# MAGMA OCEAN REDOX EVOLUTION AND ITS INFLUENCE ON AN OUTGASSED ATMOSPHERE

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Introduction: Magma oceans were likely ubiquitous in terrestrial planets early evolution [1]. The giant impact argued to have resulted in the formation of the Moon likely induced large-scale melting of the Earth's mantle resulting in a magma ocean. Such a magma ocean must have led to widespread chemical equilibration between the mantle and the atmosphere for volatile elements. While subsequent processes like volcanism [2] or impacts [3] may have altered the atmospheric composition, the initial composition set by the magma ocean stage was crucial for its subsequent evolution. The speciation of volatile elements in the atmosphere is governed by the oxygen fugacity (fO_2) in the magma ocean. Since oxidized and reduced species can have very different solubilities in silicate melts, the fO_2 also plays a crucial role in volatiles outgassing. Here we self-consistently calculate the evolution of the fO_2 in a deep crystallizing magma ocean in order to compute the evolution of the outgassed atmosphere's composition in C-O-H system.

Model: The fO_2 in the magma ocean is computed assuming it to be controlled by the ratio between ferrous- and ferric-iron oxides. The respective abundances of these oxides is tracked by treating ferric and total iron as incompatible elements (the former being more incompatible than the latter, with $D_{Fe3+}=0.27$ and $D_{Fe}=0.94$). The molar ratios of the gaseous species of the H and C redox couples are then computed by considering the following reactions to be at equilibrium:

$$2H_2+O_2=2H_2O$$

$$2CO+O_2=2CO_2$$
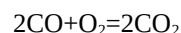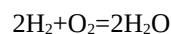
Finally, the partial pressures of these species are computed by considering mass conservation of each element, partitioned between crystals, silicate melt, and gas, with species-specific solubility values. For this step, we distinguish between two magma ocean crystallization scenarios: 1) equilibrium crystallization where the magma ocean is characterized by a melt fraction higher than 40% and is in equilibrium with the whole cumulates pile at all times, and 2) fractional crystallization where the magma ocean is fully liquid and in equilibrium only with the mass of crystals formed over the current crystallization step.

In order to resolve the temporal evolution of the magma ocean crystallization, we adopt a thermal evolution model based on [4]. The convective heat flux in the magma ocean is equated to the radiative flux through a grey atmosphere. Greenhouse effect is parametrized via an opacity factor dependent on the atmospheric mass of the different gaseous species.

Results: The model described above provides an evolution framework for the temperature (i.e. crystallization advancement), ferric-to-total iron ratio ($Fe^{3+}/\Sigma Fe$), the fO_2 of the magma ocean and the partial pressures in the atmosphere. It requires a set of initial conditions, which we vary as the parameters of our study. The initial fO_2 is set at IW-2 either at the surface or at the bottom of the magma ocean (corresponding to a core-mantle equilibration occurring at shallow or deeper depth, respectively). This choice corresponds to different initial values of $Fe^{3+}/\Sigma Fe$, computed using the pressure-dependent fO_2 parametrization from [5]. The bulk H and C budgets are set by assuming an equivalent of 1 to 10 Earth ocean of water and a C/H ratio between 1 and 10.
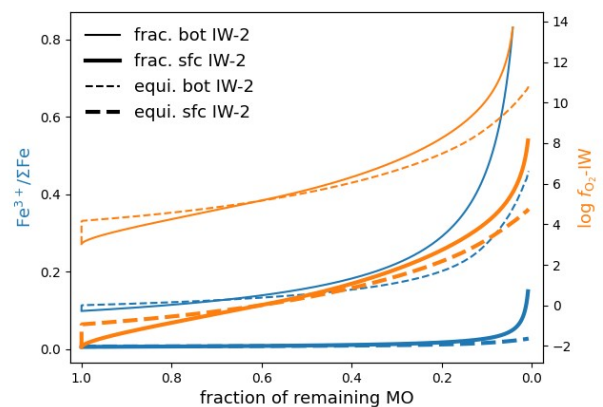

Figure 1: Evolution of $Fe^{3+}/\Sigma Fe$ and fO_2 of terrestrial magma ocean for fractional (solid lines) and equilibrium (dashed lines) crystallization scenarios, with an initial fO_2 in the magma ocean set at IW-2 at the surface (thick lines) or at the bottom (thin lines).

Figure 1 represents the evolution of $Fe^{3+}/\Sigma Fe$ and fO_2 in the magma ocean as a function of crystallization. The higher incompatibility of ferric iron compared to ferrous iron leads to a progressive increase in $Fe^{3+}/\Sigma Fe$ and, in turn, of the fO_2. This increase is distinctly higher for fractional crystallization (solid

lines) than for equilibrium crystallization (dashed lines) due to the large amount of remaining trapped melt in the latter case.

The evolution of fO_2 is then used to compute the gaseous redox speciation in the atmosphere, which influences the elemental solubility and has thus a double effect on the atmospheric composition, influencing both speciation and ougassing. Based on a fractional crystallization case with fO_2=IW-2 at the surface initially, Figure 2 shows the time-evolution of the mass mixing ratios of the gaseous species in the atmosphere as well as the total atmospheric pressure, until full crystallization of the magma ocean, for three different C and H budgets.
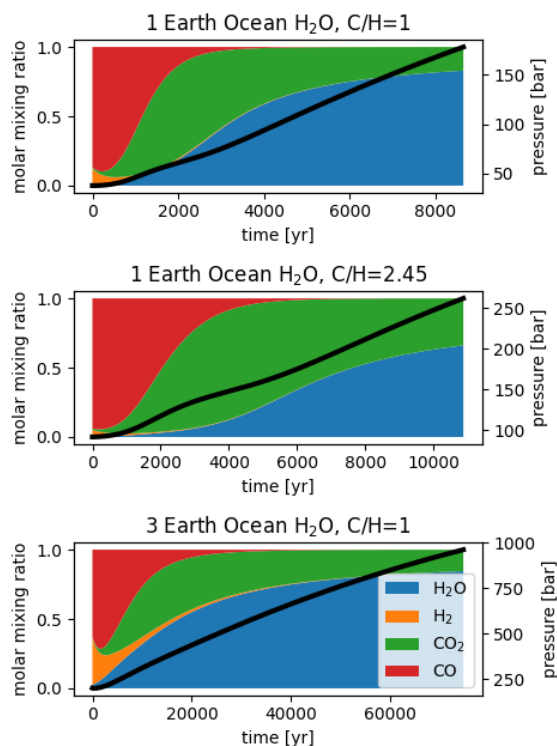

Figure 2: time-evolution of the molar mixing ratios (read off the left y-axis) and total pressure in the atmosphere (read off the right y-axis) for the equivalent of 1 Earth ocean of water and a C/H ratio of 1 (top panel), 1 Earth ocean of water and a C/H ratio of 2.45 (middle panel) and 3 Earth ocean of water and a C/H ratio of 1 (bottom panel). Notice that both the x-axis and the right y-axis change between the panels.

As the magma ocean crystallizes and the fO_2 increases accordingly, more oxidized species (H_2O and

CO_2) are outgassed. The surface fO_2 (which is used for atmospheric speciation) in this case starts at IW-2, corresponding to an initially mildly reduced atmosphere. As at a give fO_2, C-bearing species have in general a lower solubility than H-bearing ones, the atmosphere is initially dominated by CO. Increasing the bulk volatiles budget (from the top panel to the bottom one) increases the final total pressure. The final atmosphere is largely oxidized, thus dominated by H_2O and CO_2, in a ratio set by the bulk C/H because, in the fractional crystallization case illustrated here, outgassing is almost complete. Finally, because water has the strongest greenhouse power, increasing the bulk hydrogen budget significantly prolongs magma ocean crystallization, while modifying C/H at constant H budget has a much lower impact.

Conclusions: The incompatibility of ferric iron in the crystallization sequence of the terrestrial magma ocean leads to a progressive increase in the fO_2 and to a shift towards an oxidized atmosphere as the magma ocean crystallizes. While an oxidized atmosphere has already been suggested if core-mantle equilibration occurred at the bottom of the magma ocean [5], our result suggests that it actually is a systematic outcome of the magma ocean crystallization.

References: [1] Elkins-Tanton L. T. (2012) *AREPS*, **40**, 113–139. [2] Ortenzi G. *et al*., (2020) *Sci. Rep.,* **10**, 10907. [3] Zahnle K. J. *et al*., (2020) *Planet. Sci. J.,* **1**, 11. [4] Nikolaou A. *et al*., (2019) *Astrophys. J.,* **875**, 11. [5] Deng J. *et al*., (2020) *Nature Comm.,* **11**, 2007.