ATMOSPHERIC INGASSING AND OUTGASSING DURING TERRESTRIAL PLANET ACCRETION: IMPLICATIONS FOR WATER, HELIUM-3 AND MANTLE OXIDATION.

Z.D. Sharp[1] and P.L. Olson[1] Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque NM, USA, zsharp@unm.edu, peterleeolson@unm.edu

Introduction: The sources of volatiles to the Earth are unresolved. Multiple ideas have been proposed for Earth's hydrogen, incuding direct ingassing from the solar nebula [1], late delivery by carbonaceous chondrites (the Late Veneer) [2], addition from accreting asteroids and comets as Earth was growing [3,4], scattering of wet planetesimals onto Earth-crossing orbits [4] and delivery of small bodies as the snow line migrated to 1 AU [5]. High $^3He/^4He$ ratios in deeply-sourced mantle rocks require a primordial source for ^3He, either as direct ingassing from a dense nebular atmosphere [6,7] or early addition of planetesimals that had been irradiated by solar wind from the early Sun [8]. All of these models have merits, but there are a number of inconsistancies that exist. Here we show that nebular ingassing explains much of the data and eliminates the inconsistencies inherent in the other models.

The late veneer model has received considerable acceptance because it explains the high highly siderophile element (HSE) abundance of the mantle and the D/H ratio of the presumed carbonaceous chondrite source matches that of the bulk Earth [9]. However, the isotope ratios of some HSEs ($^{187}Os/^{188}Os$ and $^{100}Ru/^{101}Ru$) are similar to anhydrous enstatite and ordinary chondrites but not water-rich carbonaceous chondrites [10,11]. The late veneer model does not explain the high $^3He/^4He$ ratio of the primitive mantle, making a late veneer C chondrite source problematic. The addition of solar-irradiated corposular material explains both He and Ne isotope ratios [12], but it is hard to envison how He delivered from impacts would be incorporated into the growing planet rather than being degassed and lost to space. We show that nebular ingassing is an efficient mechanism for ingassing of both H and He as long as the nebula persisted until Earth reached ~80‰ of its present size. The subsequent degassing of H_2 following nebular dissipation would raise the $f(O_2)$ of Earth's mantle such that the HSEs sourced in the metal component of later impacts would dissolve into the mantle, explaining the high HSE abundance observed in the mantle today.

Modeled ingassing and outgassing: Here we use a boundary layer model of atmosphere-ocean gas exchange to quantify the acquisition and loss of hydrogen and helium to a magma ocean from a nebular atmosphere during terrestrial planet accretion. Our model assumes that surface pressure and temperature increase with planet mass to maintain a global magma ocean during the nebular atmosphere lifetime, that the gas transfer velocity is limited by the solubility and age of the magma ocean surface, and that iron species control the magma oxidation state.

For a wide variety of accretion scenarios our predicted hydrogen ingassing on Earth is several ocean mass equivalents, and still more if core sequestration occurs (Fig. 1). In addition, Earth would have acquired several hundred petagrams of helium-3 from the same nebular atmosphere, more than 100 times the present day inventory [13].

After the dissipation of the nebula, the drop in atmospheric pressure would cause the mantle to be oversaturated with respect to H_2 and degassing into the thin proto-Earth atmosphere would occur. Using the same modeling approach as for ingassing (loss across the surface layer and a 'surface age'), the total H_2 concentration of the mantle would decrease as long as there was a continual high rate of bombardment to maintain a fresh surface layer (Fig. 2). Loss of H_2 would have a dramatic effect on raising the $f(O_2)$ of the mantle [14]. Modeling the $f(O_2)$ using the reaction

$$3\ FeO + H_2O = Fe_3O_4 + H_2 \text{ and } Fe^{3+}/Fe^{2+}$$

in basalt as a proxy for $f(O_2)$ [15], we find that a $Fe^{3+}Fe^{2+}$ ratio equivalent to the fayalite-magnetite-quartz (FMQ) buffer would be reached several million

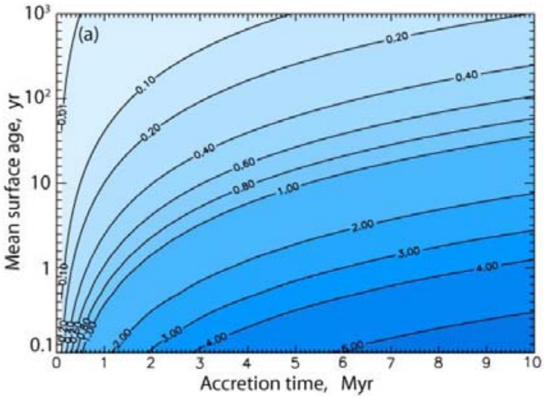

Fig. 1. Final H_2 abundance (in ocean equivalents) from nebular ingassing into a magma ocean as a function of the average age of the surface layer and duration of accretion (age of nebula). A mean surface age of 1 year and accretion time of 5 Ma will generate 3 ocean equivalents H_2.

years after dissipation of the solar nebula (Fig. 3).

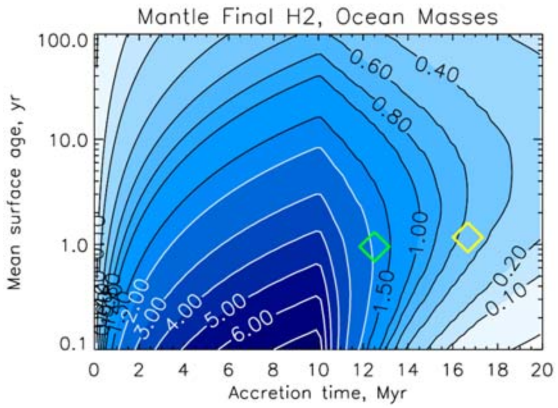

Fig. 2. Final H_2 abundance (in ocean equivalents) assuming that the nebula dissipated at 10 Ma. After that time, H_2 would be lost from Earth's mantle by degassing to space. Green and yellow diamonds both lead to a final *f*(O_2) of FMQ with 2 and 0.4 ocean equivalents addition, respectively. The lower water content for the yellow diamond is due to continued loss of H_2 long after nebualr dissipation.

Raising the *f*(O_2) of the growing Earth has important ramifications for the source of mantle HSEs. Metal grains delivered by accretion following the *f*(O_2) increase would dissolve into the silicate mantle, liberating HSEs in chondritic proportions. The high *f*(O_2) of the the mantle would partially or completely oxidize iron from the impactor, sourced either as emulsified core material from a differentiated body, or discrete metal grains from a chondrite impactor. The high HSE abundance commonly attributed to the late veneer can also be explained by early incorporation of impact material into an oxidized mantle. The Moon-forming Giant Impact event would result in a larger fraction of HSEs being incorporated into the lunar core compared to Earth, explaining the HSE discrepancy between the two bodies.

Overall, the model rectifies some of the problems with previous models and removes some constraints imposed by those models. For example, the D/H ratio of nebular-sourced hydrogen is far lower than the present-day mantle [16,17] and requires additional components of high D/H material [18]. This could be satisfied by some combination of chondrites and comets [14]. It therefore allows for high D/H ratio comets to be a volatile contributor without violating the bulk Earth D/H value. The model also does not require carbonaceous chondites as the late veneer source, eliminating the Os and Ru isotope ratio discrepancy between C-chondrites and Earth's mantle.

Our model also predicts negligible hydrogen and helium-3 ingassing for Mars, but shows that vast amounts (tens of ocean mass equivalents of hydrogen) are possible during the accretion of super Earth-sized terrestrial planets.

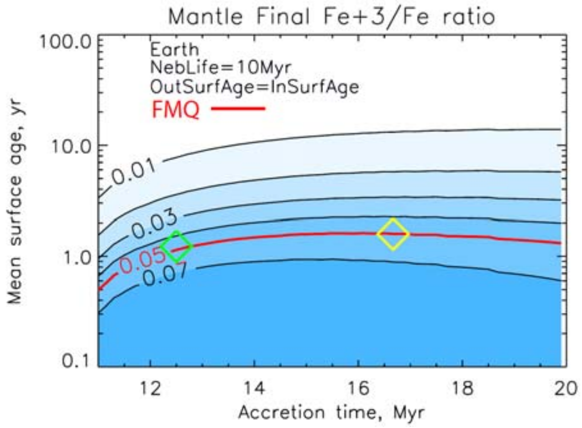

Fig. 3. Calculated Fe^{3+}/Fe_{total} ratios of mantle following degassing of H_2 after nebular dissipation. The FMQ contour is shown in red. A mean surface age of ~1 year will raise the Fe^{3+} concentration from zero to 0.05 in several million years. Any additional material delivered after this time will add HSE to the silicate mantle.

References: [1] Ikoma, M. and H. Genda (2006) *The Astrophysical Journal*, *648,* 696-706. [2] Albarède, F. (2009) *Nature*, *461,* 1227-1233. [3] Raymond, S.N., T. Quinn, and J.I. Lunine (2006) *Icarus*, *183,* 265-282. [4] Morbidelli, A., et al. (2000) *Meteoritics & Planetary Science*, *35,* 1309-1320. [5] Sato, T., S. Okuzumi, and S. Ida (2016) *Astronomy & Astrophysics*, *589, 19 pp.* [6] Mizuno, H., K. Nakazawa, and C. Hayashi (1980) *Earth and Planetary Science Letters*, *50,* 202-210. [7] Porcelli, D., D. Woolum, and P. Cassen (2001) *Earth and Planetary Science Letters*, *193,* 237-251. [8] Trieloff, M., et al. (2000) *Science*, *288,* 1036-1038. [9] Alexander, C.M.O.D., et al. (2012) *Science*, *337,* 721-723. [10] Walker, R.J., et al. (2002) *Geochimica et Cosmochimica Acta*, *66,* 4187-4201. [11] Fischer-Gödde, M. and T. Kleine (2017) *Nature*, *541,* 525-527. [12] Ballentine, C.J., et al. (2005) *Nature*, *433,* 33-38. [13] Tolstikhin, I.N. and B. Marty (1998) *Chemical Geology*, *147,* 27-52. [14] Sharp, Z.D. (2017) *Chemical Geology*, *448,* 137-150. [15] Helgason, Ö., S. Steinthorsson, and S. Morup (1989) *Hyperfine Interactions*, *45,* 287-294. [16] Deloule, E. and F. Robert (1995) *Geochimica et Cosmochimica Acta*, *59,* 4695-4706. [17] Deloule, E., F. Robert, and J.C. Doukhan (1998) *Geochimica et Cosmochimica Acta*, *62,* 3367-3378. [18] Dauphas, N., F. Robert, and B. Marty (2000) *Icarus*, *148,* 508-512.