OXIDIZED OR REDUCED EARLY ATMOSPHERES OF TERRESTRIAL PLANETS? MAGMA OCEAN ATMOSPHERE CONTROL AND THE IMPORTANCE OF METAL-MAGMA EQUILIBRATION. M.M. Hirschmann[1], [1]University of Minnesota (Dept. of Geology and Geophysics 108 Pillsbury Hall, Minneapolis, MN 55455. *Marc.M.Hirschmann-1@umn.edu*).

Introduction: The compositions of the earliest atmospheres on terrestrial planets are central to the development of earliest planetary environments, including the climate, habitability, and possibilities for the origin of life. Miller and Urey [1] assumed the early atmosphere of Earth was reduced, consisting chiefly of CH_4, H_2, and NH_3. It is now commonly assumed that early atmospheres of Earth and other terrestrial planets consist chiefly of H_2O and CO_2 [2-7], in part because terrestrial volcanic gases on Earth have been more oxidized at least for the last 3.9 Ga [8]. On the other hand, thermodynamic calculations show that gases evolved from chondritic meteorites consist chiefly of CH_4, H_2O, H_2, and NH_3 [9-10] owing to equilibration with Fe metal. Consequently, early atmospheres degassed directly from accreting material may be similar to that originally proposed by Miller and Urey [1]. However, reaction with underlying magma ocean can potentially profoundly modify the composition of the early planetary atmospheres by imposing an oxygen fugacity related to Fe^{3+}/Fe^{2+} equilibrium in the magma.

Magma ocean-atmosphere interactions Planetary atmospheres likely equilibrate with a magma ocean at some point in the early history of terrestrial planets. A significant fraction of early planetary atmospheres may develop by near-surface degassing of accreting planetesimals [9-10]. However, volatiles may be implanted directly into the interior of growing terrestrial planets and atmospheres generated from impact degassing may be modified by extensive exchange and equilibration with underlying magma oceans [5-7]. Magma oceans crystallize from the bottom upwards and do not develop permanent solid carapaces [11]. Vigorous convection actively replenishes the surface layer, allowing extensive volatile exchange between the early atmosphere and the entire magma ocean on short time scales compared to crystallization times [7].

Oxygen fugacity in magma oceans Magma oceans associated with core formation or with planetismal impacts will react with metal, and this controls their oxygen fugacity and that of the overlying atmosphere. But the oxygen fugacity imposed on the atmosphere depends on the depth at which the magma equilibrates with metal. Metal will be present episodically near the magma-ocean interface at the instant after an impact, which, if equilibrium is achieved, would impose an atmospheric oxygen fugacity ~1-2 log units below that fixed by the Fe-FeO (IW) buffer. But iron droplets settle rapidly through a magma ocean [12] and the

magma ocean quickly becomes nearly free of Fe metal, except at its base. The resulting magma ocean will be equilibrated with metal at a mean depth related to interactions with Fe as it settles through the magma column or with the ponded Fe below.

The proportions of Fe^{3+} and Fe^{2+} in a magma ocean will be set by equilibration with metal at the mean depth of equilibration and vigourous convection will homogenize the Fe^{3+}/Fe^{2+} ratio throughout the magma column. But, a constant ratio of Fe^{3+}/Fe^T in the magma will not enforce a constant oxygen fugacity, as the different molar volumes of Fe^{2+} and Fe^{3+} in magmas require that the reaction $FeO_{magma} + \frac{1}{4}O_2 \Leftrightarrow FeO_{1.5\ magma}$ depend on pressure. Therefore the oxygen fugacity in shallow portions of a well-mixed magma ocean may be quite different from near its base.

Low pressure partial molar volumes and compressibilities of Fe^{3+} and Fe^{2+} in silicate melts [13], and the Fe^{3+}/Fe^T speciation of glasses quenched from 0.4-3 GPa [14] indicate that the partial molar volume of FeO in silicate melts is smaller than that partial molar volume of $FeO_{1.5}$. This reduces Fe^{3+}/Fe^T along fixed buffers with increasing high pressure and so decompression at fixed Fe^{3+}/Fe^T causes magmas to become more reduced relative to the buffer (Fig. 1).

If the trend evident in Fig. 1 were to apply throughout the pressure range of a magma ocean, then well mixed magmas in equilibrium with metal at depth would be even more reduced at lower pressure, and the atmosphere above such magma oceans would be highly reduced, as illustrated in Fig. 2A. If this actually occurs in real magma oceans, it raises some interesting chemical and dynamical issues, because such magmas would respond to the reducing conditions by precipitating metal, leading to chemical and density zonation in the magma column. However, it is likely that it does not, at least in magma oceans where significant pressures are achieved.

We predict that at high pressures [>3 GPa], the trend in Fig. 1 reverses, such that melts of the same Fe^{3+}/Fe^T become more reduced with increasing pressure. If so, magma oceans would be reduced at depth and comparatively oxidized in their shallow reaches, and early planetary atmospheres above magma oceans could consist chiefly of H_2O and CO_2, as in Fig. 2B. This should occur because Fe^{3+} in magmas likely takes
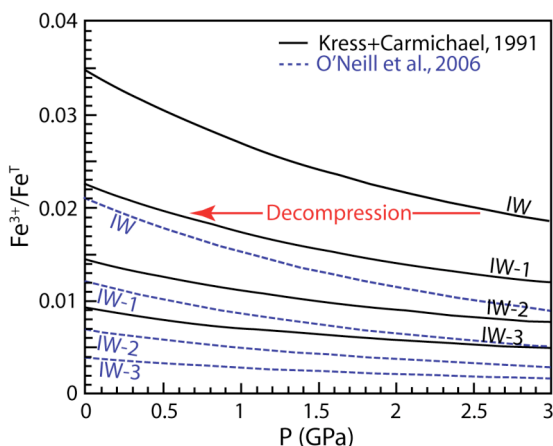
Fig. 1. Fe^{3+}/Fe^T of silicate melts as a function of pressure at oxygen fugacities fixed by the iron-wüstite (IW) buffer and IW-1, IW-2, and IW-3, based on two different thermodynamic models [13,14]. As illustrated by the red arrow, decompression at fixed values of Fe^{3+}/Fe^T leads to reduction relative to IW for both calculations. Quantitative differences between the models are likely because the amount of Fe^{3+} present at these reducing conditions is small and because both are extrapolated from models calibrated under more oxidizing conditions.

on higher coordination states at high pressure, as the partial molar volume of VI coordinated Fe^{3+} in silicate melts is 25% smaller than IV coordinated Fe^{3+} [15] and so high coordinated Fe^{3+} should become more stable in melts at high pressures, leading to reduction with isochemical compression. This is analogous to what occurs in solid peridotite, for which Fe^{3+} is increasingly stabilized in the high coordination environments provided by high pressure minerals (garnet, wadsleyite, ringwoodite, perovskite) resulting in more reduced conditions with increasing pressure [16].

Discussion This prediction requires experimental verification, but if accurate has several consequences. At low pressure, the Fe^{3+}/Fe^T ratio of silicate magma in equilibrium with Fe metal is very low (~0.01-0.03, Fig. 1). But minerals in Earth's lower mantle in equlibrion with Fe metal have high the Fe^{3+}/Fe^T (~0.3 [16]). If similar ratios applied to metal-saturated magmas at ≥25 GPa (i.e., ≥700 km in Earth; ≥1800 km for Mars),

then such magmas, once advected to the near-surface would be highly oxidized (~IW+5), resulting in an $H_2O+CO_2+N_2$ atmosphere.

If deep high-pressure magma oceans are related to early oxidizing atmospheres and shallow low pressure magma oceans to reducing atmospheres, then smaller planets that equilibrate with iron at low pressure may yield early atmospheres rich in CH_4 and H_2, whereas larger terrestrial planets, equilibrating with iron at higher pressure, may yield protoatmospheres rich in CO_2 and H_2O. This may set terrestrial planets on different evolutionary paths, with differences for the preservation potential of the atmospheres, the evolution of their climate, and development of conditions conducive to the development of life.

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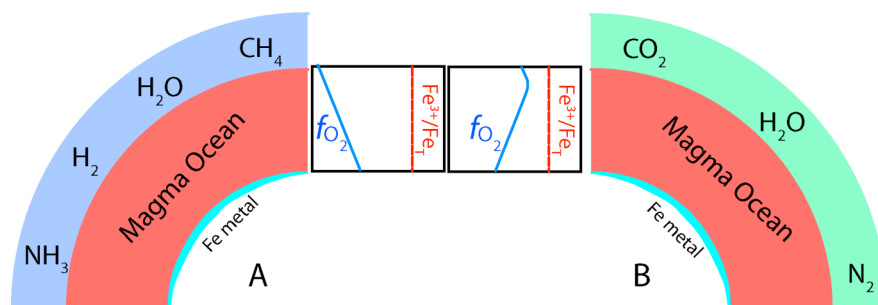
Fig. 2. Schematic illustration of the relationship between magma ocean oxygen fugacity gradients and the composition of the overlying atmosphere. In both A and B, the magma ocean is in equilibrium with Fe-rich metal at its base and is well mixed, such that the proportions of Fe^{3+} and Fe^{2+} are homogeneous throughout. However, in A, it is supposed that isochemical decompression of magma leads to reduction, based on low pressure thermodynamic models [13,14] and the overlying atmosphere is reduced. In B, it is supposed that isochemical decompression of magma at high pressure leads to oxidation, and so to an oxidized atmosphere.