EXPERIMENTAL INVESTIGATION OF THE ROLE OF OXYGEN FUGACITY ON DEGASSING OF PLANETARY MAGMA OCEANS. H. Zhang, A. C. Withers and M. M. Hirschmann, Dept. of Earth Sciences, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, MN, 55455 (zhan1442@umn.edu).

Introduction: The oxidation state of a magma ocean (MO) during early planetary formation and differentiation may have a crucial influence on the compositions of early planetary atmospheres and on the geochemical differentiation of planetary interiors [1]. Yet the redox conditions that created the early atmosphers of terrestrial planets remain uncertain. Earlier studies argued for both oxidized and reduced early terrestrial atmosphers [2-5]. Importantly, magma ocean- atmosphere interactions have a key influence on the oxidation state and composition of early atmospheres of terrestrial planets. Volatile species are exchanged extensively between shallow MOs and primitive atmospheres (Fig. 1) and so the oxygen fugacity (fO$_2$) in shallow parts of a MO affects the composition and speciation of early atmospheres.
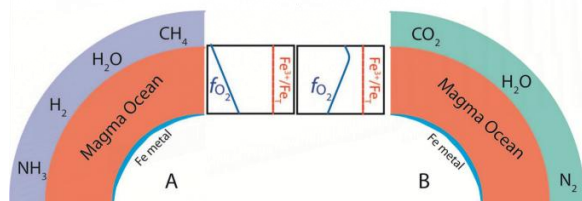

Fig 1. Schematic illustration of the relationship between MO fO$_2$ gradients and the composition of the overlying atmosphere. In both A and B, the MO is in equilibrium with Fe-rich metal at its base and is well-mixed. In A, it is supposed that isochemical compression of a MO leads to reduction, based on low pressure observations [6, 7], and the overlying atmosphere is reduced. In B, isochemical compression of a MO at high pressure leads to lower magmatic fO$_2$, rather than higher as suggested by low-pressure models [6,7], and this causes the overlying atmosphere to by relatively oxidized.

Iron is the most abundant multi-valent element in silicate melts and so magmatic $Fe^{3+}/\sum Fe$ ratios are directly linked to MO oxidation state. In a vigorously convecting, well-mixed MO the oxygen fugacity (fO$_2$) may be set by the $Fe^{3+}/\sum Fe$ ratio imposed by magma-metal equilibration at high pressure, since the MO is in contact with metallic iron at depth. Low pressure experiments indicate that the $Fe^{3+}/\sum Fe$ ratio decreases as pressure increases [7], which suggests a MO with fixed $Fe^{3+}/\sum Fe$ is more reduced at low pressure than at high. This is illustrated in Fig. 2, which shows the calculated influence of fO$_2$ and pressure on silicate melt $Fe^{3+}/\sum Fe$. As shown by the red arrow, decompression

of a homogeneous magma with fixed $Fe^{3+}/\sum Fe$ (Fig.3) leads to the MO becoming more reduced (relative to the IW buffer) at the surface for two different thermodynamic models [6, 7]. If this situation applies throughout the MO, then the overlying atmosphere will be highly reduced (Fig. 1A).
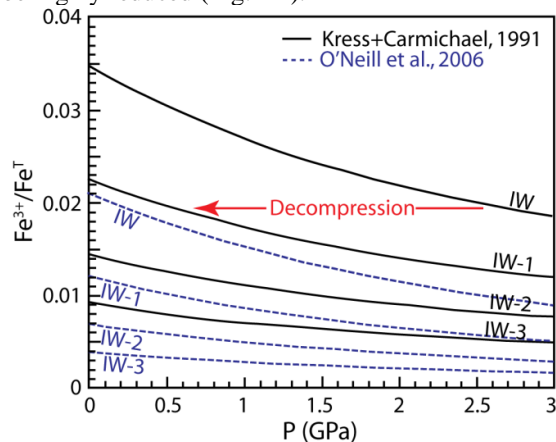

Figure 2: The $Fe^{3+}/\sum Fe$ of silicate melts changes with pressure at oxygen fugacities fixed by the iron-wüstite (IW) buffer [8] and 1, 2, and 3 orders of magnitude below the IW buffer, from existing thermodynamic models[6, 7]. As the red arrow shows, isochemical decompression at a fixed value of $Fe^{3+}/\sum Fe$ leads to reduction relative to IW buffer for both models. Quantitative differences between models are likely because both are extrapolated from models calibrated under more oxidizing conditions.

Whether the situation in Figs. 1A and 2 applies to deep MOs, where high pressures are reached, is open to question, as the volumes and compressibility of Fe^{2+} and Fe^{3+} in silicate melts are distinct, the $Fe^{3+}/\sum Fe$ ratio may impose fO$_2$ quite different at shallow depth from that prevailing at high pressure. This could lead to the opposite condition, in which atmospheres overlying MOs are comparatively oxidized (Fig. 1B). This study investigates experimentally the effect of pressure on the relationship between oxygen fugacity and $Fe^{3+}/\sum Fe$ in a silicate melt.

Experiments: The starting composition is an andesite [7], prepared from reagent grade oxides and silicates. To facilitate Mössbauer spectrometry, 30% of the total Fe_2O_3 was added as $^{57}Fe_2O_3$. This initial material was loaded into 2 mm diameter Pt capsules and the oxygen fugacity within the capsule was controlled by the addition mixture of 10 wt% Ru+10 wt% RuO$_2$ loaded as layers on the the bottom and top of the capsule. Ru/RuO$_2$ imposes conditions close to that of the

magnetite/hematite buffer [7], which are sufficiently oxidizing that loss of Fe to the Pt capsule is negligible. Experiments up to 3 GPa were performed in a half-inch, end-load piston cylinder and those up to 7 GPa were performed in a Walker-style multi-anvil device. Experiments were performed above the liquidus at 1400-1750 °C; to achieve redox equilibrium between buffer and melt, experiments lasted for 4 h at ≤ 1600 °C and 12 min at 1750 °C. Compositions of quenched glasses were verified by EMPA (Fig. 2) and $Fe^{3+}/\sum Fe$ ratios were analyzed by Mössbauer spectrometry.

Results: Most resulting Mössbauer spectra consist of two broadened quadrupole doublets corresponding to ferric and ferrous iron; two of the spectra also include a broadened ferromagnetic absorption corresponding to Fe^{3+}. This broadening is likely owing to a lack of long-range order in next-nearest neighbor environments. The Mössbauer spectra were fitted with the xVBF method using the RECOIL software package.

We fit Fe^{2+} paramagnetic absorption to a quadrupole doublet with 2D Gaussian distributions of the center shift (CS) and quadrupole splitting (QS), with variable parameters: CS, Gaussian standard deviation of the CS distribution (σ_{CS}), QS, Gaussian standard deviation of the QS distribution (σ_{QS}), and correlation between the CS and QS distributions (ρ). We fit Fe^{3+} paramagnetic absorption to a quadrupole doublet with 2D CS and QS distributions with variable parameters: CS, QS, and σ_{QS}. Fe^{3+} paramagnetic absorption fitting do not use the σ_{CS} and ρ parameters as they should be essentially zero for Fe^{3+} absorption [9]. The fraction of Fe^{2+} and Fe^{3+} was estimated from the area of the sub-spectral components. Based on previous study of glasses with similar composition which found no difference in the relative areas of Fe^{3+} subspectra between 4.2 K and 293 K [10], we assumed that the recoil-free fractions of Fe^{2+} and Fe^{3+} are the same. Verifying low temperature investigations are in progress.

The preliminary results show that $Fe^{3+}/\sum Fe$ ratios decrease with increasing pressure and with increasing temperature (Fig. 3). The effect of temperature is approximately similar to that expected from previous thermodynamic models [6,7], but the effect of pressure is more modest, particularly above 4.5 GPa. A revised thermodynamic parameterization is in progress.

Discussions and Applications: Whereas low pressure data suggested that isochemical (constant $Fe^{3+}/\sum Fe$) self-compression of magma leads to oxidation [6,7] (Figs. 1A, 2), there is reason to suppose that self-compression of Fe^{2+} and Fe^{3+} in a MO at high pressure leads to the opposite effect, as Fe^{3+} may be stabilized by taking on higher coordination states, leading to higher $Fe^{3+}/\sum Fe$ under reduced conditions. This

would lead the trends in Fig. 2 to reverse at higher pressure, in which case isochemical compression would yield reduction (Fig. 1B). Data up to 7 GPa do not verify this hypothesis, but rather suggest that the magnitude of reduction of compression is significantly more modest than supposed based on low pressure constraints. Reversals may occur at higher pressure, and experiments above 7 GPa are planned.
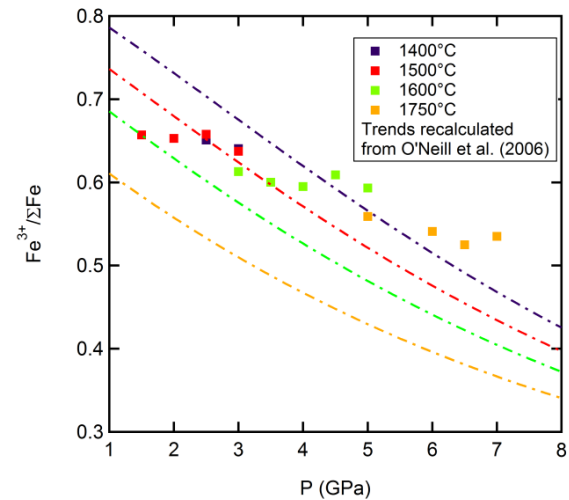

Figure 3: $Fe^{3+}/\sum Fe$ in quenched andesitic glasses from 1.5 to 7 GPa and 1400-1750 °C and trends calculated from the thermodynamic model at similar temperatures [7].

Regardless of behavior above 7.5 GPa, it is clear that the oxidation state of atmospheres overlying MOs may be related to the depth at which equilibrium is established between Fe-rich alloy and silicate, with differences for the potential early atmospheres, climate, and origin of life. If shallow MOs are related to reducing atmospheres and deep high pressure ones related to oxidizing atmospheres, then smaller planets that equilibrate with iron at low pressure may yield early atmospheres rich in CH_4 and H_2 (Fig.1A). Larger ones equilibrating with iron at higher pressure, may yield early atmospheres rich in CO_2 and H_2O (Fig. 1B).

References: [1] Hirschmann M.M. (2012) *Earth and Planetary Science Letters, 341–344*, 48-57. [2] Miller S.L. and Urey H.C. (1959) *Science, 130*, 245~251. [3] Delano J.W. (2001) *Origins of Life and Evolution of Biospheres, 31*, 311-341. [4] Matsui T. and Abe Y. (1986) *Earth Moon Planets, 34*, 223-230. [5] Kasting J.F. (1993) *Science, 259*, 920-926. [6] Kress V. and Carmichael I. (1991) *Contributions to Mineralogy and Petrology, 108*, 82-92. [7] O'Neill H.S.C. et al. (2006) *American Mineralogist, 91*, 404-412. [8] Campbell A.J. et al. (2009) *Earth and Planetary Science Letters, 286*, 556-564. [9] Alberto H.V. et al. (1996) *Journal of Non-Crystalline Solids, 194*, 48-57. [10] Jayasuriya K.D. et al. (2004) *American Mineralogist, 89*, 1597-1609.