THE FATE OF H ON MINI-NEPTUNES AND SUPER-EARTHS.

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Summary: Small-radius $R < 4_{Earth}$ exoplanets are found in two modes: an $R > 1.8\ R_{Earth}$ mode with density much less than rock, and an $R < 1.8\ R_{Earth}$ mode with bulk density indicating Earth-like composition [1-2]. Low-density mini-Neptunes around stars with solar or near solar metallicity probably have H_2-rich atmospheres, based on elemental abundances, cosmochemistry, the position and insolation-dependence of the radius break between the two planets, and planet evolution models [3]. The nature of the atmospheres on the $R < 1.8\ R_{Earth}$ Super-Earths is not known. Hypotheses (which could both be true) include (a) Super-Earths today have radii that are boosted by high-molecular weight atmospheres outgassed from the planetary interior [4], and/or (b) many Super-Earths had H_2-dominated atmospheres, now lost [5].

How much H do mini-Neptunes contain, and where is it? Key H stores include H/H_2 in the volatile-rich envelope ("atmosphere"); H_2O in the atmosphere; H/H_2 contained within silicate (magma or rock) [6]; and H_2O dissolved in the rock, for example as OH. Another possibility is H dissolution into liquid Fe metal and sequestration in a Fe-metal core. Chemically reduced carbon compounds may also contain H; for simplicity we omit consideration of them here. The H content of mini-Neptunes is a key parameter for models of planet growth and atmosphere loss – as well as for determining if a mini-Neptune can evolve into a Super-Earth.

The prevailing view:

Basic and sophisticated models agree that if a Super-Earth (in a ~10 day orbit, typical for known exoplanets) gathers ~1% of its own weight in solar-composition gas, then its radius today will be approximately double the bare-rock radius, neatly explaining the bimodality [7]. Because they match data, such models have influenced planet formation theory, and motivate the idea that many Super-Earths are "evaporated cores" of mini-Neptunes.

However, these models treat the remaining 99% of the planet's mass – rock plus Fe-metal – as chemically inert. To the contrary, the volatile-silicate boundary is high-pressure (~10 kbar), both permeable and chemically reactive, and hot (>liquidus temperature for silicates). Magma above the liquidus is runnier than water, so if the magma convects, then the magma and atmosphere will be equilibrated on geologic timescales.

A thought experiment:

Consider a silicate magma that is redox-buffered by a reaction like

$$(1\text{-}x)\mathrm{Fe} + \tfrac{1}{2}\,\mathrm{O_2} = \mathrm{Fe_{1-x}O} \qquad (1)$$

i.e. an Fe-"FeO" buffer. With x ~= 0.05, this can be thought of as the iron-wüstite / IW buffer; however we apply the buffer to temperatures above the wüstite melting point. To fix ideas, we neglect all elements except for Fe, Mg, Si, O, and H, suppose that 1600 K < T < 2500 K so that the rock is molten but the vapor pressure of the magma is a small fraction of the total atmospheric pressure [8], and suppose further that pressures at the interface are <1 kbar so that for the purposes of order-of-magnitude calculation we can treat the atmospheric gases as ideal. The oxygen fugacity fO_2 is then given by standard data [compiled in table 10-16 of ref. 9]. fO_2 scales as the square of the activity of wüstite (e.g., [10]). This is confirmed by the output of our Gibbs free energy minimization code, IVTAN, for the Fe-Mg-Si-O-H system. For example, if Fe/(Fe+Mg) = 0.1 in the magma, then (setting activities proportional to concentrations) fO_2 is $\sim 10^2 \times$ lower than the IW buffer – adopting a $\log_{10}$ scale, this is "IW-2". The H_2/H_2O ratio in the envelope is set by fO_2 [9], via $H_2 + \frac{1}{2} O_2 = H_2O$. Thus, the net reaction is $FeO + H_2 = Fe + H_2O$. The H_2 solubility at the top of the magma layer is approximated following [6,11], and the H_2O solubility at the top of the magma layer is approximated by [12]. We then find mass balance for H between the four reservoirs.

The main result is that even for IW-2 or IW-4, it is very easy for most H to be stored in the magma as H_2O, even when the atmosphere is mostly H_2, and even when H is derived from the nebula and not from outgassing. This is because H_2O is much more soluble in silicate magma than is H_2. This is in addition to the previously noted [6] effect of H dissolution into the magma. As a result, the fate of H in mini-Neptunes is to cycle between the atmosphere and the magma, and the mole ratio of (H stored in the atmosphere)/(H stored in the magma) is small. Thus the fraction of H in the atmosphere is small, and this holds more strongly if H dissolves in an Fe-metal core. It is interesting that planet formation even from enstatite chondrites (which are extremely reducing) predicts mantle oxygen fugacity of ≥(IW-3.2) according to the model of [13]. Oxidation states similar to that carbonaceous chondrites, ordinary chondrites, or achondrites predict higher mantle FeO than for enstatite chondrite composition. Buffers like (1) can be overwhelmed if so much H is added from the nebula that *all* Fe is reduced to Fe^0. The amount of H needed for this will be controlled by the oxidation state of the embryos

(±pebbles) that collide to form the rock+metal cores, as reflected by silicate FeO content.

Discussion.
On Earth, most reducing power is sequestered at the center of the planet as an Fe core. But this is increasingly difficult at the T > 4000K temperatures predicted by mini-Neptune evolution models [14], because metal and silicate are increasingly miscible at T > 4000K [15].

Open questions include: (1) *Can the inflated radii of mini-Neptunes be explained by H_2O delivery to Fe-metal-rich worlds, and subsequent outgassing of H_2, without accretion of nebular H_2?* This has been shown to be (just) stochiometrically possible [16]. However, adding the requirement of chemical equilibrium, and considering C delivery, strongly supports the prevailing view that the mini-Neptune densities and radii require accretion of nebular gas. (2) *What is the maximum exoplanet radius boost for outgassing?* This is important for interpreting the densities of short-period Super-Earths detected by Kepler and TESS, and for constraining the origin of the volatile envelopes of small-radius exoplanets closer to the habitable zone.

At the conference, we will present our answers to these open questions, and discussion of the fate of H on mini-Neptunes and Super-Earths with magma-ocean surfaces at higher T and P.

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