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Non-ideal liquidus curve in the Fe-S system and Mercury's snowing core

Bin Chen,[1] Jie Li,[1] and Steven A. Hauck, II[2]

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[1] We conducted multi-anvil experiments to investigate the melting behavior of the iron-sulfur system at moderate pressures. Our data reveal a positive departure from ideal solution behavior at 14 GPa, as indicated by the presence of two inflection points on the liquidus curve of iron-rich compositions. In contrast, the shape of the liquidus curve at 10 GPa is consistent with nearly ideal mixing between end-member components. Combined with existing data at lower pressures and above 20 GPa, our results suggest a negative liquidus temperature gradient under conditions found at shallow depths in Mercury's core. At the present time, the core is most likely precipitating solid iron in the form of snow, at a single depth or in two distinct zones. Formation and segregation of iron snow would alter the thermal and chemical state of the core and influence the origin and surface expression of the planet's magnetic field. **Citation:** Chen, B., J. Li, and S. A. Hauck, II (2008), Non-ideal liquidus curve in the Fe-S system and Mercury's snowing core, *Geophys. Res. Lett.*, *35*, L07201, doi:10.1029/2008GL033311.

1. Introduction

[2] Mercury, the innermost and smallest planet in the solar system, is enigmatic in many aspects, including the origin of its anomalously high metal to silicate ratio, the mechanism of its global magnetic field generation, and the physical state of its core [*Ness et al.*, 1975; *Morgan and Anders*, 1980; *Stevenson et al.*, 1983; *Harder and Schubert*, 2001; *Solomon et al.*, 2001; *Solomon*, 2003]. Addressing these mysteries is among the primary scientific objectives of NASA's MESSENGER mission to Mercury [*Solomon et al.*, 2001]. In the absence of seismological data from the planet, little is known directly about Mercury's core. Recent Earth-based radar measurements of Mercury's rotation led to discovery of a relatively large physical libration, implying that Mercury's core is at least partially molten [*Margot et al.*, 2007]. Notably, the existence of a global magnetic field is consistent with a convection driven dynamo in a liquid outer core. Operation of the dynamo seems to require a liquid layer of a thickness at least 4% of the core radius [*Stevenson*, 2003; *Stanley et al.*, 2005] and models of Mercury's thermal evolution constrained by inferences of limited radial contraction, as recorded in lobate scarps, suggest a molten layer with a thickness more than 50% of the core's radius [*Hauck et al.*, 2004]. An initially molten iron or iron-nickel planetary core would have cooled and solidified by the present day, unless a volatile element like sulfur is alloyed with the iron to reduce its freezing temperature [*Stevenson et al.*, 1983; *Harder and Schubert*, 2001]. In order to better understand the physical state of Mercury's core, we investigate the melting behavior of the iron-sulfur (Fe-S) binary.

2. Experimental Method

[3] Using a 1000 US ton Walker-type multi-anvil apparatus, we measured the liquidus curves of the Fe-rich portions of the Fe-S system at 10 and 14 GPa [*Li et al.*, 2001]. Stoichiometric mixtures of Fe and FeS were dried and packed into MgO capsules. High temperature was generated using a cylindrical rhenium furnace and monitored with a rhenium-tungsten thermocouple, ignoring the pressure effect on the electro-motive force (emf). Pressure was calibrated from known phase transitions in Bi, ZnS, GaP at room temperature and in SiO_2, $CaGeO_3$ and $MgSiO_3$ at high temperatures. In each experiment, the sample was compressed to the target pressure at room temperature and then heated to the target temperature. After equilibrating at high pressure and high temperature, the experiment was quenched by shutting off the power to the furnace. Recovered run products were polished, carbon-coated, and analyzed using a Scanning Electron Microscope (SEM) and an Electron Probe Microanalyzer (EPMA).

3. Results and Discussion

[4] The liquidus curves of Fe-rich alloys at 10 and 14 GPa are constructed on the basis of our experimental data and existing data on the melting temperatures of iron and the eutectic temperatures of the Fe-S binary [*Boehler*, 1993; *Fei et al.*, 1997]. The shape of liquidus curve reflects the nature of interactions between end-member components in a solution [*Dehoff*, 2006]. The curve at 10 GPa is relatively smooth, consistent with nearly ideal mixing in the liquid. The curve at 14 GPa contains two inflection points, revealing a positive departure from ideal solution behavior. At 1 bar, there is moderate repulsion between the Fe and FeS components in the liquid, leading to a positive departure from ideal solution behavior [*Brett and Bell*, 1969]. As pressure increases, the curve gradually straightens with decreasing eutectic temperature, probably due to a growing attraction between the Fe and FeS components. Our new data reveal that upon the formation of the intermediate compound Fe_3S_2 at around 14 GPa [*Fei et al.*, 1997] the liquidus curve becomes similar to that at 1 bar, indicating moderate repulsion between the Fe and Fe_3S_2 end-members. No structural changes in liquid or solid iron have been observed near 14 GPa [*Shen et al.*, 1998, 2004], but as

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[1] Department of Geology, University of Illinois at Urbana-Champaign, Urbana, Illinois, USA.

[2] Department of Geological Sciences, Case Western Reserve University, Cleveland, Ohio, USA.

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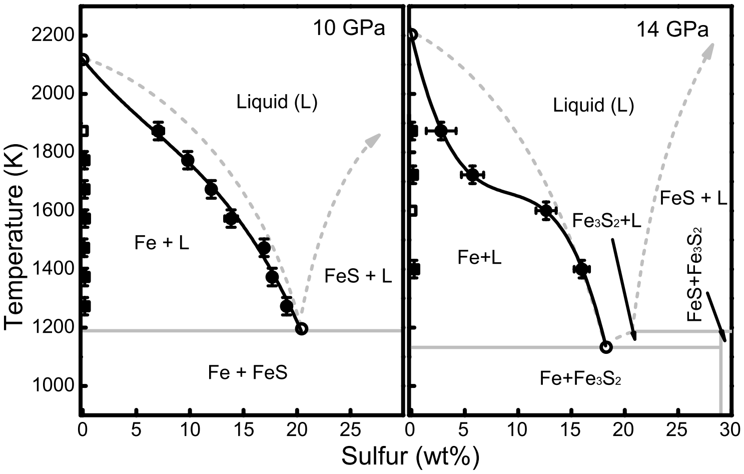

Figure 1. Phase relations in the Fe-rich portion of the Fe-S binary, showing (left plot) a nearly ideal liquidus curve at 10 GPa and (right plot) a positive departure from ideal solution behavior at 14 GPa, indicated by the two inflection points on the liquidus curve. The curves are polynomial fits to our data on coexisting liquid (solid circles) and solid (open and solid squares) at various temperatures and existing data on pure iron and eutectic melts (open circles) [*Boehler*, 1993; *Fei et al.*, 1997]. The open squares indicate that solid phase is missing in the polished sections, but can be inferred from the sulfur contents of the starting material and the liquid phase. The missing solid phases are assumed to be nearly sulfur free, as found in other run products. Approximate ideal liquidus curves (dashed grey) [*Fei et al.*, 1997] are shown for comparison. Uncertainty in temperature is estimated as ±30 K. Uncertainties in sulfur contents are one standard deviations of multiple analyses.

pressure increases, Fe-S eutectic melt evolves discontinuously towards a compact structure, with a non-uniform contraction at pressures between 13 and 17 GPa [*Morard et al.*, 2007]. The change in Fe-S interaction may be related to the pressure-induced spin crossover in solid iron, occurring at 13 GPa at 300 K [*Rueff et al.*, 1999]. A spin crossover may cause changes in the relative sizes of iron and sulfur atoms, and the strength and configuration of the Fe-S chemical bonds.

[5] The non-ideality at 14 GPa leads to substantial reductions in the liquidus temperatures of Fe-rich alloys (Figure 1). These results have direct implications for understanding the nature and evolution of Mercury's core. The sulfur content of Mercury's core is poorly constrained. Early theories of planetary accretion based upon the condensation sequence of species from the solar nebula predict severe depletion of volatile elements in Mercury, because of its proximity to the Sun [*Morgan and Anders*, 1980]. Only a small amount of sulfur is sufficient to account for the decoupled motion between the mantle and core, but a much higher sulfur content may be needed to allow the operation of a core dynamo [*Stevenson*, 2003; *Stanley et al.*, 2005], and to explain the planet's limited contraction over the past four billion years [*Hauck et al.*, 2004]. Incorporating a significant amount of sulfur in the core, however, would require extensive radial mixing in the solar nebula during planet formation [*Harder and Schubert*, 2001]. In applying our data to Mercury, we consider a wide range of composition from a sulfur-free core to a fully molten core containing 12 wt% sulfur.

[6] We estimate the adiabatic gradient in Mercury's core to be about 11 K/GPa, assuming the gradient is independent of the average core temperature (Figure 2). The pressure inside Mercury's core varies from about 7 GPa to more than 40 GPa [*Harder and Schubert*, 2001]. The liquidus of Fe-S alloys exhibit a number of peculiar features within this range, including a peak near 10 GPa, a negative gradient between 10 and 14 GPa, and a kink between 20 and 25 GPa (Figure 2). Beyond the kink, the liquidus temperature gradient is steeper than the adiabatic gradient for sulfur contents higher than about 7 wt%; it is negative or shallower than the adiabatic gradient for sulfur contents lower than about 7 wt%.

[7] The differentiation of Mercury's core would have depended on its sulfur content. If the core contains less than about 7 wt% sulfur, a cooling adiabat first crosses the liquidus at the high pressure end (Figure 2). In this case, an initially molten core starts freezing at the center. The inner core boundary (ICB) moves outwards, similar to the present-day Earth's core (Earth-like state). As the solid inner core grows, the liquid outer core becomes increasingly enriched in sulfur. When the inner core radius reaches about 1200 km, the core adiabat intersects the liquidus both at the ICB and near the core-mantle boundary (CMB), at the low-pressure peak of the liquidus (Figure 2). From this point in time, precipitation of solid iron occurs simultaneously at the ICB and as shallow "snow" near the CMB (Figure 3), resembling the likely present state of Ganymede's core [*Hauck et al.*, 2006] and a possible future state of the Martian core [*Stewart et al.*, 2007]. As iron snow sinks and sulfur-rich residual liquid rises from the snow zone and ICB, a gradient in sulfur concentration develops in the liquid: at shallower depths the liquid becomes enriched; at greater depths the sulfur concentration is determined by the injection of rising liquid from the ICB and the dissolution of sinking snow from near the CMB. Even though the iron snow may not accumulate at the inner core immediately, it eventually contributes to the inner core growth by reducing the sulfur concentration and hence raising the liquidus temperature of the deep liquid. Further growth of the inner

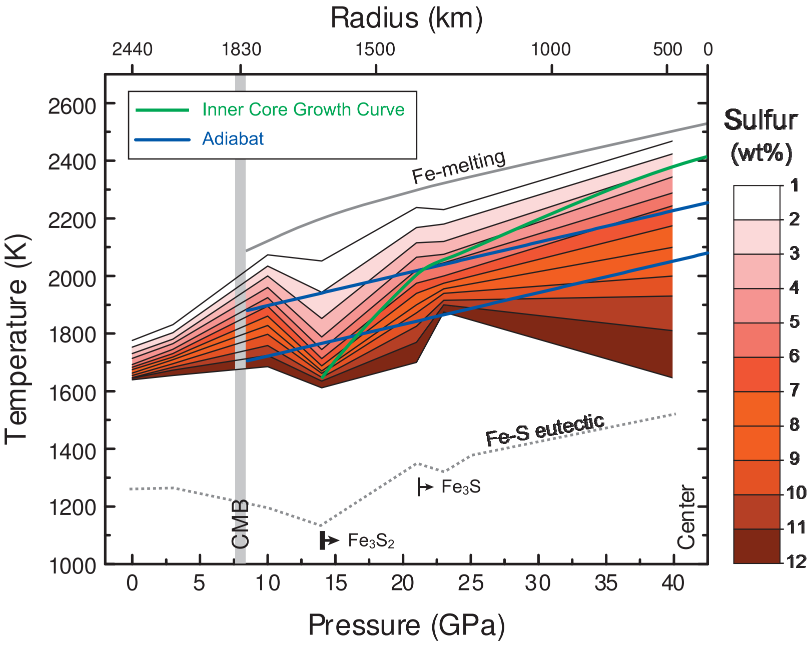

Figure 2. Liquidus of Fe-S alloys containing 1 to 12 wt% sulfur (red contours divided by thin lines), showing a peak near 10 GPa and a kink between 20 and 25 GPa. The melting curve of pure iron (black solid) and eutectic curve of Fe-S binary system (black dotted) are shown as references [*Boehler*, 1993; *Fei et al.*, 1997]. The two inflections in the eutectic curve coincide with the stabilization of Fe_3S_2 near 14 GPa [*Fei et al.*, 1997] and Fe_3S near 21 GPa [*Fei et al.*, 2000]. Depth and pressure relations in Mercury's core are from *Harder and Schubert* [2001]. Blue lines are adiabatic temperature profiles in Mercury's core with the core-mantle boundary (CMB) temperature at 1700 and 1900 K, respectively. We use constant material properties from *Christensen* [2006] and *Turcotte and Schubert* [2002], taking the thermal expansion = 3×10^{-5} K^{-1}, specific heat = 700 J kg^{-1} K^{-1}, and the core density = 8200 kg m^{-3}. The green curve represents the inner core growth path for a core containing 3 wt% sulfur. Data sources of liquidus are: 1 bar and 3 GPa, *Brett and Bell* [1969]; 10 and 14 GPa, this study; 21 GPa, *Fei et al.* [2006]; 23 GPa and 40 GPa, *Stewart et al.* [2007] with a polynomial fit applied to experimental data at 23 GPa. Due to limited data coverage, the liquidus curve at 40 GPa is uncertain, giving rise to uncertainties in the liquidus temperature gradients of intermediate sulfur contents between 23 and 40 GPa.

core is determined by a number of factors, including the cooling rate and the rates of sulfur diffusion and iron dissolution in the liquids. The green curve in Figure 2 delineates the approximate inner core growth path of a core containing 3 wt% sulfur, calculated without considering chemical gradients in the liquid and the contribution of snowing solid iron.

[8] The evolution of the core, alternatively, would have been different if its sulfur content is higher than about 7 wt%. A cooling adiabat first crosses the liquidus at the low-pressure peak near the CMB (7–8 wt% S), almost simultaneously at both the low-pressure and high-pressure peak (8–10 wt% S), or at the high-pressure peak (10–12 wt% S) (Figure 2). Iron precipitates in the form of snow, and produces a compositional gradient in the liquid, with sulfur enriched above the snow zone and depleted below it (Figure 3). An inner core may not form until the sulfur content of deep liquid is sufficiently low to allow solid iron to precipitate at the ICB. If only one snow zone is present, the core is in a Ganymede-like state. If two distinct snow zones have formed, the liquid core would be divided into three layers: a sulfur-rich top layer, a middle layer that receives sinking iron snow from above and sulfur-rich residual liquid from below, and a sulfur-poor bottom layer in which sinking iron from the deep snow zone is likely to dissolve (Figure 3). Further evolution depends on the rate the core cools relative to the rate sulfur diffuses, and how quickly snowing solid iron dissolves in the liquids.

[9] With the estimated present-day temperature at the CMB between 1700 and 1900 K, we find three possible core states at the present time: a Ganymede-like state, an Earth-like state, and a double-snow state (Figure 3). The Ganymede-like state with a single snow zone and a solid inner core is applicable over a wide range of sulfur contents and present-day temperatures at the CMB (Figure 2). The radius of the inner core is determined by the core's sulfur content and temperature. If the sulfur content is below 4 wt%, the solid inner core would occupy more than 50% of the core's radius. Such a large inner core may not be compatible with the observation of limited contraction on the planet [*Hauck et al.*, 2004]. For only a few specific combinations of sulfur content in the core and current temperature at the CMB, Mercury's core would be in the Earth-like state, with iron precipitating at the ICB. The double-snow state is the most likely state if sulfur is the predominant light element in Mercury's core, and the planet is at an early stage of inner core growth, with the inner core radius below about 1200 km. The present-day core would consist of two distinct zones of iron snow formation in a layered outer liquid core and possibly a small solid inner core (Figure 3).

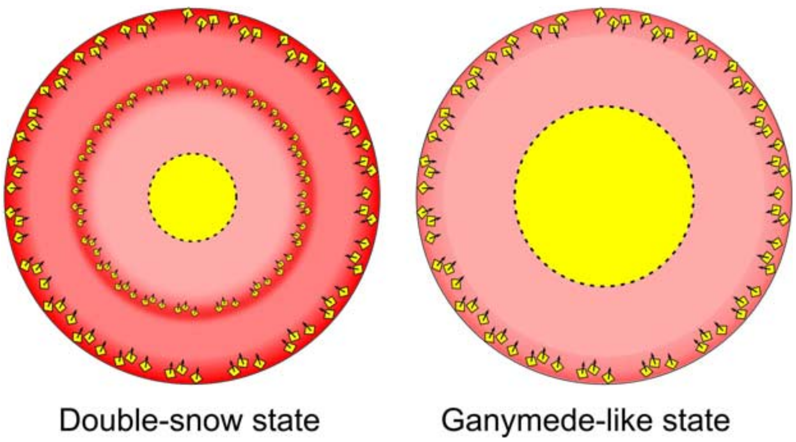

Figure 3. Schematic illustrations of the likely states of Mercury's core at the present time. In the double-snow state, the core consists of two distinct zones (red bands) where iron snow (yellow squares) forms, a thick liquid outer shell (pink) and a small solid inner core that is less than about 1200 km in radius (yellow). The iron snow sinking towards the center (indicated by arrows) leads to a compositional gradient in the liquid, with sulfur enriched immediately above the snow boundaries (red) and depleted in the bottom layer (light pink). The middle layer (dark pink) has an intermediate sulfur concentration; it receives iron snow from above and sulfur-rich liquid from below. In the Ganymede-like state, the core has a single snow zone in a liquid outer shell, and a solid inner core. The radius of the inner core is determined by the core's sulfur content and temperature.

[10] The inferred double-snow state of Mercury may be unique among the terrestrial planets and terrestrial-like satellites with iron-sulfur cores, as it results from the simultaneous presence of two segments in the core where the liquidus temperature gradient is negative or shallower than the adiabatic temperature gradient. The negative liquidus gradient between 10 and 14 GPa is due to the positive departure from ideal solution behavior near 14 GPa, whereas the negative or shallow liquidus gradient above 23 GPa appears to be associated with pressure-induced changes in the eutectic composition and temperature [*Stewart et al.*, 2007]. Only on Mercury do the core conditions span the pressure range over which both segments of negative or shallow liquidus gradient are present. The range is not found in less massive satellites such as the Moon (core pressure < 10 GPa) and Ganymede (core pressure < 14 GPa), and is lower than found in cores of larger planets such as Mars (core pressure > 20–25 GPa) and the Earth (core pressure > 136 GPa) [*McBride and Gilmour*, 2004].

[11] The nature of Mercury's core exerts direct control on the origin and characteristics of the planet's global magnetic field. Mariner 10 discovered an intrinsic field on Mercury, about one thousand times weaker than the Earth's [*Ness et al.*, 1975]. Convection in the fluid region of the core is considered a likely mechanism to produce Mercury's field, although the energy sources for a self-sustaining dynamo are not well understood [*Stevenson et al.*, 1983]. More importantly, most dynamo models for Mercury predict a dipole field that is at least several times stronger than observed [*Stanley et al.*, 2005]. A recent deep dynamo model suggests that a sub-adiabatic stable layer at the top of Mercury's fluid core may subdue the surface expression of a strong field inside the core [*Christensen*, 2006]. Inferred from our experimental data, the snowing core states open up new dynamo scenarios, where the driving force for convection may originate in multiple locations inside the core, and includes gravitational segregation of solid iron, in addition to the chemical buoyancy of a sulfur-rich melt and latent heat associated with iron precipitation. The style of convection may be double diffusive, with heat and the lighter sulfur-rich liquid moving outwards and solid iron moving inwards. If the solid iron sinks fast and does not melt until much greater depth, then the release of latent heat within a shallow snow zone would increase its temperature, enhancing convection above it. Dynamic models are needed to explore the effect of variable thermal and chemical gradients on the origin of the planet's magnetic field and its expression on the surface.

[12] More detailed knowledge of the melting behavior of Fe-S binary and constraints on the rates of growth and dissolution of iron crystals and sulfur diffusion in the liquid would yield a refined understanding of the thermal and chemical state and evolution of Mercury's core. The presence of other volatile elements in the core needs to be considered. The radio science, laser altimeter, and magnetic experiments onboard the MESSENGER spacecraft are expected to address major questions about the size of Mercury's core and potentially the extent to which the core is molten. Our inferred core states provide a new context into which forthcoming observational data can be placed, connecting the physical state of the enigmatic innermost planet with its composition and accretion history, and the formation and evolution of the terrestrial planets in general.

[13] A snowing core is conceivably a widespread phenomenon in the solar system that occurs in planetary bodies with different core compositions and temperatures. Some cores (e.g., Ganymede) may have had snow in their history [*Hauck et al.*, 2006] while others (e.g., Mars) may expect it in the future [*Stewart et al.*, 2007]. New data on the liquidus temperatures of various compositions over a wide range of pressures will allow us to construct the core history of the terrestrial planets as well as icy satellites and Kuiper Belt Objects (KBOs).

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B. Chen and J. Li, Department of Geology, University of Illinois at Urbana-Champaign, 1301 W. Green Street, Urbana, IL 61801, USA. (binchen2@uiuc.edu; jackieli@uiuc.edu)

S. A. Hauck II, Department of Geological Sciences, Case Western Reserve University, 222 A.W. Smith Bldg., 10900 Euclid Avenue, Cleveland, OH 44106-7216, USA. (hauck@case.edu)