SPATIAL PARTITIONING OF SULFUR IN THE MERCURY'S CRYSTALLIZING MAGMA OCEAN.

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Summary: To explain the high sulfur content and low FeO content of the Mercury's surface lavas, it has been proposed that Mercury is deprived of oxygen compared to the Earth, Moon and Mars [1]. Such reducing conditions would lead to significant differences between the evolution of the Mercury magma ocean (MMO) and the canonical Lunar magma ocean. Here, we investigate the formation of sulfide layering produced by the solidification of a global magma ocean in Mercury. We use experimentally determined sulfur solubility in silicate melts [2] to predict the depth at which sulfides precipitate. The model produces primordial sulfide layers whose thickness and locations depend upon the oxygen fugacity and initial sulfur content of the Mercurian magma ocean. A geodynamic model is then used to test under which conditions the initial mineralogical layering can be preserved during the very early evolution of the Mercury's mantle.

Introduction: Much of the surface of Mercury is covered by lavas dating from 4.2 Ga to 3.8 Ga [e.g., 3]. One of the most intriguing aspects of this old planetary surface is the high sulfur (2-7 %Wt) and low FeO (<0.5 Wt %) content of these lavas. A possible explanation is low oxygen fugacity that would significantly affect phase equilibria [e.g., 1, 4] . In a highly reduced silicate MO, iron exists mainly either as Fe or FeS. The absence of FeO in the silicate mantle eliminates flotation of feldspar, as occurred on the Moon. Likewise, compositional overturn driven by a dense illemenite-rich layer overlying high #Mg mafic cumulates also would not occur. The early Mercury mantle dynamic would mainly be governed by thermally driven density contrasts, radioactive heating (to some extent linked to sulfides formation) and density contrast induced by the presence of retained melt. In this preliminary work, we use mass-balance and a sulfur solubility model to predict an idealized initial sulfur stratification in the MMO. A geodynamic model is then used to evaluate the preservation of such stratification.

Initial sulfur stratification – We consider the evolution of an essentially iron-Free MMO occurring after core mantle segregation (or formation of an FeS layer). We assume that a vigorously convecting molten magma ocean overlies a solid cumulate pile. The oxygen fugacity is equal and uniform in both layers. For simplicity, sulfur content at sulfur saturation (SCSS) in the melt depends only on oxygen fugacity and temperature.

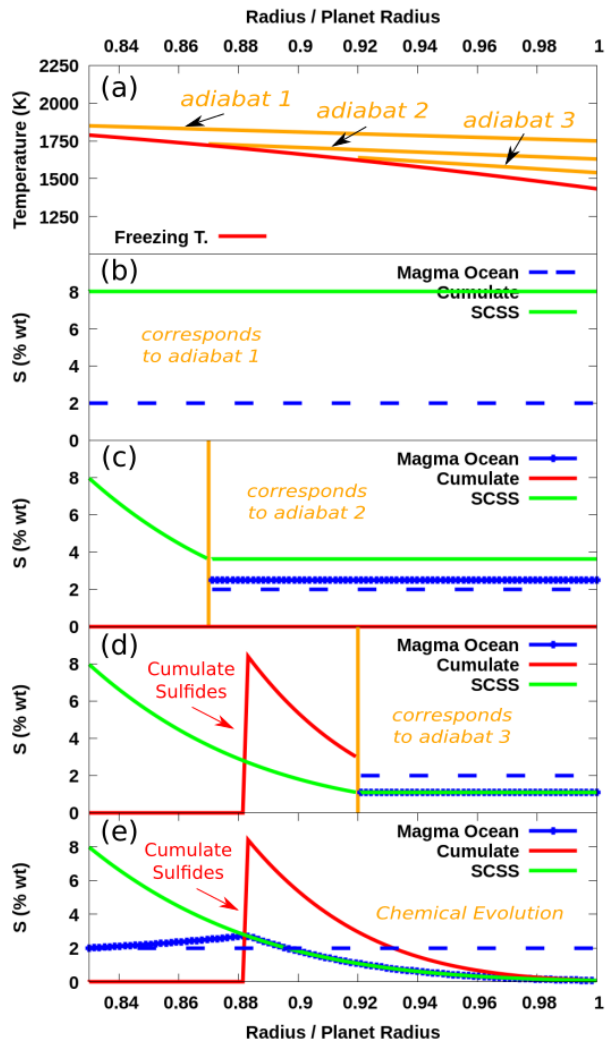

Figure 1 : *Precipitation of negatively buoyant sulfides during Mercury's magma ocean solidification at IW = -6 and with an initial sulfur content of 2 % Wt. (a) A cumulate pile forms at the bottom of the magma ocean when the adiabat (orange) intersects the idealized freezing temperature. (b) Prior to solidification, the magma ocean (containing 2 % Wt of S) is below saturation conditions (8 % Wt of S). (c) Crystallization of S-free silicates phases increases the sulfur content of the magma ocean. As the temperature of the solidification front decreases, the SCSS decreases. (d) The magma ocean has reached sulfur saturation. In order to keep the magma ocean at saturation conditions, sulfides precipitate. (e) Sulfur stratification associated to the crystallization sequence depicted in (b), (c) and (d).*

The temperature in the molten region follows an adiabat, whereas it follows the freezing temperature in the cumulate pile. As temperature increases with depth, SCSS also increases with depth. The density of sulfides remains poorly constrained, therefore two end-member models are considered: (1) sulfides perfectly float in the magma ocean (2) sulfides perfectly settle and accumulate when they form. In the first case, we assume that sulfides exsolve at shallow depth (in the top thermal boundary layer of the MO) and are buoyant enough to not be entrained by convection. In the second case, we assume that the saturation condition (SC) in the molten layer is dictated by the temperature at the solidification front. For instance, sulfides might exsolve at shallow depth, where it is cold, and then dissolve near the solidification front as they would settle and/or be entrained by convection. It is important to note that sulfides can also precipitate as liquid at high temperature. If they are negatively buoyant, they would be trapped in the cumulate pile and freeze later upon cooling. Our approach is based on the following mass-balance in which the total amount of sulfur is conserved,

$$\int_{R_c}^{R} C_s^c(r) r^2 dr + C_s^{MO}(R) \int_{R}^{R_p} r^2 dr = C_s^{init} \int_{R_c}^{R_p} r^2 dr$$

where R_c is the radius of the core, R_p the radius of the planet, R the depth of the solidification front, $C_s^c(r)$ the sulfur concentration in the cumulate pile at radius r, $C_s^{MO}(R)$ the sulfur concentration of the magma ocean and C_s^{init} is the bulk sulfur content of the Mercury's mantle after core-mantle segregation. We depict in Figure 1, a case where sulfides are negatively buoyant. If the magma ocean is below SC, $C_s^c(r) = 0$ (Fig. 1c). If the magma ocean reaches SC, $C_s^c(r) \neq 0$ and the composition of the magma ocean is set to the SCSS (Fig. 1d), $C_s^{MO}(R) = SCSS((T(R), f_{O_2})$ where $SCSS$ is a polynomial fit determined experimentally by [2], $T(R)$ is freezing temperature defined arbitrary halfway between the liquidus and the solidus of a dry lherzolite (see Figure 1.a) [6] and fO_2 the oxygen fugacity. Figure 2 shows the effects of varying initial sulfur content, oxygen fugacity and sulfides buoyancy on the initial sulfur stratification of the Mercury's mantle.

The idealized model presented here demonstrates that the low fO_2 of Mercury can lead to a variety of sulfide layering in the mantle. We are currently investigating the preservation of such primordial sulfur stratification in the Mercury's mantle using a geodynamical model developed for the Lunar magma ocean [6,7]. In particular, the last sulfides to precipitate in the MMO would be enriched in radioactive elements such as U, Th and K that could significantly affect the early thermal evolution of Mercury and the composition of magmas erupted on the surface. We are also investigating the evolution of sulfide composition, which should have significant effects on sulfide saturation and buoyancy.

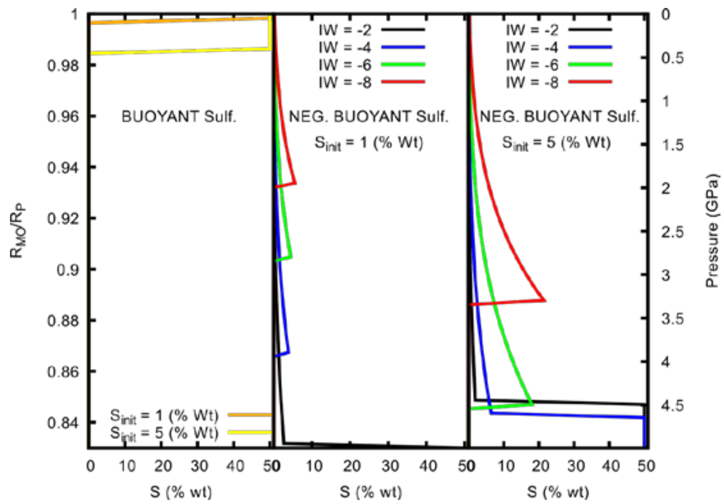

Figure 2: *Primitive sulfur stratification imposed by Mercury's magma ocean solidification. (left) Buoyant sulfides. Sulfides exsolve close to surface due to the low surface temperature that induces very low saturation conditions. If surface temperature is low enough (< 1000K) and oxygen fugacity high enough (IW > -8), the size of this "sulfides" crust depends only on the initial sulfur content. (middle) Negatively buoyant Sulfides -* $\boldsymbol{C_s^{init}} = 1\%$ *Wt. As low* fO_2 *increases SCSS, more reducing conditions delays sulfide saturation in the MO and decreases the depth at which sulfides start to precipitate. (right) Negatively buoyant Sulfides – For* $\boldsymbol{C_s^{init}} = 5\%$ *Wt., the Mercury's magma ocean can be super-saturated in sulfur prior to silicate precipitation if IW < -4. A sulfide layer forms at the bottom of the mantle.*

References – [1] Nittler *et al.* (2011) *Science 333*, 1847-1850. [2] Namur *et al.* (2016) *EPSL 448*, 102 – 114. [3] Head *et al.*, (2011) *Science 333*, 1853-1856. [4] Namur and Charlier (2014), *LPS XLV*, Abstract #1312 [5] Katz *et al.* (2003) *G3* 3. [6] Boukaré *et al.*, (2018), EPSL, in revision. [7] Boukaré *et al.*, (2017), *LPS XLVIII*, Abstract #2494.