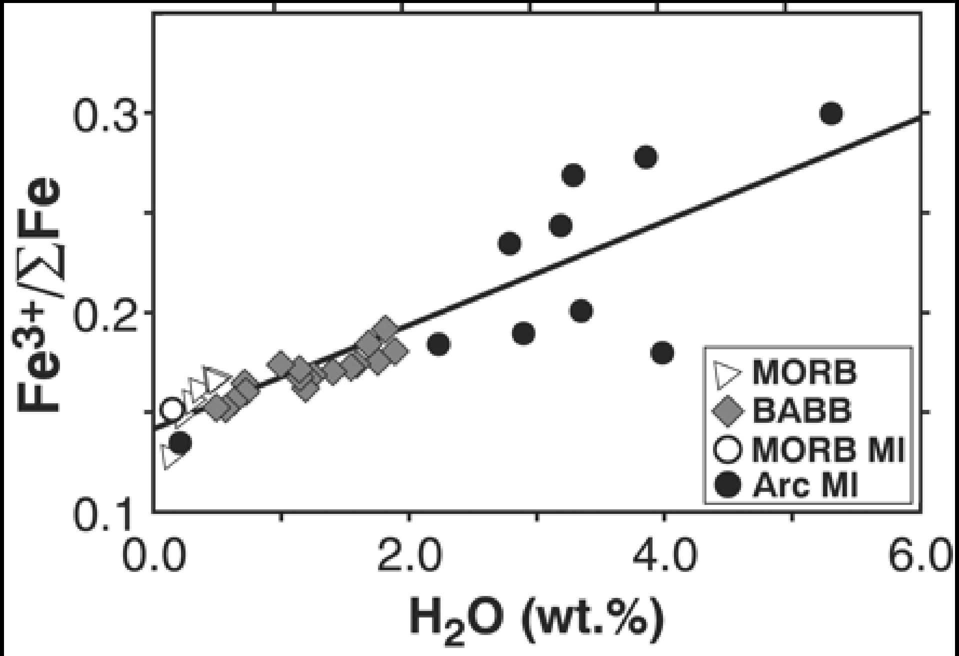
Plot of average Ba/La versus measured $Fe^{3+}/\Sigma Fe$ for MORBs, BABB and arc basalts



- The ratio of Ba (fluid mobile) to La (fluid-immobile) is a proxy for the influence of slab-derived fluid
- Because the Ba/La ratio is minimally influenced by magmatic processes, it is considered a true reflection of the mantle source

- In the basalt samples from the Mariana arc and back-arc basin, Ba/La ratios of lavas progressively increase with increasing $Fe^{3+}/\Sigma Fe$ ratios
- Covariation of the Ba/La ratio with $Fe^{3+}/\Sigma Fe$ thus suggests that oxidation is direcly related to the addition of H_2O from the subducted slab

Melt oxidation is linked to the mantle source



- The observed trend indicates the magnitude of magmatic oxidation associated with the addition of fluids from the subducted slab
- $Fe^{3+}/\Sigma Fe$ increases on average by 0.026 with each weight% increase in magmatic H_2O

Water may not act as an efficient oxidizing agent in Earth's upper mantle

- Magmatic oxidation due to loss of H2 may be responsible for oxidizing basalt pillow cores at low pressure, but whether H2O can dissociate to liberate H2 in the mantle wedge remains controversial
- Direct transport of Fe^{3+} could oxidize the mantle wedge of subduction zones.
  - Dilute aqueous fluids are inefficient carriers of Fe^{3+}, but as slab-derived components become more acidic, more saline, or more melt like Fe^{3+} may become highly mobile.
- Alternatively, fluid-mobile elements such as S could oxidize the mantle wedge of subduction zones without requiring direct transport of Fe^{3+}.
  - Sulfur reduction will take place provided that the oxygen fugacity of the mantle wedge remains below the sulfur-sulfur oxide buffer, or approximately QFM+2.

Summary

- This study present integrated measurements of redox-sensitive ratios of oxidized iron to total iron ($Fe^{3+}/\Sigma Fe$), determined with Fe K-edge μ-XANES spectroscopy, and pre-eruptive magmatic H_2O contents of a global sampling of primitive undegassed basaltic glasses and melt inclusions covering a range of plate tectonic settings.
- Magmatic $Fe^{3+}/\Sigma Fe$ ratios increase toward subduction zones (at ridges, 0.13 to 0.17; at back arcs, 0.15 to 0.19; and at arcs, 0.18 to 0.32) and correlate linearly with H_2O content and element tracers of slab-derived fluids.
- These observations indicate a direct link between mass transfer from the subducted plate and oxidation of the mantle wedge.