

HYDROGEN ISOTOPIC FRACTIONATION IN THE TERRESTRIAL MAGMA OCEAN. K. Pahlevan¹, L. Schaefer¹, L. Elkins-Tanton¹, S. Desch¹, S. Karato². ¹School of Earth and Space Exploration, Arizona State University (kaveh.pahlevan@asu.edu), ²Dept. of Geology & Geophysics, Yale University.

Introduction: Questions on the origin of terrestrial water have centered on the source (“Where did Earth’s water come from?”) and isotopic signatures (“What was the source D/H?”) [e.g. 1,2]. A recent report of an isotopically distinct mantle H reservoir [3], as well as earlier inferences of distinct deep H reservoirs in the Earth [4,5], prompt a different question: what is the origin of the H isotopic heterogeneity in the Earth? To address this question, we have developed a model of the degassing of the terrestrial magma ocean and overlying atmosphere including equilibrium magma-vapor partitioning, vapor-phase speciation, and isotopic fractionation. We find that the generation of endogenous H isotopic heterogeneity on the Earth is possible and depends critically on the oxidation state of the magma ocean during its crystallization/degassing [e.g. 6].

Context: Models of the Moon-forming giant impact extensively melt and partially vaporize the silicate Earth and deliver a substantial mass of metal to the Earth’s core. The subsequent evolution of the terrestrial magma ocean and overlying vapor atmosphere over the ensuing $\sim 10^{5-6}$ years has been largely constrained by theoretical models with remnant signatures from this epoch [7] proving somewhat elusive.

Here we report calculations of equilibrium hydrogen isotopic fractionation between the magma ocean and overlying steam atmosphere to determine the extent to which H isotopes trace the evolution during this epoch. By analogy with the modern silicate Earth, the magma ocean-steam atmosphere system is often assumed to be chemically oxidized ($\log fO_2 \sim QFM$) with the dominant atmospheric vapor species taken to be water vapor [8]. However, the terrestrial magma ocean – having held metallic droplets in suspension – may also exhibit a much more reducing character ($\log fO_2 \sim IW-1$) such that ocean-atmosphere equilibration renders molecular hydrogen the dominant H-bearing atmospheric species. This variable – the redox state of the magma ocean – has not been explicitly included in prior models of the evolution of the magma. Here we take the magma ocean fO_2 as a free parameter and calculate the consequences for a range of redox states.

We couple equilibrium isotopic fractionation with magma ocean crystallization calculations to forward model the behavior of hydrogen isotopes during this epoch and find that the distribution of H isotopes in the silicate Earth immediately following crystallization represents an oxybarometer for the terrestrial magma ocean. Whether such endogenous isotopic heterogeneity

can survive as an observable signature in the modern silicate Earth is an open question.

Liquid-Vapor Equilibration: Before using equilibrium thermodynamics, we can ask: is there rapid equilibration between the magma ocean and overlying atmosphere? On the modern Earth, the timescale for pCO_2 equilibration with the oceans is $\sim 10^2$ years [9] but, to our knowledge, no equivalent calculation for the timescale of magma ocean equilibration has been done. Here, using a boundary layer analysis [e.g. 10], we make an estimate of the timescale for magma-atmosphere equilibration under the assumption that diffusion through the magma surface boundary layer, rather than the ascent of bubble plumes [11], dominates the equilibration process. Using this approach, we can write the timescale (τ_{eq}) for ocean-atmosphere chemical equilibration:

$$\tau_{eq} = 3 \times 10^3 \text{ years} * (\delta_T / 1 \text{ cm}) * (H / 10^3 \text{ km}) \quad (1)$$

where the result is expressed in terms of δ_T , the thickness of the *thermal* (versus chemical) boundary layer, and H is the depth of the magma ocean. This calculation suggests that equilibration with the atmosphere via processing the magma ocean mass through a chemical boundary layer is rapid relative to evolutionary timescales in the problem (10^{5-6} years [e.g. 12]). More work is required to quantify the competing role of degassing via bubble plumes near the surface. However, boundary layer diffusion alone suggests that ocean-atmosphere equilibration may be rapid. We note that, as with the analogous metal-pond-magma-ocean problem [13], either reservoir (ocean or atmosphere) can present the rate-limiting step to equilibration at the interface. Here we have assumed that exposure of the magma to boundary layers (“aeration”) is the rate-limiting step rather than atmospheric exposure to magma. The analogous calculation for the atmosphere shows that this assumption is justified due in part to the high atomic diffusivities and high convective velocities in the vapor atmosphere. Having demonstrated that rapid ocean-atmosphere equilibration is possible, we next describe the thermodynamic model we use to calculate the equilibrium partitioning.

Equilibrium Model Description: We have developed a model to describe the degassing behavior of H (as H_2 or H_2O) from the magma ocean, and subsequently calculate the behavior of deuterium as a passive tracer. Here, we briefly describe the model components in turn.

Atmosphere. We adopt a two-component (H_2 - H_2O) thermodynamic model to describe a “pure” steam atmosphere whose oxygen fugacity (fO_2) is determined via equilibration with the underlying ocean. The only other volatile element of high enough abundance in the atmosphere to potentially alter the speciation of H is carbon, but CH_4 is known to be unstable at the relevant conditions (e.g. [8]).

Ocean. We use the pseudo-one-component magma ocean model described in [14]. We assume that the magma ocean is well-mixed and utilize the model to relate the atmosphere equilibration temperature (which determines isotopic partitioning) to the depth of the magma ocean (which determines the extent of degassing). OH is assumed to be the dominant magmatic H-bearing species *at the surface* for the full range of conditions here considered, consistent with recent experiments [15].

Crystals. The driving force for magma ocean degassing during crystallization is the exclusion of volatiles from crystals. The mineral-melt partition coefficient of OH in nominally anhydrous mantle minerals is low, typically ~ 0.005 - 0.02 [6]. Hence, we adopt a crystal-liquid partition coefficient of 0.01, noting that the results of the degassing history are insensitive to this number, so long as it is sufficiently small. Crystals are treated as sinks for mass and hydrogen.

Isotopic Fractionation. Following recent calculations of equilibrium H isotopic fractionation in the proto-lunar disk [16], we calculate the magma-vapor isotope fractionation under the assumption that OH(v) approximates the bonding environment for hydrogen in the magma, OH(l).

Species	H	H_2	H_2O	OH	MgOH
K_{eq}	1	1.22	1.80	1.77	1.79

Table 1. Listed are the equilibrium constants (at 10^3 K) for isotopic exchange reactions between given vapor species and atomic hydrogen. $K_{eq}(H)=1$ by definition. The equilibrium constant represents the tendency of a species to concentrate deuterium at equilibrium, and is high for species that feature the OH vibrational stretch. Since magmatic H is always dominated by OH, it is the presence of H(v) or H_2 (v) in the vapor that determines the magnitude of liquid-vapor isotopic fractionation. From [16].

Results: We find that the redox state of the magma ocean determines not only the vapor speciation and liquid-vapor partitioning of hydrogen but also the equilibrium isotopic fractionation during the crystallization epoch (Figure 1).

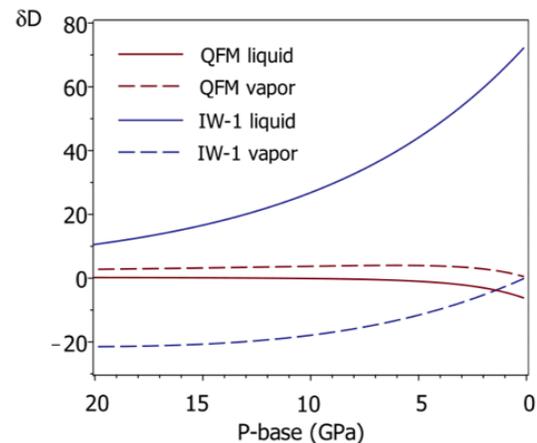


Figure 1 H isotopic evolution accompanying crystallization of an oxidizing (QFM) and reducing (IW-1) magma ocean. An oxidizing magma ocean generates small (<10 per mil) isotopic variations, while a reducing magma ocean results in ~ 70 per mil δD variability among its crystallization products.

Conclusions: We have calculated the timescale for ocean-atmosphere equilibration via boundary layer diffusion and find that it is short relative to evolutionary timescales, motivating equilibrium calculations. Liquid-vapor isotopic fractionation of H is substantial under reducing conditions and can generate measurable D/H variability in the crystallization products but is muted in an oxidizing magma ocean. The distribution of H isotopes on Earth immediately following crystallization acts as an oxybarometer for the magma ocean.

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