EARTH'S WATER: NEBULAR INGASSING AND STORAGE OF HYDROGEN IN EARTH'S CORE.

S. J. Desch[1], J. Wu[1] and P.R. Buseck[1,2], [1]School of Earth and Space Exploration, Arizona State University, PO Box 871404, Tempe AZ, 85287-1404, School of Molecular Sciences, Arizona State University, PO Box 871604, Tempe AZ, 85287-1604. steve.desch@asu.edu

Introduction: Understanding the origins of Earth's water is key to assessing the structure and history of Earth and other terrestrial planets, including Venus, and to assessing the likelihood that rocky exoplanets possess various amounts of water. The origins of Earth's water are constrained by its total amount of water (or more precisely, hydrogen), and the D/H ratio of that hydrogen. Earth contains one "ocean" (1.4 x 10^{21} kg) of water in its hydrosphere, another 0.25-4 ocean's worth dissolved (as OH) in the mantle [1], and perhaps another ocean's worth dissolved in its transition zone [2,3], totalling about 3 oceans' worth, or about 0.1% of Earth's mass [4]. Earth's core is known to be about 7wt% light elements, possibly including substantial amounts of hydrogen [5]. The D/H ratio of crustal waters is 156 x 10^{-6} (VSMOW), and hydrogen in the mantle has D/H = 149 x 10^{-6} [6]. Mantle hydrogen is not completely homogeneous: deep mantle samples show a ratio D/H < 120 x 10^{-6} [7].

These constraints are nearly but not completely met if Earth gained its water from chondritic building blocks, especially carbonaceous chondrite material, as proposed by [8,9]. Carbonaceous chondrites are up to ~10wt% water (structurally bound in clays), and numerical simulations of planetary accretion routinely predict that Earth could have accreted ~10% of its mass from beyond 2.7 AU, the source region of carbonaceous chondrites [10]. It is more probable for Earths to accrete many tens of oceans' worth of water, but 3 oceans' worth is not improbable [11]. Furthermore, the D/H ratio of both ordinary and carbonaceous chondrites is ~ 140 x 10^{-6}, similar to the value for bulk Earth [8]. Chondrites are an excellent but not perfect match to Earth's water: while close, models generally predict more water than inferred for the Earth's mantle and surface, and the D/H ratio in chondrites is not as high as in the Earth's mantle or surface.

Additional sources of water or hydrogen appear needed. Observations of rocky exoplanets strongly suggest those with radii > 1.5 Earth radii have substantial H_2/He atmospheres [12,13], and imply that Earth may have accreted an envelope of gas from the solar nebula, then ingassed hydrogen into its magma ocean. Theoretical models robustly predict that even Earth-mass planets should accrete thick (~1000 bar) H_2/He atmospheres from their parent protoplanetary disks, and even a 0.3 Earth mass planetary embryo can accrete a 10-bar H_2/He atmosphere [14]. The surface temperatures of these early-forming embryos are likely sufficient to sustain magma oceans, especially with the blanketing effects of thick atmospheres. They may dissolve hydrogen into their magma oceans, that eventually partitions into their cores [15].

Even as Earth's mantle may acquire significant contributions of hydrogen from ingassing from an accreted proto-atmosphere, it also is expected to lose significant hydrogen to dissolution into iron droplets, forming high-pressure iron hydrides that can be sequestered in the Earth's core [15]. H_2O in the atmosphere dissolves into the magma ocean, or H_2 dissolves and then oxidizes to form H_2O. H_2O and H_2, and Fe and FeO, reach an equilibrium depending on the redox state of the mantle. At high pressures ~ 50 GPa [16], H_2 dissolves in Fe blebs to form FeH_x hydrides. As these sink into the core, hydrogen is stored there.

We present preliminary results from a model of Earth's water, in which a significant fraction of its hydrogen is ingassed from proto-atmospheres into the magma oceans of the embryos from which Earth accreted. In this model, a significant fraction of Earth's hydrogen is also sequestered into the core. For reasonable assumptions, the total mass and D/H ratio of hydrogen in Earth's mantle match the observed values.

Model for Earth's Hydrogen: We assume that Earth grew from planetary embryos whose hydrogen primarily came from chondritic material, structurally bound H_2O with D/H = 140 x 10^{-6}. We assume they also accreted H_2/He atmospheres from the solar nebula, with D/H ~ 21 x 10^{-6}, notably lighter than other reservoirs of hydrogen [17]. Earth's bulk D/H ratio is a mass-weighted average of its chondritic and nebular reservoirs. The mass of hydrogen dissolved in the magma ocean is determined by the partial pressures of H_2 and H_2O in the atmosphere, and their solubilities. The mass fraction of the mantle that is H_2 is x_{H2} = 100 (P_{H2} / 1000 bar) ppm [15] and the mass fraction that is H_2O is x_{H2O} = 0.04 (P_{H2O} / 1000 bar)$^{1/2}$ [18]. We take P_{H2O} / P_{H2} = 0.1, consistent with equilibrium of the atmosphere with the expected redox of the magma ocean [15]. From this we find that the ratio of hydrogen in the atmosphere to hydrogen in the magma ocean is ≈ 0.9 (P_{H2} / 1000 bar)$^{1/2}$, so that in general most of the hydrogen will reside in the mantle (in equilibrium).

Hydrogen in the atmosphere and magma ocean will have nearly the same D/H ratios. We assume an isotopic fractionation factor $0.95 < \alpha_{am} < 1$, so that the mantle D/H is slightly higher, by about 2%, than the atmosphere. We assume that on relatively short timescales (< 10^8 yr), the magma ocean stage ceases and chemical communication between the mantle and atmosphere is cut off. Eventually the atmosphere is lost, and the bulk D/H ratio of Earth, $(D/H)_{tot}$, is the ratio in the mantle. As Earth's core forms it incorporates more hydrogen. We track the progress of core by defining q, the ratio of hydrogen in the core to the entire planet.

As each metal bleb sinks to the core it carries hydrogen with a D/H ratio set by the mantle ratio $(D/H)_m$, and the isotopic fractionation factor α as hydrogen partitions between silicate and iron melts at ~ 50 GPa. From the D/H ratio of hydrogen in the bleb itself, we calculate the ratio in the core, $(D/H)_c$, to grow as

$$d[\,(D/H)c\,] / dq = (D/H)_{bleb} - (D/H)_c / q.$$

This equation can be numerically integrated to the q at which all the originally accreted hydrogen is in the core, except for ≈3 oceans' worth of hydrogen remaining in the mantle, eventually to reside in the mantle and transition zone, plus outgassed to the hydrosphere.

A key input parameter is α, the isotopic fractionation factor as H partitions at ~ 50 GPa between being dissolved in the silicate melt and dissolved in the metal blebs as iron hydrides. This quantity has not been measured directly, due to the difficulty of performing in situ experiments on high-pressure iron hydrides, but multiple lines of evidence suggest α < 1, i.e., a negative isotope effect. One reasonable way to assess the possible range of α is to use the following relationship: $\alpha=[(D/H)^{iron\text{-}liquid}/(D/H)^{H2\text{-}gas}]\cdot[(D/H)^{H2\text{-}gas}/(D/H)^{H2O\text{-}fluid}]\cdot[(D/H)^{H2O\text{-}fluid}/(D/H)^{silicate\text{-}melt}]$. In the light of the only reported experiment comparing D and H solubilities in iron liquid [19], the first item of the formula, $(D/H)^{iron\text{-}liquid}/(D/H)^{H2\text{-}gas}$, can be best evaluated by using Sieverts' law while assuming Henry's law is obeyed. The other two items at ~50 GPa and relevant temperature are approximated by extrapolating the experimental results from [20,21]. For the interested conditions in the magma ocean, we consider $0.68 < \alpha < 0.87$.

Results: A family of solutions with two parameters—the isotopic fractionation factor a, and the mass of H_2/He proto-atmosphere accreted—exists in which Earth's mantle retains 3 oceans' worth of hydrogen with its observed ratio. As an illustrative example, if future experiments confirm α = 0.75, and Earth did not accrete an atmosphere, Earth must have accreted 7.6 oceans of hydrogen from chondrites, of which 1.8 oceans' worth end up in the core (with D/H = 101 x 10^{-6}), 3.0 oceans end up in the mantle (D/H = 156 x 10^{-6}), and 2.8 oceans end up in the atmosphere (D/H = 148 x 10^{-6}), eventually to be lost. If α = 0.75 and Earth accreted a massive proto-atmosphere with P_{H2}≈900 bar, adding 30 oceans' worth of hydrogen (with D/H = 21 x 10^{-6}), then it must also have accreted 39 oceans' worth of hydrogen from chondrites, for a total of 69 oceans' worth. Of this, 63.2 oceans must end up in the core (D/H = 83 x 10^{-6}). The increased contributions of isotopically light hydrogen from the solar nebula can be offset by the negative isotopic fractionation that occurs during core formation. For intermediate values of P_{H2}, for every ocean's worth of hydrogen ingassed from the proto-atmosphere, roughly two more oceans' worth of hydrogen must be stored in the core. Similar results obtain across the range of likely α.

Conclusions: Earth probably acquired much of its hydrogen from chondrites, but could have acquired significant fractions of hydrogen from ingassing of nebular hydrogen into the magma oceans of its constituent embryos. Ingassing makes mantle hydrogen isotopically light, but storage of hydrogen in the core raises the mantle's D/H ratio. A family of solutions exists with more ingassed hydrogen offset by hydrogen stored in the core. The discovery of isotopically light hydrogen in the deep mantle strongly suggests a significant ingassed component [7], which we conclude implies a significant amount of hydrogen in Earth's core.

References: [1] Hirschmann, MM (2006) AREPS 34, 629. [2] Pearson, DG et al. (2014) Nature 507, 221. [3] Schmandt, B et al. (2014) Science 344, 1265. [4] Mottl, MJ, et al. (2007) Chem. Erde 67, 253. [5] Hirose, K, Labrosse, S & Hernlund, J (2013) AREPS 41, 657. [6] Hallis, L et al. (2012) EPSL 359, 84. [7] Hallis, L et al. (2015) Science 350, 795. [8] Alexander, C et al. (2012) Science 337, 721. [9] Safarian, AR et al. (2014) Science 346, 623. [10] Morbidelli, A, et al. (2000) MAPS 35, 1309. [11] Raymond, SN, Quinn, T & Lunine, JI (2004) Icarus 168, 1. [12] Weiss, LM & Marcy, GW (2014) ApJL 783, L6. [13] Rogers, LA (2015) ApJ 801, 41. [14] Stokl, A, E Dorfi & H Lammer (2015) A&A 576, A87. [15] Hirschmann, MM, et al. (2012) EPSL 348, 38. [16] Siebert, J et a. (2013) Science 339, 1194. [17] Geiss, J & Gloeckler, G (1998) Space Sci. Rev. 84, 239. [18] Fricker, PE & Reynolds, RT (1968) Icarus 9, 221. [19] Baum, BA et al. (1971) Russ. J. Chem. Phys. 45, 1062. [20] Rolston, JH, Hartog, J & Butler, JP (1976) J. Chem. Phys. 80, 1064. [21] Dalou, C, LeLosq, C & Mysen, BO (2015) EPSL 426,158.