HYDROGENATION OF THE MARTIAN CORE BY HYDRATED MANTLE MINERALS WITH IMPLICATIONS FOR THE EARLY DYNAMO. J. G. O'Rourke* and S.-H. Shim, School of Earth and Space Exploration, Arizona State University, Tempe, AZ, *jgorourk@asu.edu.

Introduction: Mars is unique because its lower mantle may store orders of magnitude more water than the basal mantles of smaller (Mercury) and larger (Earth) planets that are composed of different silicate mineral phases. Most models treat the core of Mars as an iron/sulfur alloy [1,2]. However, hydrogen may enter the core via redox reaction with hydrated silicates during accretion [3] and at later times at the core/mantle boundary (CMB) [4]: Fe (core) + H_2O (mantle) = 2H (core) + FeO (mantle). The partition coefficient for hydrogen between solid ringwoodite and liquid iron at CMB pressures was measured as ~26 (molar ratio) [4], meaning that nearly all hydrogen would enter the metal at thermodynamic equilibrium. One study inferred a partition coefficient of ~0.2 based on sample analyses after quench to ~1 bar [5], but some unknown amount of hydrogen escaped the metal during decompression in those experiments. Recent work suggests that Fe-S-H may form immiscible fluids in the Martian core [6], as proposed for the Fe-Si-O system in Earth's core [7]. In any case, mantle dynamics control the rate at which hydrated silicates are delivered to the CMB to react.

Previous studies disagreed about whether the core of Mars can become hydrogenated over time. One study proposed that nearly all hydrogen from a putative Late Hesperian/Early Amazonian ocean is now stored in the core [4]. However, later work argued that transport in the basal mantle is too slow to deliver much hydrogen to the core [8]. Our now-published study [9] revisited this debate (Figure 1). We found that most of the water that the Martian mantle originally contained could have been lost to the core. Calculated hydrogen fluxes across the CMB are high enough to form a stable layer in the core that could await detection today [10] and possibly caused the early demise of the dynamo.

Methods: We incorporated redox reaction at the CMB into a previously published, parameterized model for thermal evolution with mantle dynamics in the stagnant-lid regime [11]. Convective overturn of the boundary layer in the lower mantle determines the total heat flow out of the core and the flux of hydrogen into the core. The total mass flux is approximately

$$\left(\frac{dM_H}{dt}\right)_{cmb} = 2A_C\rho_M\Delta C_{H,BL}\left(\frac{D_{H,BL}}{\pi t_{ov}}\right)^{\frac{1}{2}},$$

where A_C is the surface area of the CMB, ρ_M is the density of the lower mantle, $\Delta C_{H,BL}$ is the difference between the hydrogen content of the core and lower mantle, and t_{ov} is the overturn timescale. The most critical parameter is $D_{H,BL}$: the effective diffusivity of hydrogen in the boundary layer. The diffusivity of hydrogen in solid wadsleyite and ringwoodite has been estimated to range from ~10^{-10} to 10^{-5} m^2/s near the CMB of Mars, although recent experiments [12] and simulations [13] favor values towards the middle of this range (i.e., 10^{-8} to 10^{-7} m^2/s). However, the core is plausibly hotter than the wet solidus of the mantle. Partial melting of the mantle boundary layer could raise the effective diffusivity of hydrogen to orders of magnitude above its diffusivity in solid silicates.

We used an updated model of the core to better compute the thermodynamic budget for convection and any dynamo. In particular, the thermal conductivity of the core is tuned so the dynamo dies ~500 Myr after accretion, consistent with observations [14]. Fluid dynamics with spherical geometry, rotation, chemical stratification, and magnetic fields are very complicated. Future work is required to describe all the phenomena that may occur [15].

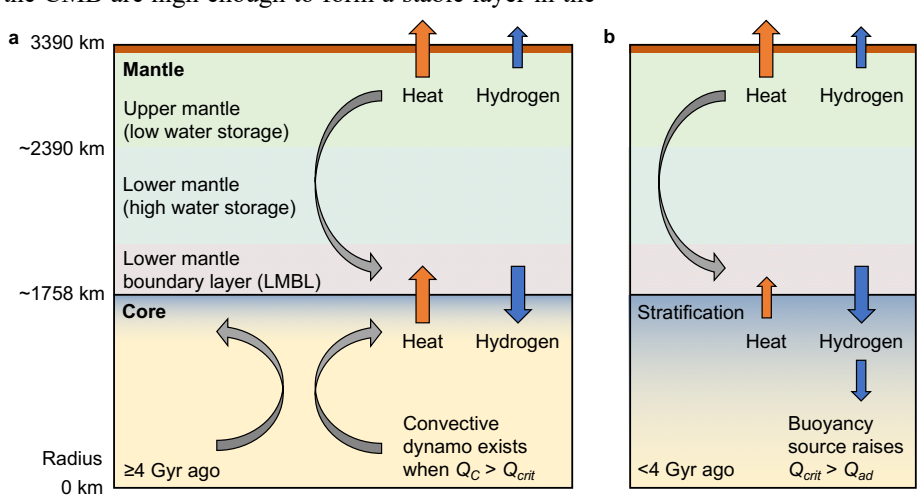

Figure 1. Convective overturn of the lower mantle drives cooling of the core and hydrogenation, which produces a stratified layer and can sap energy from the dynamo [9].

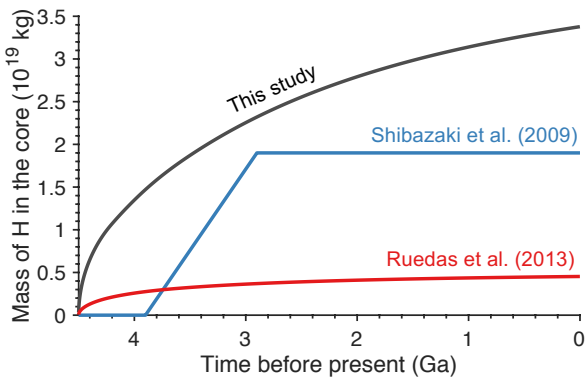

Figure 2. Mantle convection delivers an ocean-worth of H to the core. Our model (black) [9] with $D_{H,BL} = 10^{-6}$ m^2/s compared to scaling analysis (blue) [4] and a diffusion calculation (red) [8].

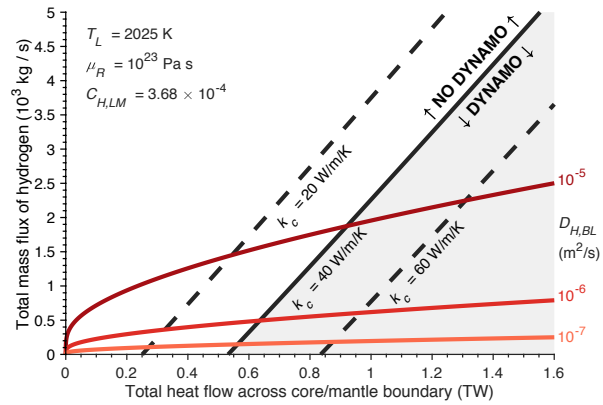

Figure 3. Hydrogenation increases the minimum heat flow required to drive a dynamo. Black lines are the critical mass fluxes above which the convecting system does not have enough energy to mix hydrogen throughout the entire core for plausible values of thermal conductivity in the core (~20–60 W/m/K). A stratified, hydrogen-rich layer would grow at the top of the core and/or convection in the deeper core would cease. Unlike chemical processes in Earth's core such as inner core growth that lower the critical heat flow below the "adiabatic limit" for thermal convection in the absence of chemical processes, hydrogenation raises the critical heat flow. Hydrogenation could shorten the lifespan of the dynamo by ~500 Myr or more relative to predictions from standard models.

Results: Figure 2 shows the cumulative amount of hydrogen that is lost to the core from the mantle. In our nominal model, the viscosity structure and evolution of the mantle potential temperature are consistent with petrologic studies [16] and dynamical simulations [17]. The temperature of the core near the CMB is 2700 K initially and exceeds the dry solidus of the mantle for ~4 Gyr before decreasing to ~2300 K after 4.5 Gyr. If the effective diffusivity of hydrogen is $D_{H,BL} \geq 10^{-7}$ m^2/s, then the equivalent of the proposed ocean [4] is lost to the core. The FeO content of the mantle is predicted to increase by ~0.25 wt% over time if $D_{H,BL} \sim 10^{-6}$ m^2/s.

Figure 3 illustrates the potential impact on the dynamo of hydrogenation. Adding buoyant material to the top of a convecting system can sap gravitational energy, reducing the total dissipation available for a dynamo. This effect is mathematically equivalent to raising the thermal conductivity of the core, which is also an entropy sink. For example, if the lower mantle was initially water-saturated, then $(dM_H/dt)_{cmb} \sim 400$ kg/s at ~500 Myr, which could shut down the dynamo at that time given a thermal evolution that would otherwise sustain it until ~1 Gyr or longer. However, hydrogen that remains in a stratified layer at the top of the core only weakly affects the convecting system. Future work is necessary to determine how hydrogen that crosses the CMB actually affects convection.

Implications: Any study of the water budget of Mars must consider the core as reservoir of hydrogen. Redox reaction at the CMB should be incorporated into dynamical simulations of mantle convection. Our parameterized models suggest enough water to form a global ocean with a depth >0.25–1 km has been effectively lost to the core and the mantle FeO-content has increased. The depth of this "lost ocean" could be as large as ~7 km if the basal mantle were water-saturated and partial melting speeds transport near the CMB.

Elevated CMB heat flow could have persisted beyond the Noachian if hydrogenation subdues the dynamo. Standard models assume that CMB heat flow was sub-adiabatic after ~500 Myr, otherwise thermal convection in the core would sustain the dynamo. However, high heat flow is perhaps preferred to stabilize mantle plumes under Tharsis and Elysium [18]. In general, Mars-sized planets could be uniquely ill-suited to maintaining long-lived global magnetic fields.

References: [1] Khan et al. (2018) *JGR:Planets*, *123*, 575–611. [2] Rivoldini et al. (2011) *Icarus*, *213*, 451–72. [3] Gudkova & Zharkov (2004) *PEPI*, *142*, 1–22. [4] Shibazaki et al. (2009) *EPSL*, *287*, 463–70. [5] Clesi et al. (2018) *Sci. Ad.*, *4*, e1701876. [6] Shim et al. (2019) *EPSC-DPS*, #188. [7] Arveson et al. (2019) *PNAS*, *116*, 10238–43. [8] Ruedas et al. (2013) *PEPI*, *220*, 50–72. [9] O'Rourke & Shim (2019) *JGR:Planets*, *124*, doi:10.1029/2019JE005950. [10] Helffrich (2017) *PEPS*, *4*, 24. [11] Fraeman & Korenaga (2010) *Icarus*, *210*, 43–57. [12] Sun et al. (2015) *GRL*, *42*, 6582–9. [13] Caracas & Panero (2017) *PEPS*, *4*, 1–11. [14] Acuña et al. (1999) *Science*, *284*, 790–3. [15] Bouffard et al. (2017) *JCP*, *346*, 552–71. [16] Filiberto (2017) *CG*, *466*, 1–14. [17] Plesa et al. (2018) *GRL*, *45*, 12198–209. [18] Kiefer & Li (2016), *MPS*, *51*, 1993–2010.