Mercury's Early Natargraphite (Carbon) Crust and Sulfide Solubility Bolster Explosive-style Volcanism.

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Introduction: Density and compressibility ranges for Mercury's melt compositions indicate the formation of a buoyant, floatation graphite (carbon) crust during a global magma ocean [1] that was subsequently followed by partial melting and effusive volcanism for ~1 Gyr [2-4]. Using observational data collected from the **ME**rcury **S**urface, **S**pace **EN**vironment, **GE**ochemistry, and **R**anging (MESSENGER) spacecraft, volcanic vent distributions [5-7] and a compositional analysis of surface rocks signify early sulfur- and carbon-driven explosive volcanism during secondary crust evolvement [8]. A highly reducing, sulfur-rich primordial mantle that is capped by a layer of low-density carbon and results in significant pyroclastic eruptions is unique to the terrestrial planets in the solar system. This exotic environment is investigated using a recently developed sulfide solubility model for mercurian partial melts and accompanied by a discussion of eruption influences associated with the post-differentiated graphite crust.

"Natargraphite" definition: In the following discussion, the floatation carbon crust is referred to as "natargraphite," where the prefix *natar-* is derived from the Latin word *natare*, meaning *to swim*, that closely resembles *to float*. This more appropriately defines the outer layer of buoyant graphite formed from Mercury's magma ocean stage.

Mercury's volatile interior: Elevated K/Th and near chondritic K/Cl ratios [9-10] in conjunction with large surface concentrations of sulfur (S) observed by MESSENGER [4] imply Mercury's silicate interior is S-rich relative to the other terrestrial planets and indicates S is a primary volatile clouting the primitive explosive volcanism [8]. To further scrutinize the gross S, compositional experiments representative of mercurian lavas were performed using chemical data of the surface rocks to determine an empirical parameterization for predicting S content at sulfide solubility (SCSS) [11]. This S solubility framework is dependent on oxygen fugacity, melt composition and magma temperature. **Fig. 1** models the SCSS for Mercury's interior with an estimated mantle thickness of ~410 km, oxygen fugacity of 5.4 $\log_{10}$ units below the iron-wustite buffer and a magma density of 3.2 g cm^{-3}. The results indicate primitive partial melts are likely to remain sulfide globule free and S saturated [11] from a decrease in SCSS as the magma encounters lower pressures and temperatures in the shallow subsurface.

Influences of natargraphite crust: Mercury's natargraphite crust formation is analogous to lunar magma ocean crystallization models in which an underlying anorthositic floating crust formed following the Moon's differentiation [12]. The areal extent of pyroclastic deposits on Mercury's surface juxtaposed to the Moon's indicates a greater concentration of shallow magma volatiles that can significantly enhance the explosivity of early eruptions [5]. This implication is explored for the young near-surface mercurian melts through a dialogue of S oversaturation (i.e. excess sulfur compounds) and S exsolution (i.e. separation of gaseous sulfur).

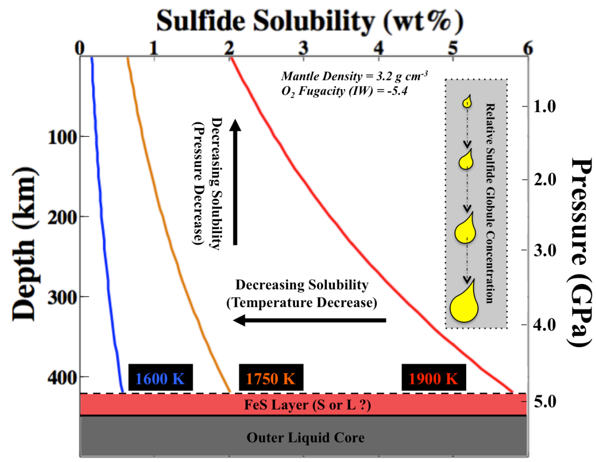

Fig. 1: Pressure effects on SCSS for mercurian melts at 1600 K (blue line), 1750 K (orange line), and 1900 K (red line). Sulfide globules are likely to remain concentrated in the lower mantle near the FeS layer that is either in a solid or liquid state outside the core.

Sulfur oversaturation. Relatively rapid decreases in pressure may result in silicate melts on Earth that can derive oversaturation of magmatic volatiles such as S [13-14]. A recent experimental model demonstrates a concentration of 100–200 ppm S can satisfy mid-ocean ridge basalt sulfide sources parental to Earth's ocean floors at temperatures as low as 1600 K [15]. On Mercury, a primitive partial melt that ascends in natargraphite is likely to undergo a decrease in temperature from near-surface cooler conditions and a decrease in density by carbon assimilation and graphite oxidation [8]. It is thus more proper to assume that a decrease in SCSS for primordial mercurian melts at trivial depths is probable to exsolve additional S analogous to Earth's modern volcanism.

Fig. 2 represents three arbitrary cooling scenarios for a 1750 K magma body in the shallow subsurface of Mercury. The provided cooling schemes indicate as much as 70–250 ppm S oversaturation may institute within the oxidized partial melts. The minimum excess S constraint for Earth-like sulfide sources can therefore be satisfied on Mercury and exsolve S toward the surface to contribute to the early explosive-style volcanism.

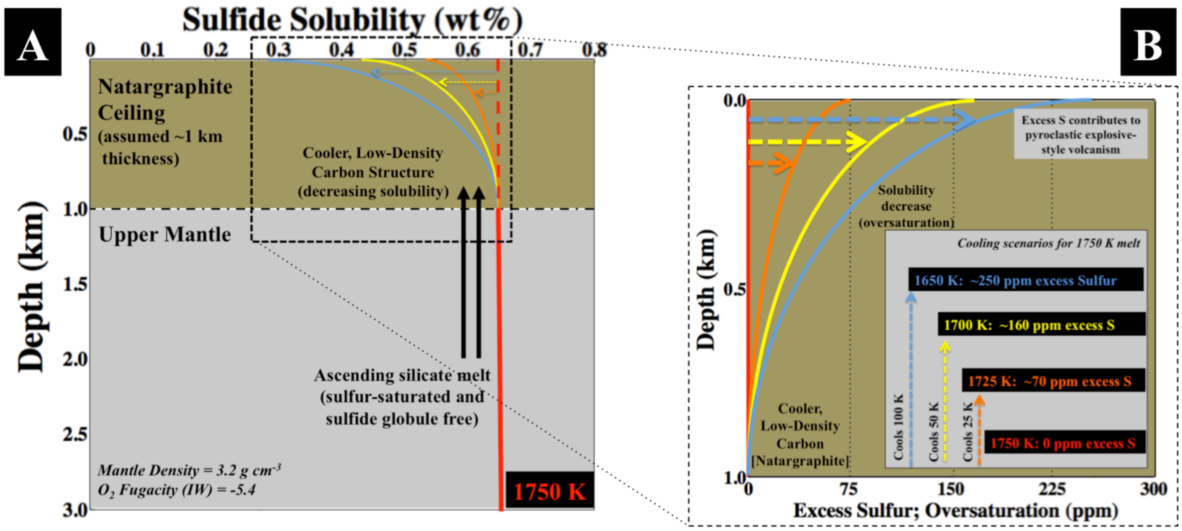

Fig. 2: Cooling scenarios for partial melts on Mercury with a natargraphite crust. Panel [A] models a magma body with a temperature of 1750 K that ascends to a ~1 km thick natargraphite ceiling. Panel [B] demonstrates the total amount of excess sulfur that could separate from the saturated melt (red line) if cooled 25 K (orange line), 50 K (yellow line), or 100 K (blue line). The oversaturation of sulfur from primitive partial melts contributes to the early explosive volcanism on Mercury.

Sulfur exsolution. On Earth, S vapor separation from tholeiitic systems (i.e. alkaline-rich magmas) are expected to exsolve the volatile at a minimum pressure of ~10 MPa [16]. The excess S that partitions from the primitive partial melts on Mercury is likely to supply to the pyroclastic volcanism as a gaseous compound due to magma temperatures being above, and pressures below, the critical point of S (1314 K, 20.7 MPa). Assuming primordial mercurian melts are analogous to Earth's tholeiitic systems, extensive separation of S compounds would presume to occur at a minimum depth of ~0.8 km.

Surface analyses of the areal extent of pyroclastics on Mercury indicate a higher explosivity of early eruptions in comparison to young lunar volcanism [6-7]. Post-differentiation resulted in a denser floatation anorthositic crust for the Moon and a less dense natargraphite layer for Mercury. This suggests primitive partial melts in shallow magma chambers on Mercury may have undergone a more abrupt decrease in pressure than lunar melts that results in further excess S to segregate. The generation of elevated explosivity for primordial mercurian eruptions can therefore be dependent on the total graphite oxidation and natargraphite thickness. The estimated thickness of the natargraphite layer is ~0.1 m–21 km [1] and the disassociation of gaseous S compounds is predicted to ensue near a depth of ~0.8 km. For a high probability of large early explosive eruptions, a minimum thickness of ~0.1 m–0.8 km could provide the necessary environment for primitive mercurian melts to subsidize additional S to the pyroclastic volcanism.

Summary: Mercury's ancient global floatation graphite crust, referred to here as natargraphite, is significant and unique to the terrestrial planets. Oversaturation of sulfur in shallow magma chambers that trifle the natargraphite ceiling contribute to the early explosive-style volcanism on Mercury. The minimum excess sulfur constraint for Earth-like sulfide sources can be satisfied for primordial volcanism on Mercury and exsolve gaseous sulfur that can supply the pyroclastic eruptions. Extensive separation of vaporous sulfur compounds is expected at a depth of about 0.8 km assuming the primitive mercurian melts are analogous to Earth's tholeiitic magmas. A minimum low-density graphite thickness limitation of ~0.1 m–0.8 km can gratify the generation of greater explosivity for the adolescent eruptions on Mercury compared to early lunar volcanism that is associated with a floatation crust composed of denser anorthosite.

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