

**OXIDATION STATES OF FE IN SILICATE MELTS AS A FUNCTION OF PRESSURE AND IMPLICATIONS FOR REDOX EVOLUTION OF THE EARLY MANTLE.** K. Armstrong,<sup>1</sup> D.J. Frost<sup>1</sup>, C.M. McCammon<sup>1</sup>, D. Rubie<sup>1</sup>, and T. Boffa-Ballaran<sup>1</sup> <sup>1</sup>Bayerisches Geoinstitut, University of Bayreuth, Universitätsstrasse 30, Bayreuth, D-95447 Germany. katherine.armstrong@uni-bayreuth.de

**Introduction:** Siderophile elements are depleted in the Earth's mantle, indicating that during differentiation, mantle silicates reacted with iron metal. Presently, the uppermost mantle is 4-5 log units more oxidized than it would be if it were in equilibrium with iron, and studies of ancient rocks suggest that this more oxidized state was attained by 3.9 Ga [1]. The mechanism by which the mantle was oxidized is unclear, but has implications for the timing of accretion, differentiation, and volatile delivery to the early Earth, as well as evolution of the early atmosphere.

It has been well established that during the late stages of accretion, planetesimals would have impacted the early Earth with sufficient energy to create a global magma ocean (e.g., [2]). If a magma ocean is chemically homogenous,  $\text{Fe}^{3+} / \sum \text{Fe}$  in the magma ocean would be governed by depth-dependent metal-silicate equilibrium ([3] and references therein). Metal would sink through the magma ocean and final equilibration should occur at the base. At shallow pressures silicate melts in equilibrium with liquid metal contain practically no  $\text{Fe}^{3+}$ . However it is possible that silicate melts, like many silicate minerals start to favour the formation of  $\text{Fe}^{3+}$  over  $\text{Fe}^{2+}$  at high pressure [3]. For example, even at equilibrium with metallic iron, the lower mantle mineral bridgmanite contains significant  $\text{Fe}^{3+}$  [4]. Although this results from an energetically favourable coupled substitution of  $\text{Fe}^{3+}$  and Al in the bridgmanite crystal structure, it is possible that pressure similarly stabilizes the  $\text{Fe}_2\text{O}_3$  component in silicate melts;  $\text{Fe}^{3+}$  in garnet coexisting with iron metal also increases with increasing pressure, with no coupled substitution.

If the same behaviour occurs in melts, a large magma ocean would experience a redox gradient, where the top would be at a much higher relative oxygen fugacity compared to the base ([3] and references therein). Sinking magma would at some depth precipitate metallic iron, forming ferric from ferrous iron; if the iron metal produced separated to the core continuous oxidation of the mantle would occur. Crystallisation of this magma ocean would produce an oxygen fugacity gradient similar to that in the Earth's mantle today.

Existing experimental results on redox equilibria in silicate melts are restricted to low pressures (<5 GPa). Up to this pressure, the  $\text{Fe}^{3+} / \sum \text{Fe}$  ratio of a silicate melt in equilibrium with Ru-RuO<sub>2</sub> decreases with pressure [5], thus precluding disproportionation with in-

creasing depth up to these pressures. However, magma oceans in the early Earth are believed to have extended to pressures of several 10s of GPa, and it is entirely possible that the observed trend is reversed at high pressure.

Here we report the results of high pressure experiments which show a flattening of the trend previously reported at lower pressures [5]. This may indicate that at even higher pressures the  $f\text{O}_2$  of a silicate melt with a fixed  $\text{Fe}^{3+} / \sum \text{Fe}$  ratio may start to decrease relative to the Ru-RuO<sub>2</sub> buffer and at some depth reach metallic iron saturation.

**Experimental Methods:** Starting material of andesitic bulk composition was prepared from reagent grade oxides and carbonates ground under ethanol in an agate mortar and pestle after [5]. (In wt%: SiO<sub>2</sub> – 57.3, TiO<sub>2</sub> – 3.0, Al<sub>2</sub>O<sub>3</sub> – 14.8, Fe<sub>2</sub>O<sub>3</sub> – 9.4, MgO – 2.1, CaO – 7.4, Na<sub>2</sub>O – 4.4, and K<sub>2</sub>O – 1.1.) Oxides were fired at 1000°C for three hours to ensure dryness before weighing, and bulk composition was further devolatilized and decarbonated after preparation by slowly raising the temperature to 1000°C and baking for 12 hours.

The powder was sealed in 2.0 mm outer diameter welded Pt capsules. One experiment was equilibrated at 17 GPa and 2100°C for one hour in a 5000 tonne multianvil press, and another at 10 GPa and 1900°C for 30 minutes in a 1200 tonne multianvil press. Both used a 10 mm edge length Cr<sub>2</sub>O<sub>3</sub>-doped MgO octahedron and WC cubes with 11 mm edge length truncations. Temperature was monitored with a W97Re3 – W75Re25 (type D) thermocouple. The  $f\text{O}_2$  was buffered by the addition of ~20 wt% Ru + RuO<sub>2</sub> (mixed 1:1 by weight) at the bottom of the capsule [5].

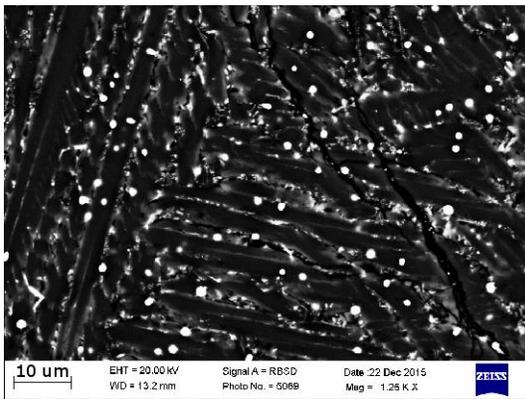
Recovered capsules were cut in half vertically. One half was mounted in epoxy and polished for SEM and electron microprobe analyses, the other was prepared for XRD and Mössbauer spectroscopy.

**Results:** Both samples melted completely but crystallized on quenching. Backscattered electron images, EDX chemical maps, and electron microprobe analyses indicate a very homogeneous composition throughout both samples (figure 1).

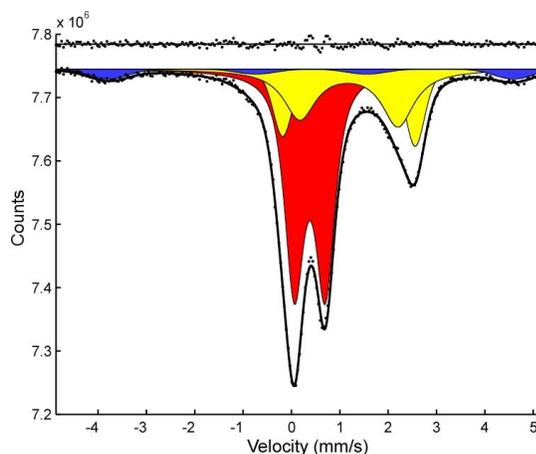
XRD analyses revealed that the dominant phase in both samples is clinopyroxene, and that both contain minor amounts of coesite. SEM and microprobe analyses clearly show the presence of Ru metal, however

the concentration was too low for the diffraction peaks to appear from beneath those of clinopyroxene.

Transmission Mössbauer spectra were collected over a 500  $\mu\text{m}$  diameter spot in the centre of selected samples that were parallel ground to a thickness of 500  $\mu\text{m}$ , giving an effective Mössbauer thickness of roughly 10 mg Fe/cm<sup>2</sup>. All spectra were similar, showing a dominant Fe<sup>3+</sup> doublet with less intense Fe<sup>2+</sup> doublets and a Fe<sup>3+</sup> magnetic sextet (Figure 2). To first order the relative abundance of iron species is given by the relative areas of subspectra, demonstrating that even by visual inspection the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio is greater than one. The quantitative determination of the bulk Fe<sup>3+</sup>/ $\Sigma\text{Fe}$  ratio of all samples measured is  $0.60 \pm 0.05$ .



**Figure 1:** BSE image of a sample synthesized at 17 GPa. Long quench crystals can be observed and the small bright points are nuggets of Ru metal.

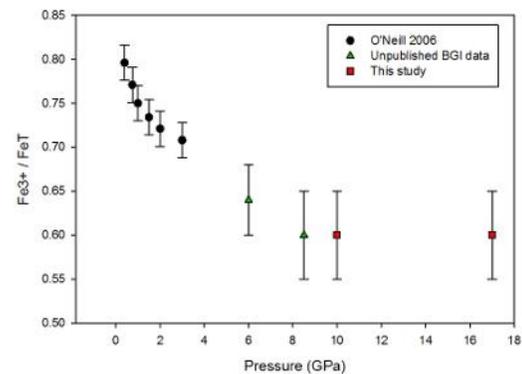


**Figure 2:** Room temperature Mössbauer spectrum of a sample quenched from 15 GPa. Subspectra are shaded as follows: Fe<sup>2+</sup> in cpx (yellow), Fe<sup>3+</sup> in cpx (red), Fe<sup>3+</sup> in magnetic oxide (blue).

**Discussion:** Figure 3 summarizes the results of this study and previous work all performed with the same

melt bulk composition and at an oxygen fugacity fixed by the Ru-RuO<sub>2</sub> buffer. Previous unpublished work performed in a multianvil at the BGI at 6 and 8 GPa is shown. Up to 8 GPa it was possible to quench the silicate liquid to a glass, however, by 10 GPa the liquid crystallises during quenching. The question remains as to how faithfully the Fe<sup>3+</sup>/ $\Sigma\text{Fe}$  ratio of the crystalline material reflects that of the initial melt. XRD analyses indicate that clinopyroxene is the only iron bearing phase. Although Mössbauer spectra show that a magnetic phase is also present, the Fe<sup>3+</sup> in this phase is accounted for in the bulk measurement. Similarity between results at 8 and 10 GPa on glass and crystallised samples respectively indicate that the results are robust.

Although the Fe<sup>3+</sup>/ $\Sigma\text{Fe}$  ratio does not continue to decrease at pressures between 8 and 17 GPa, there is no evidence that silicate melt Fe<sup>3+</sup>/ $\Sigma\text{Fe}$  ratios increase at the Ru-RuO<sub>2</sub> buffer.



**Figure 3:** Fe<sup>3+</sup>/FeT versus pressure. The trend of Fe<sup>3+</sup>/ $\Sigma\text{Fe}$  decreasing has not reversed but has flattened, suggesting that at sufficient pressure, increasing amounts of Fe<sup>3+</sup> may be stabilized in a silicate melt.

One final anomalous observation is that coesite appears to be in a sample quenched from 17 GPa and 2100°C, which is at least 5 GPa higher than the proposed stability field. Extensive pressure calibrations of the multianvil assembly used imply that it is unlikely that the pressure has been so severely overestimated. It is more likely that coesite forms metastably during rapid quenching or that thermal contraction causes pressures to drop rapidly in the assembly during quench.

**References:** [1] Delano J.W. (2001) *Orig. Life Evol. Biosph.*, 31, 311-341. [2] Drake M.J. & Righter K. (2002) *Nature*, 416, 39-44 [3] Hirschmann M.M. (2012) *Earth Planet. Sci. Letters*, 341-344, 48-57. [4] Frost D. J. & McCammon C.M. (2008) *Annu. Rev. Earth Planet. Sci.* 36, 389-420 [5] O'Neill H. St. C. et al. (2006) *Am Mineral.* 91,404-412