Bottom-up versus top-down solidification of the cores of small solar system bodies: Constraints on paradoxical cores

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1. Introduction

The degree to which other differentiated bodies in the solar system mimic the structure of Earth's core, with a solid central inner core and a less dense liquid outer core, enriched in lighter elements, is unclear. The style of core solidification hinges on the relative slopes of the adiabat, the temperature gradient on which a convecting medium in the absence of internal heat sources converges, and the melting curve of the material (Fig. 1). For Earth, the pattern is largely uncontroversial: despite early suggestions to the contrary (Higgins and Kennedy, 1971), there is little doubt that the adiabat in Earth's core is shallower than the melting curve, and an inner central core formed and has likely grown as Earth undergoes secular cooling. This paradigm for Earth's core evolution not only explains the gross liquid and solid inner core dichotomy, but also provides driving forces for the geodynamo beyond top-down cooling, through release of the latent heat of fusion, and segregation and buoyant ascent of light-alloying enriched material as the core grows.

Considerable recent attention has been devoted to shallow solidi slopes and inflections within (particularly) the iron–sulfur phase diagram, with potential applications to Mars, Mercury and Ganymede (Hauck et al., 2006; Stewart et al., 2007; Chen et al., 2008). Indeed, the possibility of solidification of solid iron at shallow core depths ("snow") followed by its descent, redissolution and resultant compositional stratification of the cores of these bodies has been proposed (Hauck et al., 2006; Stewart et al., 2007; Chen et al., 2008). The implications of this possibility for the dynamo were explored for Earth's core long ago (Malkus, 1973) in response to Higgins and Kennedy's (1971) proposal that there might be a "paradox" associated with Earth's core. Higgins and Kennedy's (1971) contention was that the slope of the adiabat was greater than that of the melting curve (Fig. 1), and the presence of an inner core thus required a thermally stably stratified, non-adiabatic core. Yet, despite the refutation of the existence of a core "paradox" for Earth, the idea that asteroidal cores are likely to solidify from their top-down because of the relatively steep low-pressure adiabat of liquid iron has been appreciated for a number of years (Haack and Scott, 1992; Chabot and Haack, 2006), and the suggestion that the adiabat may be steeper than the melting curve in the lunar core has apparently been disregarded or overlooked (Kennedy and Higgins, 1975; uncited to date in the ISI database). Most recently, the idea that the adiabat might be steeper than the melting curve in Ganymede's core for a compositional range of 3 wt.% S or more has been suggested (Bland et al., 2008).

The importance of this problem for core dynamics in medium and relatively small-sized bodies is profound: does crystallization of a core proceed via formation of iron-rich dendrites at its top that might detach and descend (Haack and Scott, 1992), and/or via descent of...
fine-grained iron snow, with resultant enrichment of the deep core in iron and the shallow core in light-alloying elements, resulting in stable stratification? Or, does a solid inner core naturally form in most iron-rich cores of planetesimals/moons, with associated exclusion of light-alloying elements and chemically buoyant fluid evolution whose upwelling could fuel a magnetic dynamo?

The goal of this study is to characterize the size range of objects for which the slope of the pressure-dependent adiabat of liquid iron, and iron–nickel with moderate amounts of sulfur or other lighter alloying components, may exceed the slopes of the melting curves of iron alloys (Fig. 1). This effect hinges on the high-thermal expansions of iron alloys, and complements the phase diagram–associated reversals of magnitude of the adiabat and liquidus that have been proposed to exist in sulfur-rich cores in Mars, Mercury and Ganymede, and likely applies to all iron-rich cores of bodies in a given size range.

An additional goal of this study is to examine, clarify and illuminate the current constraints on parameters critical in determining the convective style within liquid cores of modestly-sized solar system bodies (loosely defined as spanning from asteroids to moons and Mercury). In particular, there is a dichotomy of results on the thermal expansion of liquid iron at ambient pressures, and the shifts in density and thermal expansion produced by sulfur content have not always been accurately applied in models of planetary interiors. These are not casual shortcomings: for example, thermal expansion is the thermodynamic parameter whose magnitude produces the most marked variations in the slope of the adiabat. Hence, uncertainties in this parameter fundamentally impact the view of how cores evolve, and how magnetic fields might (or might not) be generated.

2. Methods

The slope of the adiabat in pressure–temperature space can be described equivalently by either:

\[ dT / dP = \alpha(P) T / \rho(P) C_p = \gamma T / K_c(P) \]  

where \( \alpha(P) \) is the pressure-dependent thermal expansion, \( T \) is the temperature at which the adiabatic gradient is being calculated, \( \rho(P) \) is the pressure-dependent density, \( C_p \) is the heat capacity at constant pressure (which, for liquid iron, is relatively constant in value: Desai, 1986), \( \gamma \) is the Gruneisen parameter and \( K_c(P) \) is the pressure-dependent isentropic bulk modulus. Clearly, one can in principle calculate the adiabat of iron-rich core materials at any pressure and temperature conditions, as long as the thermodynamic parameters are known at these conditions. Yet, the thermodynamic properties of liquid iron or liquid iron-rich alloys are not easy to measure, and hence the direct constraints on the parameters of Eq. (1) are not as well determined as might be hoped across the suite of pressure and temperature conditions likely to be present in planetary cores. As the Gruneisen parameter is difficult to directly measure, the most straightforward means of calculating the adiabat is through the thermal expansion. Indeed, a considerable amount of temperature-dependent density data have been collected (particularly on end-member liquid iron), and the systematics through which parameters such as thermal expansion may be extrapolated to high pressure are well-known. Therefore, the parameters of Eq. (1) may be assessed, and the pressure dependence of the adiabat calculated, with reasonable accuracy to pressures spanning those present within the suite of moons in the solar system.

The basic algorithm that I utilize for constraining the adiabat to ~10 GPa involves calculating the density and bulk modulus at high pressures using available elasticity data on liquid iron and iron alloys using the Birch–Murnaghan equation of state (Birch, 1978):

\[ P = 3K_0 f \left[ 1 + 2f \frac{5}{3} \left[ 1 + af + \ldots \right] \right] \rho \]  

where \( K_0 \) is the zero-pressure bulk modulus, \( a \) is \( 1.5(\partial K / \partial P - 1) \) and \( f \) is the Eulerian strain variable defined as \( 0.5 \left[ (V / V_0)^{2/3} - 1 \right] \), where \( V \) is the volume at pressure and \( V_0 \) is the zero-pressure volume. Notably, over the pressure ranges considered, the type of equation of state used (such as Vinet (Vinet et al., 1987), as opposed to Birch–Murnaghan) makes no significant difference. The thermal expansion is constrained at high pressures using two means:

\[ \alpha / \alpha_0 = K_0 / K \]  

and

\[ \alpha / \alpha_0 = K_0 / K (\rho / \rho_0)^{0.5} \]  

where the subscript “0” denotes the ambient pressure value of the parameter. The former expression is the well-known proposal that \( \alpha K = \text{constant} \) (e.g., Birch, 1968), while the latter is the preferred equation for extrapolating to high pressure of Duffy and Ahrens (1993). Because of the sensitivity of the adiabatic gradient to the thermal expansion, the manner in which \( \alpha \) is extrapolated is important for determining the possible range of values of the adiabat at even the modest pressures present in the cores of moons.

3. Liquid iron results

The state of knowledge on liquid iron thermal expansion at ambient pressures is illustrated in Fig. 2. Because of the technological importance of liquid iron, a wide variety of probes have been utilized to measure its density at high pressures. These include Archimedean (Lucas, 1960; Kirshenbaum and Cahill, 1962; Lucas, 1972), pycnometric (Sato, 2003: quoted as a personal communication in Assael et al., 2006), bubble-pressure (von Frohberg and Weber, 1964), levitated drop (Saito et al., 1969; Brillo et al., 2006), heated wire (Hixson et al., 1990; Beutl et al., 1994) and gamma-ray attenuation techniques (Drotning, 1981; Nasch and Steinemann, 1995). Assael et al. (2006) review these data with a goal of establishing a reliable reference value for the thermal expansion of liquid iron. Most of the studies of the density of liquid iron fall close to a general trend, with the recommended value of Assael et al. (2006) being \( 1.32 \times 10^{-5} / \text{K} \) for the thermal expansion of liquid iron; this value appears to be relatively constant with temperature up to at least 2500 K. The two studies that show systematically lower values are the gamma-ray attenuation studies, and values derived largely from these studies (a thermal expansion of \( 8.2–9.2 \times 10^{-5} / \text{K} \)) have been widely adopted.
within the geophysical and planetary literature (e.g., Anderson and Ahrens, 1994; Nasch and Manghnani, 1998; Cammarano et al., 2006; Hauck et al., 2006; Riner et al., 2008). The rationale for why these values have been adopted relative to the larger number of studies that yield a higher thermal expansion is unclear. Moreover, why the gamma-ray attenuation studies yield a smaller thermal expansion value than virtually all other techniques is not apparent, but may be related to temperature-induced shifts in geometry of the high-temperature samples, producing a temperature dependence of the attenuation coefficient of the experimental assembly (Assael et al., 2006).

4. Results

The importance for planetary bodies of these differing thermal expansions is shown in Fig. 3. Here, the adiabat is calculated using Eq. (1) at both ambient and high pressures, using a zero-pressure adiabatic bulk modulus for liquid iron of 109 GPa, in accord with both sound velocity measurements (Kurz and Lux, 1969; Nasch and Manghnani, 1998) and an inversion for high-pressure liquid iron properties (Anderson and Ahrens, 1994). The pressure derivative of the bulk modulus of liquid iron is ill-constrained, and I choose a range of values from 4.66 (Anderson and Ahrens, 1994) up to a value of 7 in order to evaluate the sensitivity of the calculations to this parameter. The bulk modulus and density at high pressures are each evaluated using the Birch–Murnaghan equation, Eqs. (3) and (4) are each used to calculate the thermal expansion at high pressures, and the calculation of the adiabat progressively increments the temperature with pressure within Eq. (1). A heat capacity of 835 J/kg/K is used, and is assumed to be constant with pressure and temperature, in accord with the observed temperature independence of this value (Desai, 1986).

The melting relations for iron in Fig. 3 are from the measurements to 5.8 GPa of Strong et al. (1973). These are generally regarded as quite accurate, and their initial melting slope agrees with that calculated thermodynamically from the Clausius–Clapeyron equation. The experimentally-observed slope is (within resolution) constant, and the discontinuity at 5.2 GPa is caused by the δ-γ-liquid triple point, above which the melting curve steepens, in accord with thermodynamic requirements. Clearly, if the lower value of the thermal expansion of liquid iron of 9.2 × 10^{-5}/K is correct, then the slope of the adiabat is less than that of the melting curve at all pressures, and top-down crystallization of iron-rich asteroidal bodies, as proposed by Haack and Scott (1992), is not expected. However, if the larger value of the thermal expansion of liquid iron is correct, the adiabat is steeper than the melting curve at all conditions of asteroidal interiors and may, depending upon the pressure derivative of the bulk modulus and thermal expansion formulation, be steeper until the pressure of the δ-γ-liquid triple point, or approximately to the pressures present within the lunar core.

5. Roles of nickel and sulfur

Iron-rich meteorites typically contain between ~4 and 16% nickel, and sulfur is usually invoked as the dominant light-alloying component present in the cores of small to Mars-sized objects (e.g., Haack and Scott, 1992; Scott et al., 2002; Breuer et al., 2007). Hence, we assess the effect of these added components on the adiabatic gradient at high pressures. The effects of nickel and sulfur on the thermal expansion of iron are shown in Fig. 4. As with pure liquid iron, there are two sets of values available for the thermal expansion of iron-rich nickel alloys (Nasch and Manghnani, 1998; Seifter et al., 1998). The effect of nickel in both studies appears to quite modestly decrease the thermal expansion of the liquid (Fig. 4), which is in accord with the overall similarities in thermodynamic parameters between these two metals. For comparison, values of the thermal expansion of liquid sulfur-bearing alloys (limited to FeS composition) are systematically larger than those of iron, although the two measurements of this parameter
are somewhat discrepant (Nagamori, 1969; Kaiura and Toguri, 1979). Because of the potentially competing and compensating effects of Ni and S on the thermal expansion, adiabats are calculated for the iron–sulfur (and implicitly nickel) using the two separate thermal expansion coefficients of liquid iron. This assumption will likely minimize the inferred slopes of the adiabat, as the effects of sulfur on the thermal expansion appear likely to be greater than that of nickel (Fig. 4). The effects of sulfur content on heat capacity are interpolated between that of end-member iron and the Fe–FeS compositions of Kanda et al. (1986). In passing, it is notable that the temperature dependence of the thermodynamic properties in the iron–sulfur system may be anomalous. For example, Nasch et al. (1997) found a positive temperature dependence of the sound velocity of an Fe 52.5% Ni–10% S liquid at ambient pressure; if this corresponds to a temperature-induced increase in the bulk modulus of the liquid, then the proportional relation between d\(\alpha\)/d\(P\) and d\(k\)/dT implies that d\(\alpha\)/d\(P\) may be positive in liquid Fe–S systems. If this is the case, Eqs. (3) and (4) would markedly underestimate the value of the thermal expansion in this system, and hence the adiabatic gradient, at high pressures.

Fig. 5 shows the calculated adiabats for the two sets of thermal expansions. In these calculations, the zero-pressure adiabatic bulk modulus of Nasch et al. (1997) determined from sound speed measurements on a Fe–Ni–10 wt.% S melt is used for the 10 wt.% S liquid, with the bulk modulus calculated using the zero-pressure density of 5330 kg/m\(^3\) for this composition (Kaiura and Toguri, 1979; Sanloup et al., 2000), and a d\(k\)/dT of 6 (e.g., Balog et al., 2003). The bulk modulus and density of Fe–5 wt.% S liquid are interpolated between the Fe–10 wt.% S composition and pure iron liquid. Notably, the density of Fe–10 wt.% S liquid of 5330 kg/m\(^3\) has been reported in parameterized models as the density of end-member FeS (Fe–36.5 wt.% S) liquid (Hauck et al., 2006; Williams et al., 2007; Bland et al., 2008). However, liquid FeS has a measured density of ~3890 kg/m\(^3\) at 1500 K (Kaiura and Toguri, 1979; Kress et al., 2008). Hauck (pers. comm.) reports that while the value of 5330 kg/m\(^3\) for end-member FeS liquid in Table 1 of Hauck et al. (2006) is in error, the correct value from Kaiura and Toguri (1979) was used in their calculations. Interpolated densities in the Fe–FeS system using this high end-member (where utilized) would produce an underestimate (by about a factor of 3) of the effect of sulfur on core densities, illustrating the key role of ensuring that accurate thermodynamic data for iron-alloy liquids are incorporated in parameterizations used in planetary modeling.

The phase equilibria constraints on the liquidus of the Fe–S system at modest pressures are surprisingly sparse. Following Chen et al. (2008), I determine the liquidus from fits at the 5 and 10 wt.% compositions to the ambient pressure phase diagram, the 3 GPa data of Brett and Bell (1969) and the 10 GPa phase diagram of Chen et al. (2008); such fits show no strong evidence for curvature within the 0–10 GPa pressure range.

Clearly, the addition of sulfur markedly lowers the liquidus slope and produces modest steepening of the adiabat (Fig. 5). The net effect is that for even low thermal expansions, cores of small bodies (roughly up to the size of Callisto) with modest amounts of sulfur (~5 wt.% S) will initiate their solidification from the top-down. For high-thermal expansions, a 5 wt.% S core will not approach its liquidus slope until substantially in excess of 10 GPa — and, at pressures of ~14 GPa, the phase diagram topology shifts due to the onset of an Fe3S2 phase (e.g., Stewart et al., 2007; Chen et al., 2008). The situation for 10 wt.% S alloys is more extreme. Neither low- nor high-thermal-expansion adiabats have slopes approaching those of the liquidus at pressures below 10 GPa. Hence, core crystallization should begin from the top-down in all smaller solar system bodies (the moon, Ganymede, etc.) with cores of this composition. In effect, Fig. 5 quantifies the trade-offs between differing estimates of thermal expansion and sulfur content in producing cores that crystallize from the top-down, and illustrates the uncertainties in drawing firm compositional boundaries on top-down behavior (Bland et al., 2008): these uncertainties are exacerbated by the limited phase equilibria data on the dependence of the liquidus on sulfur content at these pressure conditions. Nevertheless, bottom-up crystallization scenarios of bodies with core pressures below 10 GPa appear to require sulfur-poor cores and a low thermal expansion of liquid iron alloys (Fig. 5). Indeed, even for the lower values of thermal expansion, a sulfur content of ~3 wt.% should be marginally sufficient to produce top-down crystallization in a low-pressure asteroidal body (Figs. 3 and 5); because of the large effect of sulfur on the liquidus, modestly higher sulfur contents dramatically increase the size of objects that would undergo top-down crystallization (Fig. 5).
6. Conclusions

Initial top-down core crystallization is likely to be common among smaller solar system bodies, and is a direct consequence of the relatively large adiabatic gradients within such bodies. This type of behavior has been previously recognized for the Mercury and Martian cores, but primarily as a manifestation of sulfur- and pressure-induced shifts in topology of the phase diagram (Hauck et al., 2006; Stewart et al., 2007; Chen et al., 2008), rather than as a fundamental manifestation of the large thermal expansions of iron-rich liquids. However, the precise pressure- and composition range of this behavior hinge on the rather controversial thermal expansion of liquid iron and its alloys.

Nevertheless, the phenomenon of the adiabat being steeper than the liquidus for a large suite of parameter ranges implies that compositionally stratified cores may be the norm in smaller bodies in the solar system, rather than the exception. This is not to say that dynamos absolutely cannot exist in such cores: for example, Singer and Olson (1984) have calculated that gravity waves may be able to power a dynamo in a compositionally stratified core, as might descent of sinking iron particles (Hauck et al., 2006) or extreme tidal effects (Arkani-Hamed et al., 2008) — but atypical mechanisms for dynamo generation are likely required within such cores. While high heat flows (or heating from extinct radionuclides) in the fully molten core regime could drive early core convection and dynamo action (e.g., Staggman et al., 2003; Weiss et al., 2008), the likely generation of compositional stratification during solidification implies that a natural mechanism for shutting off dynamos of smaller bodies may exist. In such instances, the duration of a fully molten core and possible associated dynamo will be controlled by a range of parameters, including the initial temperature, size and thermal conductivity of the body, but will also hinge on the liquidus temperature (and hence sulfur content) of the core as well (e.g., Hauck et al., 1990). Indeed, the –100–300 K liquidus depression generated by 5–10 wt.% S in the Fe–FeS system to 10 GPa (Chen et al., 2008) will, for core cooling rates of order 1 K/MY. for 100–1000 km sized bodies (Haack et al., 1990), expand the lifespan of an all-liquid sulfur-bearing core relative to a pure iron core by in excess of 1015 yr.

With respect to the known extant dynamo of Ganymede, other mechanisms for dynamo generation may need to be invoked, such as its core lying on the sulfur-rich side of the Fe–FeS eutectic, with FeS crystallizing buoyantly at the top and generating descent of iron–its core lying on the sulfur-rich side of the FeS–FeS–Fe eutectic at 30 kbp. Earth Planet. Sci. Lett. 6, 479–482.


