CRYSTALLIZATION OF MERCURY'S SULFUR-RICH MAGMA OCEAN. S. W. Parman[1], E. M. Parmentier[1] and S. Wang[1], [1]Department of Earth, Environmental and Planetary Sciences, Brown University, Providence RI 02906. Email: stephen_parman@brown.edu

Introduction: The flotation of buoyant phases during the solidification of Mercury's magma ocean (MMO) would have a substantial effect on its evolution. On the Moon, plagioclase was the buoyant phase, forming the anorthositic flotation crust that acted as stagnant lid, lowering heat flow and slowing solidification of the lunar magma ocean. However, due to the low FeO contents of the MMO, feldspar is not expected to be buoyant at any point in MMO solidification (Figure 1, [1]), and is not observed on the surface [2]. Buoyant graphite is hypothesized to form in the MMO, but this layer would be too thin (10-100 m) to form a conductive lid [1].

MESSENGER observations suggest that Mercury lavas are S-rich, likely due to very low fO_2 [2]. If the MMO was similarly S-rich, large amounts of sulfide may have been produced. Here we examine whether these sulfides could form a flotation crust and whether such a crust would be physically stable.

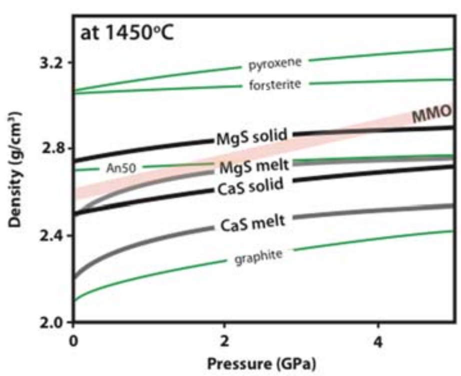

Figure 1. *Density of phases relevant to MMO crystallization. Density of liquid MMO (red band), pyroxene, forsterite, An50 feldspar and graphite from [1]. Densities of solid MgS and CaS from [3] with correction to 1450°C using a thermal expansivity of 0.000017/K. 8-9% density reduction upon melting estimated from FeS equation of state [4].*

A sulfide lid?: Early forming sulfide would be liquid FeS [5,6]. This would be much more dense (>4 g/cm^3) than the MMO and sink (Figure 1), forming a layer on top of the core [8]. Subsequent sulfides would be Mg-rich, with lesser amounts of Cr, Ca, Mn and Ni [7]. Solid MgS (niningerite) is more dense than the MMO, but MgS liquid is likely to be less dense (Figure 1). Pure MgS has an extremely high melting point (>2000°C), which decreases rapidly as it mixes with other sulfide components the range 1000-1500°C. So segregation of liquid Mg-rich sulfide is possible. However, as it cooled and solidified at the surface, it would become negatively buoyant.

Both solid (oldhamite) and liquid CaS will be buoyant in the MMO (Figure 1). Ca-rich sulfide has not been found in abundance in experiments simulating up to 70% crystallization of the MMO from log fO_2 from IW-2 to IW-7 [7]. However, as the Ca concentration of the MMO increases during fractional crystallization of olivine and orthopyroxene, Ca-rich sulfide is likely to be stabilized. As with the Mg-rich sulfide, it will be not be pure CaS but will have substantial Mg, Mn and Cr and a substantially lower melting point (1000-1500°C) than pure CaS (2500°C). Likewise, Na should reach high enough values to potentially stabilize Na-rich sulfide (djerfisherite). This would depend in part on when albite became stable during MMO crystallization. Na-rich sulfide have densities <2.4 g/cm^3, and so would be strongly buoyant in the MMO.

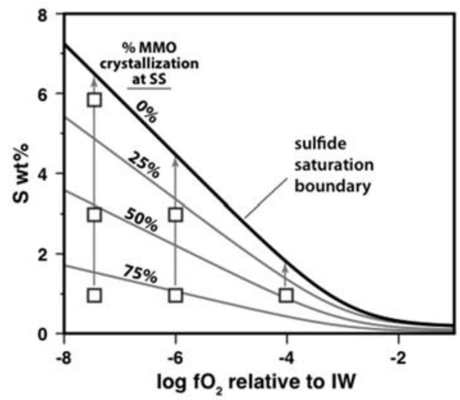

Figure 2. *Experimentally measured S solubility in silicate MMO as a function of fO_2 (thick solid line [5,7]). For S undersatureated MMO, labelled contours show amount of crystallization need to bring MMO to sulfide saturation (by fractionation of silicates). Boxes show cases of varying initial MMO S content (1, 3 and 5.8 wt%, [6]), and varying log fO2 (IW-4, -6 and -7.5). If the MMO started with <1wt% S and at IW-4), sulfide will form only after >50% solidification of the MMO.*

Ongoing experiments are quantifying the compositions of sulfides formed during late stage crystallization of the MMO. For the purposes of this abstract, we will assume that somewhere between 50 and 25% crystallization of the MMO, a buoyant sulfide does form, and that all subsequent sulfide will float to the surface to form a conductive lid.

Thickness and composition of sulfide lid: The point where sulfide will appear in the solidification of the MMO depends largely on the initial S content of the MMO and its fO_2 (Figure 2). The presence of an FeS layer at the bottom of the mantle [8] suggests that the MMO was sulfide saturated throughout the entire solidification of the intial 400 km deep MMO (thick line, Figure 2). This could produce a relatively thick lid (up to 20 km). The early sulfide would be buoyant Mg-rich sulfide melts. Later forming sulfides would be Ca-rich.

However, if there is no FeS "anti-crust" layer, then the MMO may not have been sulfide saturated to begin. While chondritic meteorites have high S contents (5-6 wt%), the Earth has less than 1 wt% bulk S, indicating substantial loss of S during accretion [9]. If this is true of Mercury as well, then 50% or more crystallization would be required to saturate the MMO with sulfide, even at IW-3 (Figure 2). In this case, a relatively thin (~5 km), Ca-rich and buoyant sulfide layer would form from the last 200 km of the MMO.

Physical stability of a sulfide lid: The stability of the solid lid depends on its buoyancy relative to underlying magma and its strength in resisting stresses imposed at its base by thermal convection. Excavation and penetration of the lid by impacting bodies is another potentially important factor influencing the heat flux that we defer to future study.

The vigor of convective motions in a highly turbulent convecting fluid has been well examined. A typical velocity of convective motions is given by

$$u = 0.6\left(\frac{\alpha g F L}{\rho c_p}\right)^{1/3}$$

[10,11]; where L is the convecting layer depth, F is the heat flux, and other symbols have their usual meaning.

Shear stresses at the base of the lid can be estimated by considering the velocity structure of the boundary layer (Figure 3). The velocity at the middle of the convecting layer can be expressed as

$$\frac{u}{u^*} = \log\left(\frac{\rho u L}{2\mu}\frac{u^*}{u}\right)^3 + 5$$

[12]; where the 'friction velocity' u^* is related to viscous stress τ in the layer of laminar viscous flow, with viscosity μ. The shear stress adjacent to the boundary is then $\tau = \rho u^{*2}$.

When a lid is present, heat flux is controlled by conduction through the lid. The thickness of the conductive lid l varies inversely with F. We assume that the strength of the lid, which is expected to be highly fragmented by impacts, is controlled by sliding friction (Bylerlee's law) so that maximum stress that can be supported in the lid is $\sigma = 0.85\rho g l/2$ where the numerical factor is the friction coefficient. We assume that frictional stresses control the strength only in the upper, cold half of the lid.

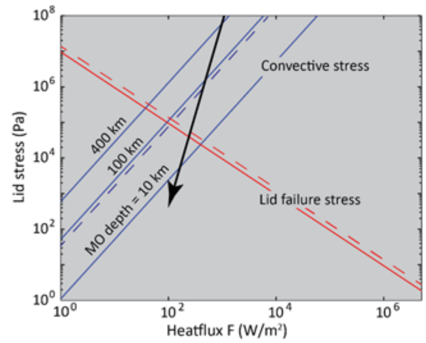

Figure 3. *Stability of a conductive lid: stress in lid due to convective shear stress (blue lines) and lid failure stress (red lines) as a function of heat flux for lid solidification temperatures of 1000°C (solid) and 1500°C (dashed). Convective lid stress shown for three magma ocean depths. The dark bold arrow shows a typical thermal evolution in which the heat flux decreases and the MO thins with time. Lid would become stable where thermal*

Figure 3 compares the stresses due to convection with the strength of the lid as defined above. Convective stresses are shown for three magma ocean depths. The lid is stable for stresses lower than the lid failure stress at a given heat flux (red lines). When the magma ocean is deep and the heat flux is high, no continuous lid can form. The first buoyant sulfide minerals are expected to crystallize at temperatures in range of 1000 - 1500°C. With surface temperatures and radiative heat fluxes in this range, as shown in figure x, convective stresses are well above the lid failure stress. A lid can become stable only as the magma ocean cools and becomes shallower due to solidification, allowing the heat flux to fall below ~10^3 W/m^2.

Conclusions: A buoyant, sulfide-rich conductive lid may form during MMO solidification. Once present, the lid will slow down cooling of the MMO reducing the vigor of convection lengthening the duration of the magma ocean.

References: [1] Vander Kaaden & McCubbin (2015) JGR Planets 120: 195-209. [2] Nittler et al (2011) Science 333: 847-1850. [3] Peiris et al (1994) J Phys Chem Solids 55: 413-419. [4] Nishida et al (2011) Amer Min 96: 864-868. [5] Berthet et al (2009) GCA 73: 6402-6420. [6] Chabot et al (2014) EPSL 390: 199-208. [7] Parman et al (2015) LPSC 46, abstract 2345. [8] Hauck et al (2013) JGR Planets 118: 1204-1220. [9] Dreibus & Palme (1996) GCA 60: 1125-1130. [10] Priestly (1959) Turbulent Transfer in the Lower Atmosphere. [11] Solomatov (2000), Origin of the Earth and Moon. [12] Tennekes & Lumley (1972) A First Course in Turbulence.