Water and the Oxidation State of Subduction Zone Magmas

Katherine A. Kelley and Elizabeth Cottrell

Science 325, 605 (31 JULY 2009)
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 ($\text{Fe}^{3+}/\Sigma\text{Fe}$) in primary, mantle-derived basaltic melts reflects mantle oxygen fugacity.
- Interpretation of bulk measurements of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios 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 $\mu$-XANES spectroscopy) to determine iron oxidation states of glasses from a suite of volcanic 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 µm)

- 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 $\text{Fe}^{3+}/\Sigma\text{Fe}$ to be systematically varied.
  - $\text{Fe}^{3+}/\Sigma\text{Fe} = \text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$
  - Oxidised; $\text{Fe}^{3+}/\Sigma\text{Fe} \to 1$, Reduced; $\text{Fe}^{3+}/\Sigma\text{Fe} \to 0$

- 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 $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of each glass is determined by Mossbauer spectroscopy.
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.
The pre-edges show a structure consisting of two overlapping peaks separated by ca. 2 eV.

The peak around 7114 eV increase with increasing oxygen fugacity \( \text{Fe}^{3+}/\Sigma \text{Fe} \).

The peak around 7112 eV decrease with increasing oxygen fugacity \( \text{Fe}^{3+}/\Sigma \text{Fe} \).

The pre-edge centroid position depends strongly on the Fe oxidation state.

This allows to construct an empirical calibration curve of “pre-edge peak energy” vs. “\( \text{Fe}^{3+}/\Sigma \text{Fe} \)”.
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 $\mu$-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.
Based on $\mu$-XANES spectral analysis, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ 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
Pre-eruptive magmatic concentration of volatiles (such as H₂O) are also known to vary with tectonic setting, and specifically to increase at subduction zones.

- New measurements of the dissolved H₂O, CO₂, and S concentrations of basaltic glasses were also conducted, either
  - by ion microprobe
  - by FTIR spectroscopy and electron microprobe

These results show that magmatic H₂O 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%).
The oxidation state of Fe in the basaltic melts increases linearly with magmatic H$_2$O contents

- Shallow magmatic processes could cause linear correlations between Fe$^{3+}$/ΣFe ratios and H$_2$O concentrations that are unrelated to the properties of the mantle source.
Melt oxidation could occur through losses of some S species (such as H$_2$S) 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$_2$O degassing are excluded
Influence of shallow magmatic processes: Fractional crystallization

Small increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and $\text{H}_2\text{O}$ contents are expected because $\text{Fe}^{3+}$ and $\text{H}_2\text{O}$ are incompatible in early-crystallizing olivine, whereas $\text{Fe}^{2+}$ is compatible.

- The trajectories of $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $\text{H}_2\text{O}$ content relative to $\text{MgO}$ content indicate that olivine fractional crystallization cannot explain the observed relation between $\text{Fe}$ oxidation state and $\text{H}_2\text{O}$ 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.
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 directly related to the addition of H\(_2\)O from the subducted slab.
The observed trend indicates the magnitude of magmatic oxidation associated with the addition of fluids from the subducted slab.

- $\text{Fe}^{3+}/\Sigma\text{Fe}$ increases on average by 0.026 with each weight% increase in magmatic H$_2$O.
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 presents integrated measurements of redox-sensitive ratios of oxidized iron to total iron ($\text{Fe}^{3+}/\Sigma\text{Fe}$), determined with Fe K-edge $\mu$-XANES spectroscopy, and pre-eruptive magmatic $\text{H}_2\text{O}$ contents of a global sampling of primitive undegassed basaltic glasses and melt inclusions covering a range of plate tectonic settings.

- Magmatic $\text{Fe}^{3+}/\Sigma\text{Fe}$ 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 $\text{H}_2\text{O}$ 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.