

CONSTRAINT ON DENSITY JUMP AT THE INNER CORE BOUNDARY FROM SILICON AND SULFUR PARTITIONING BETWEEN MERCURY'S INNER AND OUTER CORE. Yingwei Fei¹, Renbiao Tao¹, and Jing Yang¹, ¹Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C., USA (fei@gl.ciw.edu).

Introduction: New measurements of the surface chemistry and geophysical data of Mercury by the MESSENGER spacecraft have renewed the discussions on the interior compositions and led to new models of the internal structure [1-8]. It is generally considered that Mercury had accreted under reduced environment. Under highly reduced core-forming conditions (e.g., at oxygen fugacities of at least 4 log unit below the iron-wüstite buffer), silicon (Si) and sulfur (S) are expected to be the dominant light elements in Mercury's core. Previous core density models have focused on the effect of S on an iron-dominant Mercury's core and few new models have examined the combined effect of S and Si. Because of limited experimental melting and element partitioning data in the multi-component systems, those models often explore a range of composition without the rigorous chemical equilibrium constraints and melting relations in the complex systems. Here we present new experimental data on the melting relations in the Fe-Si-S system up to 36 GPa, corresponding to the center pressure of Mercury. The Si and S partitioning data between solid and liquid as a function of pressure are used to evaluate the light element distribution in the core as the growth of the solid inner core and to independently constrain the density jumps at the inner core boundary (ICB) for a series of density profiles that closely match the mass, radius and moments of inertia of Mercury. We also explore the effect of immiscible liquids in the system on the possible formation of stratified liquid layers at the top of the core.

Experiments: This study aims to obtain the melting relations and light element partitioning between metallic solid and liquid at high pressure and temperature to develop models for Mercury's core structure. We have conducted experiments in the Fe-Si-S system up to 36 GPa and 2023 K, using mixtures of pure Fe, FeS, and Fe-17wt.%Si alloy powders as starting materials. Experiments at pressures less than 25 GPa were carried out in multi-anvil device using conventional tungsten carbide cubes as the second-stage anvils with the similar experimental procedure described in our previous study in the Fe-S-C ternary and Fe-S-Si-C quaternary systems [9]. The starting materials were loaded into pre-dried MgO capsules inserted into a Re cylindrical heater. Temperatures were measured using a Type-C thermocouple and pressures were calibrated with fix points of phase transitions [10].

We have also developed new experimental configuration using large sintered-diamond cubes as the anvils, that allows us to perform experiments at conditions over the entire pressure-temperature range of Mercury's core. Pressure of the new configuration used in this study has been calibrated by the room-temperature phase transitions in zirconium at 8 and 35 GPa, characterized by sharp changes in resistance [11]. The measurements of the solubility of Al₂O₃ in Mg-bridgmanite [12] are used to establish the pressure calibration at high temperature.

The recovered samples were analyzed with a JEOL JXA-8530F Field Emission electron probe using appropriate standards, a beam current of 30 nA, and a 15-kV voltage with conventional ZAF data reduction procedure. Melt compositions were obtained with a 10- μ m defocused probe beam.

Results: Built on knowledge of melting relations in the Fe-FeS system [13], we determined the melting relations in the Fe-Si-S system at 15 GPa and 21 GPa. Additional experiments were performed at pressures between 25 and 36 GPa to determine the effect of pressure on melting relations. We obtained the change of the liquidus temperature as a function of Si and S contents. For a bulk composition of 90 wt.% Fe + 6 wt.% S + 4 wt.% Si, it melts completely at 1650 K at 15 GPa and 1900 K at 21 GPa. The melting temperature is a strong function of the S concentration. We have also determined the Si and S partitioning between solid and liquid from the eutectic temperature to melting temperature of Fe-Si alloy. The partition coefficient of Si between liquid and solid is a strong function of temperature and $\log D_{\text{Si}}$ can be linearly correlated to $1/T$. At 21 GPa, $\log D_{\text{Si}} = 0.754 - 1885/T$.

Discussion: Mercury has a large metallic core with a center pressure of ~36 GPa. Planetary formation processes involving radioactive heating, accretion energy, and giant impact likely led to a completely molten core at the early stage of the history. Subsequent cooling would lead to crystallization of a solid inner core. The evolution of the inner core is closely related to the thermal evolution of the interior and the core composition which defines the ICB temperature using its melting temperature. The light element partitioning between solid and liquid also defines the density jump at the ICB.

Crystalizing from a molten Fe-Si core, the stable crystal phase and density of the inner core depend on

the Si content. For example, a composition of Fe+16wt%Si would form an inner core with an Fe-Si alloy with D03 structure ($Fm\bar{3}m$ space group) according to recent study of phase transitions in the Fe-FeS system [14]. On the other hand, a face-centered cube (fcc) Fe-Si alloy is expected to crystallize at the center initially. As the inner core grew with further cooling, it may develop a layered structure with a denser hcp (hexagonal-close-packed) phase at the center followed with a fcc phase, because a fcc-hcp phase transition in Fe+9wt%Si occurs below the 36 GPa, with a positive Clapeyron slope [15]. The density change to a liquid outer is relatively small (~2%) because Si partitions almost equally between the liquid outer core and the solid inner core. The compositional buoyancy would not be a driving force for outer core convection, which could affect the generation of Mercury's magnetic field.

The temperature required for crystallizing an solid inner core can be constrained from the melting relations in the Fe-FeSi system [14-18] for an Fe-Si core. The Fe+16wt%Si core would solidify at about 2500 K [15]. Adding S into the core would significantly reduce the temperature to form the inner core. Based on our experimental measurements of the effect of S on the melting temperature, incorporation of 5 wt% S in the core would reduce melting temperature over 300 K. More importantly, strong partition of S into the liquid would significantly enhance the density jump at the ICB. For example, the S and Si partitioning would lead to ~12% density jump at the ICB when the liquid outer core contains about 5 wt % S. From our new data on melting relations and element partitioning, we can now calculate the density jumps at ICB as a function of radius for a model Fe-Si-S core composition. The larger the inner core grows, the bigger the density jump at ICB gets. The density difference at ICB determines the compositional buoyancy that has important implication for the generation of Mercury's magnetic field.

The Fe-Si-S system forms two immiscible liquids at pressures below 14 GPa [19, 20]. For an Fe-Si-S core, the top of the liquid outer core could be stratified because of the existence of the two immiscible liquids, S-rich and Si-rich liquids. The density difference between the two immiscible liquids could be significant, ~ 7% between the coexisting Fe-28wt%Si-2wt%S and Fe-6wt%Si-8wt%S. Considering all the possible density jumps in the core, Mercury could have four layers in the core caused by a structure phase transition in the solid inner core and two immiscible liquids in the liquid outer core. The multi-layered structure would have important effect on the dynamics and thermal structure of Mercury's core. It also adds additional variables for a model to satisfy the geophysical observations, particularly the moments of inertia of Mercury.

References: [1] Smith D. E. et al. (2012) *Science*, 336, 214-217. [2] Hauck S. A. et al. (2013) *JGR*, 118, 1204-1220. [3] Rivoldini A. and Van Hoolst T. (2013) *EPSL*, 377, 62-72. [4] Knibbe J. S. and van Westrenen W. (2015) *JGR*, 120, 1904-1923. [5] Chabot N. L. et al. (2014) *EPSL*, 390, 199-208. [6] Namur O. et al. (2016) *EPSL*, 448, 102-114. [7] Margot J. L. et al. (2018) *arXiv:1806.02024* [astro-ph.EP]. [8] Dumberry M. and Rivoldini A. (2015) *Icarus*, 248, 254-268. [9] Deng L. et al. (2013) *GCA*, 114, 220-233. [10] Bertka C. M. and Fei Y. (1997) *JGR*, 102, 5251-5264. [11] Tange Y. et al. (2011) *HPRes*, 31, 413-418. [12] Liu Z. D. et al. (2017) *JGR*, 122, 7775-7788. [13] Fei Y. et al. (2000) *Am. Mineral.*, 85, 1830-1833. [14] Fischer R. A. et al. (2012) *EPSL*, 357/358, 268-276. [15] Fischer R. A. et al. (2013) *EPSL*, 373, 54-64. [16] Kuwayama Y. and Hirose K. (2004) *AmMineral*, 89, 273-276. [17] Lord O. T. et al. (2010) *JGR*, 115, B06208. [18] Santamaría-Pérez D. and Boehler R. (2008) *EPSL*, 265, 743-747. [19] Sanloup C. and Fei Y. (2004), *PEPI*, 147, 57-65. [20] Morard G. and Katsura T. (2010) *GCA*, 74, 3659-3667.