

ON CRYSTALLIZATION AT THE INNER CORE BOUNDARY

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Abstract

It is widely believed that a mushy layer develops at the ICB while the outer core material freezes onto the inner core. This view is obtained in reference to metallurgical or analog experiments on solidification carried out in the laboratory where morphological instability almost always follows constitutional supercooling. However, morphological instability is not an automatic consequence of supercooling: supercooling and stable solid-liquid interface may coexist under certain conditions such as might perhaps occur at the ICB. If these conditions are realized, there could be both solidification on the ICB and crystallization of small solid particles in the supercooled layer (slurry layer).

We made a linear stability analysis of a unidirectionally advancing solid-liquid interface under the ICB conditions. Several values of liquidus slope against concentration of light material (m_c) are used for the stability analysis. It was confirmed that supercooling and interstability may coexist if $|m_c|$ is low although this value of $|m_c|$ is believed to be too small as the liquidus slope at the ICB. The estimated amount of supercooling in the layer is of order 0.1K, and this provides an estimate of the size and population of solid particles in the slurry layer. However, even though the value of $|m_c|$ is small, to sustain such slurry layer at the ICB is unlikely due to (i) the difficulty of continuous supply of enough number of nuclei into the layer and (ii) the Rayleigh-Taylor instability by the compositional buoyancy. It is most probable that mushy layer exists at the ICB.

Key words: Inner core boundary, mushy layer, slurry, morphological instability

1. Introduction

About twenty years ago, Loper and Roberts (1978,1981) and Fearn et al. (1981) presented theoretical arguments suggesting that the region of the outer core close to the inner core boundary (ICB) was in a state of constitutional supercooling, due to the rejection of light elements into the molten iron alloy, during crystallization of the inner core. By analogy with what occurs in the casting of metals, crystal growth and in laboratory experiments on solutions, these authors concluded that the metal crystallized as dendrites above the ICB, and therefore that a slurry zone (Loper and Roberts, 1978, 1981), in which crystals grow as suspended particles, or a mushy zone (Fearn et al., 1981), where crystallization proceeds by solidification onto dendritic crystals, existed at the ICB.

Over the years, this reasonable suggestion, based on a metallurgical analogy, became a belief and the existence of a mushy zone at the ICB is currently thought to be supported by "detailed and quantitative studies" (e.g., Buffett *et al.*, 2001). Many studies were conducted on the structure and hydrodynamics of a mushy zone and convection therein (e.g., Loper and Roberts, 1978; Worster, 1986; Bergman and Fearn, 1994). Although the existence of the constitutionally supercooled layer above the ICB has been studied properly, the details of the morphological stability (e.g. Kurz and Fisher 1989) of the solid-liquid interface, which distinguish the fate (mush or slurry) of the supercooled layer, does not seem to be studied quantitatively. Morphological instability is not a necessary consequence of constitutional supercooling: it may be possible to have constitutional supercooling and interface stability at the same time. There are, however, considerable differences between crystallization of the inner core and crystal growth or analogue experiments in the laboratory and, as pointed out by Buffett *et al.* (2001),

"transferring results from one physical setting to another without proper analysis can lead to misconceptions".

In the present paper, after summing up the usual metallurgical arguments, we will assess their validity in the case of the crystallization of the inner core. First, let us point out the differences between the laboratory, or metallurgical conditions, and those obtaining at the ICB.

In the case of ingot casting, crystal growth or analog experiments on ammonium chloride solution (e.g., Roberts and Loper, 1983; Chen and Chen, 1991), solidification is directional, heat is evacuated through the solid and the temperature gradients dT/dx (with x positive from solid to liquid) are positive and very large in the solid and the liquid, typically from about 4 K/cm for experiments on $\text{NH}_4\text{Cl-H}_2\text{O}$ (Chen and Chen, 1991) to 500 K/cm for high melting point alloys (Flemings, 1974). The velocity of propagation of the solid-liquid interface is very large, typically of the order of 0.01 to 0.1 mm/s (Flemings, 1974). On the contrary, in the case of the inner core, heat is evacuated through the liquid, the temperature gradients are negative and very small in the solid and the liquid, of the order of 10^{-4} K/m, and the velocity of propagation of the solid-liquid interface is extremely small (0.3 mm per year). These considerable differences in growth rates and temperature gradients, of about six orders of magnitude, must be kept in mind when considering the extent of the supercooled zone and the kinetics of crystallization.

An important controlling physical quantity on the morphological instability of the liquid-solid interface is the gradient of the liquidus temperature against concentration (m_c in this paper). However, m_c at the ICB condition is not constrained very well. We do not know its value at high pressure, and it may change by several orders of magnitudes for different light element in solution in the liquid core. Raghavan (1988)

gave $m_c = -1.2 \times 10^3$ for Fe-S and $m_c = -1.4 \times 10^3$ for Fe-Si, and Loper and Roberts (1981) employed $m_c = -1.1 \times 10^4$ in their analysis taking the pressure effect on m_c into account. Recent studies have suggested the importance of the oxygen as a light element in the core (e.g. Alfè et al., 2002; Rubie et al., 2004). Boehler (1993) experimentally found that iron alloys with 10 wt% and 30 wt% oxygen had melting temperatures lower than Fe and FeO, but that the melting point depression disappeared above 60 GPa. So, the liquid core alloy might have a very small $|m_c|$. On the contrary, Alfè et al. (2002) obtained m_c of order -10^4 K for Fe-O system (700K liquidus depression with 8% O) at the ICB condition by their ab initio calculations. We will investigate in detail possible situations (mush or slurry) depending on the value of m_c . It is found that morphological stability and constitutional supercooling may coexist. However, the m_c leading to this state seems far from that of the ICB. It is likely that mushy layer exists at the ICB.

2. Metallurgical background

Solute redistribution (or microsegregation) generally occurs when a dilute binary alloy, or impure metal, is cooled below the liquidus: solute atoms are rejected by the purer crystals as they form. If the bulk concentration of solute is C_∞ in the liquid, and if diffusion in the solid is negligible, the freezing solid has initially the concentration $C_S < C_\infty$. Although C_S and C_∞ are mass fractions, they are referred to as "concentrations" in the current literature; we will follow this usage here. Even though the bulk of the liquid may be homogenized by convection, there exists a diffusion zone ahead of the interface, where the concentration of solute in the liquid is higher than C_∞ . As solidification proceeds, more solute is rejected from the solid and the concentration

ahead of the interface increases, until a quasi steady state is reached (Flemings, 1974; Kurtz and Fisher, 1989; Chalmers, 1964; Hurle, 1961). Eventual steady state is attained so that the concentration of the solid increases gradually and asymptotically approaching C_∞ as the solute stays in the diffusion zone. In this paper, we consider the case of the quasi steady state in which concentration of solid is C_s and that in the liquid far from the interface is C_∞ .

Since the liquidus temperature decreases as the concentration of solute atoms increases, the liquidus temperature in the diffusion zone, ahead of the interface, is lowered by an amount depending on the solute concentration, hence on the distance x to the interface. If the temperature gradient in the liquid intersects the liquidus curve ahead of the interface, the temperature of the liquid in a zone in front of the interface is lower than the liquidus temperature, the liquid is therefore supercooled. This situation is called *constitutional supercooling* (Rutter and Chalmers, 1953). The condition for the existence of a supercooled zone is that the temperature gradient in the liquid be smaller than or equal to the gradient of the liquidus temperature Θ , close to the solid-liquid interface (Tiller *et al.*, 1953):

$$\left. \frac{dT}{dx} \right|_{x=0} \leq \left. \frac{d\Theta}{dx} \right|_{x=0} \quad (1)$$

The concentration of solute in the melt at the interface reaches a steady state value C_0 intermediate between the value with no mixing and the value with total mixing (no diffusion zone) C_∞ , assumed to be independent of time, a reasonable assumption if the extent of the liquid zone is much greater than the diffusion layer.

In steady state, $dC(x)/dt = 0$, the concentration $C(x)$ at distance x of the interface is solution of the equation

$$D \frac{d^2 C}{dx^2} + v \frac{dC}{dx} = 0 \quad (2)$$

where D is the diffusion coefficient of the solute in the liquid and v (positive) is the speed of the solid-liquid interface (growth rate) relative to the far fluid. With boundary conditions $C=C_0$ at $x=0$ and $C \Rightarrow C_\infty$ at $x \Rightarrow \infty$, the solution is :

$$C(x) = C_\infty + (C_0 - C_\infty) \exp\left(-\frac{v}{D}x\right) \quad (3)$$

In steady-state conditions, when the bulk of the liquid is stirred and homogeneized by convection, it may be assumed, following Nernst's approach (Burton *et al.*, 1953), that there exists a diffusion boundary layer of approximate thickness δ , ahead of a plane solid-melt interface. The value of δ is taken as the length scale of the exponential: $\delta=D/v$.

The gradient of the equilibrium liquidus temperature at the interface is :

$$\left. \frac{d\Theta}{dx} \right|_{x=0} = m_c \left. \frac{dC(x)}{dx} \right|_{x=0} = m_c \frac{v}{D} (C_\infty - C_0) \quad (4)$$

where $m_c = d\Theta/dC$ is the slope of the liquidus in the phase diagram ($m_c < 0$).

The actual temperature gradient ahead of the interface is obtained by writing the conservation of the heat flux at the interface :

$$k \left. \frac{dT}{dx} \right|_L = k \left. \frac{dT}{dx} \right|_S - L\rho v \quad (5)$$

where k is the thermal conductivity (assumed equal in solid and liquid metal), L is the latent heat of crystallization, ρ is the density (neglecting the volume of crystallization) and $dT/dx)_S$ and $dT/dx)_L$ are the values of the temperature gradient in solid and liquid respectively.

The solute distribution creates a gradient of supercooling $d\Delta T/dx$, with $\Delta T = \Theta - T$, ahead of the interface. The condition (1) for the existence of constitutional supercooling is $d\Delta T/dx \geq 0$, or

$$-m_c \frac{v}{D} (C_0 - C_\infty) + \frac{L\rho v}{k} \geq \left. \frac{dT}{dx} \right|_s \quad (6)$$

3. Supercooling and kinetics of crystallization at the ICB

We will first use eq.(6) to verify that constitutional supercooling must indeed exist at the ICB. We will then investigate the kinetics of growth of iron crystals in the supercooled zone. We assume that crystals grow, not only at the ICB but ahead of it, and cause the inner core to grow, by settling down and accumulating at its surface.

For supercooling to exist ahead of the ICB, there must be some crystallization at the boundary. We will therefore consider the case where the crystallization right at the ICB provides a fraction f of the total crystallized mass, the remaining fraction $(1-f)$ being provided by a rain of crystals nucleated and grown above, in the supercooled zone. The volume of crystals accreting by unit area of the inner core and unit time must, of course, be equal to the rate of growth of the inner core. This equality constitutes a robust constraint on the kinetics of crystallization and accretion.

A similar analysis on the existence of supercooling ahead of the ICB has been performed by Loper and Roberts (1981). The main difference of the analysis presented in this paper is the inclusion of the solidification ahead of the ICB. This may be done easily using temperature gradients rather than employing the mass rate of solidification as in Loper and Roberts (1981). Also, temperature gradient in the inner core is taken into account in this paper. Another difference may be found in the expression of the flux of light material at the ICB. Loper and Roberts (1981) wrote down the equation for the diffusive flux (their eq.9) and proceeded rewriting it using thermodynamic arguments: the concentration in the bulk of the outer core (i.e. C_∞) was not assumed. On the other hand, in this paper, the diffusive flux was calculated by solving a diffusion equation, assuming the value of C_∞ . We believe that diffusion with

a moving boundary is represented better by solving the diffusion equation with a reliable estimate of C_∞ , rather than relying only on the thermodynamic arguments.

Parameters

Taking for the present day growth rate of the inner core the value of Labrosse *et al.* (1997): $v = 10^{-11}$ m/s = 0.3 mm/year, the volume crystallized and deposited must be equal to 10^{-11} m³/m².s i.e., 300 cm³/m².year. In other words, the present day growth rate of the inner core could be achieved, for instance, by the addition, per square meter, of a grain of iron of volume 1mm³ every 100 seconds in average.

Let us now list the values of the parameters used in the calculations. Many of these, not unexpectedly, will result from assumptions, due to our present lack of information on the composition of the core and on the phase diagrams at high pressure of the candidate alloys.

The coefficient of self-diffusion of liquid iron D_{Fe} near its melting point (which will be used later) can be calculated from the value of the viscosity at the ICB approximately equal to $\eta = 6 \times 10^{-3}$ Pa.s (Poirier, 1988, see also de Wijs *et al.*, 1998), using the Stokes-Einstein relation: $D_{Fe} = (k_B T_m)/(3\pi a_0 \eta)$. Taking the melting temperature Θ_0 at the ICB approximately equal to 5500 K (Poirier and Shankland, 1993), and the average interatomic distance $a_0 = 3 \cdot 10^{-10}$ m, we find $D_{Fe} \approx 4.5 \times 10^{-9}$ m²/s (see also Dobson, 2002). D_{Fe} is not to be confused with the coefficient of hetero-diffusion of the light element in liquid iron $D \approx 10^{-9}$ m²/s (Poirier, 1994a).

With the above values for v and D , we find that the thickness of the diffusive layer, taken equal to the scale length, δ , is equal to about 100m for the core (whereas $0.01 < \delta < 0.1$ mm in the case of crystal growth).

The latent heat of crystallization is taken equal to $L \approx 570$ kJ/kg (Poirier, 1994a) and the thermal conductivity, assumed to be equal in the solid and the liquid, is taken equal to $k \approx 60$ Wm⁻¹K⁻¹ (Labrosse *et al.*, 1997).

The density of the outer core is $\rho \approx 12000$ kg.m⁻³, about 6 to 10% less than the density of pure liquid iron at core pressures (Anderson and Ahrens, 1994), due to the presence of light elements, whose nature and proportions are still controversial (Poirier, 1994b) although silicon and sulfur (and perhaps oxygen) seem the most likely candidates. The inner core is about 3 to 6% less dense than pure iron at the pressure of ICB (Anderson and Ahrens, 1994), consistent with the possibility for some of the light element to enter the solid phase. We make the reasonable approximation that the concentration of light element in the outer core is $C_\infty \approx 0.1$ and that the concentration in the inner core is $C_S \approx C_\infty/2 \approx 0.05$.

One of the major problems consists in estimating the value of the slope of the liquidus $m_c = \partial\Theta / \partial C$ and $m_p = \partial\Theta / \partial P$. (As we shall explain later, the pressure dependence of the liquidus temperature must be taken into account to consider the interfacial stability of the ICB.) We do not know either the nature of the major light element in the Earth's core nor the phase diagrams of the relevant alloys at the pressure of the ICB. Suppose that the slope of the liquidus near the ICB is of the same order of magnitude as the slopes measured on the binary phase diagrams of Fe-S and Fe-Si alloys, near the Fe-rich end, at atmospheric pressure. In this case, using the diagrams in Raghavan (1988), we find that $m_c \approx -1.2 \times 10^3$ K for Fe-S and $m_c \approx -1.4 \times 10^3$ K for Fe-Si. Loper and Roberts (1981) used $m_c \approx -1.1 \times 10^4$ K in their analysis. Recent studies (Boehler, 1993; Alfè *et al.*, 2002; Rubie *et al.*, 2004) have pointed out the possible importance of the oxygen in the core. The liquidus slope of Fe-O system might then be expected to be much smaller than those of Fe-S and Fe-Si system according to

the high pressure experiments conducted by Boehler (1993). Therefore, smaller $|m_c|$ might be appropriate for the Earth's core. On the contrary, Alfè et al. (2002) obtained $|m_c|$ of order 10^4 K by their ab initio calculations for Fe-O system. Now, we will use four values of $|m_c|$ for the parameter study: $m_c \approx -1.1 \times 10^4$ K (following Loper and Roberts (1981), also the value is comparable with that of theoretical estimate by Alfè et al., 2002), $m_c \approx -1.3 \times 10^3$ K (average of m_c 's for Fe-S and Fe-Si from Raghavan (1983)), $m_c \approx -1.0 \times 10^2$ K and $m_c \approx -0.2$ K. $m_c \approx -0.2$ K may be too calm as the liquidus gradient at the ICB, but we nevertheless like to have this value for a demonstrative purpose. We employed $m_p = -9 \times 10^{-9}$ K/Pa following Poirier (1994a).

Finally, the temperature gradient inside the inner core, near the ICB, is taken equal to $dT/dx|_s = -1.7 \times 10^{-4}$ K/m (Labrosse *et al.*, 1997). The adiabatic gradient in the outer core (for $x > \delta = D/v$) is $dT/dx|_{ad} = -g\alpha T/c_p$, where $g = 4.4$ m/s² and $T = \Theta_0 \approx 5500$ K are the gravity and temperature at the ICB. Taking the coefficient of thermal expansion $\alpha \approx 1.3 \times 10^{-5}$ K⁻¹, and the specific heat at constant pressure $c_p \approx 860$ Jkg⁻¹ K⁻¹ (Poirier, 1994a), we find $dT/dx|_{ad} = -3.7 \times 10^{-4}$ K/m.

The values of the parameters used are summed up in Table 1.

Constitutional supercooling near the ICB and stability of the boundary

We can now use eq.(6) to estimate whether the condition for the existence of constitutional supercooling is fulfilled. We find that the LHS member of (6) is dominated by the value of the term $L\rho v/k$. For all possible values of δ , the condition for supercooling is therefore always obtained at the ICB, even considering the gross approximations used.

In laboratory experiments on solutions of salts (ammonium chloride or sodium nitrate) for which most models have been built (e.g., Worster, 1986), the solution is vigorously cooled from below. Crystallisation therefore occurs at the surface of the solid and a zone of constitutional supercooling develops ahead of the planar interface. The interface is unstable (Mullins and Sekerka, 1964) and dendrites develop, depressing more the liquidus temperature and raising the actual temperature by the release of latent heat, thus eliminating the supercooling and rapidly creating a mushy layer where equilibrium is restored (Worster, 1986). In steady state, the solid grows by pushing ahead a mushy layer of constant thickness.

Although there is no cooling from below in the case of the core and therefore no reason to consider a priori creation of dendrites, we will investigate the stability of the interface, at ICB, using the approach taken by (Mullins and Sekerka, 1964).

The criterion they use for stability (their eq. 32) can be written :

$$-\frac{1}{2} \left[\left. \frac{dT}{dx} \right|_S + \left. \frac{dT}{dx} \right|_L \right] + \frac{d\Theta}{dx} < 0 \quad (7)$$

There are however major differences between the cases they consider and that of the inner core : the temperature gradients in the solid and the liquid are negative in our case and positive in theirs, and the liquidus temperature they consider is independent of the distance to the interface, whereas, in the core, the liquidus temperature increases with pressure, and therefore depth.

The temperature gradient in the liquid depends on f , since eq. 5 must now be written

$$k \left. \frac{dT}{dx} \right|_L = k \left. \frac{dT}{dx} \right|_S - L\rho f v \quad (8)$$

Using eq. 6, we tested the stability of the system with respect to f and m_c , and calculated the growth rate against the wavelength of perturbation for various values of

the two parameters, taking the pressure effect into account. Fig.1 shows the temperature gradients necessary to investigate the existence of constitutional supercooling of the system and interfacial stability, and Fig.2 shows the linear growth rates of sinusoidal perturbation. See Appendix A for the details of the stability analysis.

It is confirmed that constitutional supercooling ($d\Theta/dx > dT/dx|_L$) occurs almost certainly under the ICB conditions (Fig.1). There is some range in f for which the interface is stable (eq.7) for all m_c 's considered in this paper (Fig.2). However, the region in f where constitutional supercooling AND interfacial stability becomes narrower with increasing $|m_c|$. Because the region is extremely narrow and f is a quantity determined as a result of the interplay of solidification, heat transfer and crystal kinetics, it is virtually no chance to attain constitutional supercooling and interfacial stability at one time with $m_c = -1.0 \times 10^2$, -1.3×10^3 and -1.1×10^4 K. On the contrary, it might be possible to have constitutional supercooling and interfacial stability with $m_c = -0.2$ K. We found that, for $f < 0.24$ there is no supercooling; for $0.24 < f < 0.43$ the interface is stable, even though there is supercooling; for $f > 0.43$, the interface is unstable. (For the supercooled and stable region we will take $0.2 < f < 0.4$, because the second digit of the bounds of f can easily be changed by employing different values of physical quantities.)

Mushy layer or slurry layer?

Linear instability of the solid-liquid interface itself does not necessarily lead to creation of a mushy layer. For example, if the growth rate of instability is small enough such that the time-scale to fill up the supercooled layer is long compared with the time-scale of our concern (say, lifetime of the Earth), it is not necessary to consider about possible creation of mush layer.

Table 2 summarizes the maximum growth rates and corresponding wavelength of linear instability with $m_c = -1.0 \times 10^2$, -1.3×10^3 and -1.1×10^4 K. $f=1$ is employed. Corresponding time-scales are at most about 100 years, very short compared with geological time-scale. A mushy layer will then be created at the ICB.

In case that $m_c = -0.2$ K, which may not be appropriate for the ICB condition, the interface is stable when $0.2 < f < 0.4$. Therefore, a slurry layer could exist at the ICB. Even if the interface were unstable, the maximum growth rate of the instabilities, $\epsilon(t)$ (see Appendix A), would occur for a wavelength of 20 m and would be very small, of the order of 10^{-12} s^{-1} : a bump of 1 mm would grow by $0.03 \text{ }\mu\text{m}$ in one year, while the core grows by 0.3 mm. However, note here that the time constant corresponding to 10^{-12} s^{-1} is 32,000 years, which is very short compared with the age of the inner core (around 1 Ga, see Labrose *et al.*, 2001). This might indicate that a mushy layer can be created if f is sufficiently large with $m_c = -0.2$ K.

It is very likely that the mushy layer exist at the ICB. Nevertheless, a one-dimensional model of the quasi-steady slurry layer with $m_c = -0.2$ K is shown in Appendix C, and possible nucleation mechanism is presented in the Appendix B. Obtained supercooling is of order 0.1 K near the ICB and excess of light element is about 3% at the ICB. The compositional difference will provide enormous Rayleigh number and it will be almost certain that to sustain such layer is not probable: the light element will be thrown away in form of plume or blob. Also, it is found that the slurry layer must have nuclei through heterogeneous nucleation (Appendix B). To supply enough number of nuclei steadily into the slurry layer ($10^{-4} \text{ nuclei/m}^3$ in this case supposing the average final radius is 10^{-3} m) during the course of the inner core growth

seems difficult. Therefore, with even very small value of $|m_c|$, slurry layer will not be probable.

4. Conclusion

Transfer of results applicable to the crystallization of metal ingots and saline solutions cooled from below has led to the generally unquestioned acceptance that there exists a sizeable mushy layer at the inner core boundary of the Earth. The metallurgical conditions are, however, very different from the ones obtaining at the ICB, in particular, as the growth rate and the temperature gradients are smaller by six orders of magnitude.

We assessed the possibility of existence of a supercooled zone ahead of the ICB and we investigated the situation arising from crystallization of iron in this layer. Using a modified Mullins and Sekerka criterion, we found that creation of mushy layer at the ICB is likely if liquidus slope against concentration is of order 100 K or larger.

It is found that, if m_c is of order 0.1K and as long as a fraction between about 20 and 40% of the total volume increase of the inner core is produced by crystallization at the ICB, the solid-liquid boundary is stable, so that no dendrites can grow. Under these conditions, instead of a mushy layer, we may have a slurry layer, in which crystals grow from preexisting nuclei and settle down to the boundary. However, to supply enough number of nuclei continuously in the course of the inner core growth seems problematic because the nucleation is possible only through heterogeneous nucleation. Also, it seems difficult to sustain a buoyant slurry layer against Rayleigh-Taylor type instability.

In conclusion, the analysis given in this paper supports the existence of the mushy layer at the ICB.

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APPENDIX A: Linear stability of a planar interface during solidification with the pressure effect on liquidus temperature

The linear stability analysis of a planer interface during crystallization made by Mullins and Sekerka (1964) is generalized in this appendix. Mullins and Sekerka assumed that the liquidus is a function of concentration only, $\Theta = \Theta(C)$. It is necessary to take the effect of pressure on liquidus temperature into consideration to discuss the interfacial stability of the ICB. The following is a brief summary of the analysis with $\Theta = \Theta(C, P)$.

As Mullins and Sekerka (1964), we assume there is no convection in the fluid. Also, crystallization above the solid-liquid interface is neglected. Suppose an infinitesimally small sinusoidal perturbation of the form

$$x = \psi(y, t) = \varepsilon(t) \sin qy \quad (\text{A.1})$$

is applied on the interface. Although the case with one-dimensional perturbation is shown in this appendix, the results found in the following can be generalized to two-dimensional case by replacing $x = \psi(y, z, t) = \varepsilon(t) \sin q_y y \sin q_z z$ and $q^2 = q_y^2 + q_z^2$.

In the analysis, it is assumed that the temperature and concentration are in steady state with pulling velocity V (growth velocity of the interface). The effect of pressure on the liquidus temperature comes in as a part of the boundary conditions. Because the solid-liquid interface, $x = \psi$, is at the liquidus temperature $\Theta = \Theta(C, P)$, the temperature at the interface ($= T_\psi$) is written as

$$T_\psi = m_C(C_\psi - C_0) - \rho g m_p \psi + T_m - T_m \tilde{\Gamma} q^2 \psi, \quad (\text{A.2})$$

where

$$m_c = \partial\Theta / \partial\mathcal{C} (< 0), \quad m_p = \partial\Theta / \partial\mathcal{P} (> 0), \quad (\text{A.3})$$

C_ψ is the concentration at the interface, C_0 is the concentration of the interface if there is no perturbations, ρ is the density, g is the acceleration of gravity (hydrostatic pressure $dP = -\rho g dx$ is assumed), $T_m = \Theta_0$ is the melting temperature without the perturbations. The last term in eq.(A.2) represents the effect of curvature of the interface on melting represented with capillary constant $\tilde{\Gamma} = \sigma / L$, where σ is the specific liquid-solid interfacial free energy and L is the latent heat.

The interfacial velocity (including that due to perturbation) must be in agreement with diffusion considerations, the following conditions must be satisfied;

$$V + \frac{\partial\varepsilon}{\partial t} \sin qy = \frac{1}{L} \left[k \left(\frac{\partial T}{\partial x} \right)_{s,\psi} - k \left(\frac{\partial T}{\partial x} \right)_{L,\psi} \right] = \frac{D}{C_\psi(\beta-1)} \left(\frac{\partial\mathcal{C}}{\partial x} \right)_\psi, \quad (\text{A.4})$$

where k is the thermal conductivity in the solid and liquid (assumed to be identical), D is the material diffusivity, and β is the partition coefficient which is assumed to be 0.4. After some calculations, the following expression for the growth rate of the disturbance, $(\partial\varepsilon / \partial t) / \varepsilon$, is found as;

$$\frac{\partial\varepsilon / \partial t}{\varepsilon} = \frac{Vq \{-2(g\rho m_p + T_m \tilde{\Gamma} q^2)(q^* - (V/D)s) - (G + G')(q^* - (V/D)s) + 2m_c G_c (q^* - (V/D))\}}{2qm_c G_c + (G' - G)(q^* - (V/D)s)}, \quad (\text{A.5})$$

where $q^* = (V/2D) + [(V/2D)^2 + q^2]^{1/2}$, $s = 1 - \beta$, G and G' are the temperature gradient at the interface without the perturbation in liquid and solid, respectively, G_c is the concentration gradient when disturbance is zero, and κ is the thermal diffusivity of the solid and liquid, assumed to be equal.

The growth rates of perturbation are evaluated for $V = fv$ ($v = 10^{-11}$ m/s) with

$f=0.2, 0.4, 0.6, 0.8$ and 1.0 , by using the values of physical quantities listed in Table1, and plotted against wave length of perturbation ($= 2\pi/q$) in Fig.2.

The fundamental stability criterion may be obtained as Mullins and Sekerka (1964) did. The system is stable if the maximum growth rate with respect to q is negative. By eq.(A.5), the approximate criteria may be written as

$$\begin{aligned} -\frac{1}{2}(G'+G)+m_c G_c - \rho g m_p > 0 & \text{ unstable} \\ -\frac{1}{2}(G'+G)+m_c G_c - \rho g m_p < 0 & \text{ stable} \end{aligned} \quad (\text{A.6})$$

The effect of pressure on the liquidus temperature is stabilizing the system. By the definitions of m_c , G_c and m_p ,

$$m_c G_c - \rho g m_p = \frac{\partial \Theta}{\partial C} \frac{dC}{dx} + \frac{\partial \Theta}{\partial P} \frac{dP}{dx} = \frac{d\Theta}{dx}, \quad (\text{A.7})$$

and the stability criteria may be written as, by using $d\Theta/dx$,

$$-\frac{1}{2}(G'+G)+\frac{d\Theta}{dx} < 0 \quad : \text{ stable.} \quad (\text{A.8})$$

The region of stability with respect to f is shown in Fig.1.

APPENDIX B: Nucleation and growth of crystals in a supercooled layer

As originally proposed by Loper and Roberts (1978,1981), one may assume that "virtually all the solidification occurs ahead of the inner core boundary" in the zone of constitutional supercooling. Roberts and Loper therefore envisioned the existence of a slurry layer, suspension of crystals in the fluid, whose hydrodynamics they studied.

In the present work, we consider that grains of iron settle to the ICB. Crystals nucleate within the supercooled layer (the region where $\Delta T \geq 0$) and, once nucleated, they grow, with a growth rate depending on supercooling (see below). As they are denser than the fluid, they fall toward the ICB with the Stokes velocity and as they

grow, they fall faster. The inner core therefore grows, partly by crystallization at the interface and partly by accretion of a rain of crystals of various sizes (depending on the height from which they have fallen) pushing ahead a zone of average supercooling, where grains continually nucleate, grow and fall.

In the laboratory, homogeneous nucleation occurs practically only in small supercooled droplets; in most cases, heterogeneous nucleation takes place on preexisting nucleants, tiny particles of dust or other impurities. In the case of the core, the possibility of homogeneous nucleation cannot be rejected offhand.

The homogeneous nucleation rate is given by Turnbull (1950):

$$N = A \exp \left[- \frac{B \sigma^3}{(\Delta G_f)^2 k_B T} \right] \quad (\text{B.1})$$

where N is the number of nuclei formed per m^3 and second, $A \approx 10^{39} \text{ s}^{-1} \text{ m}^{-3}$ for liquid metals, $B=16\pi/3 \approx 16.75$ for spherical grains and k_B is Boltzmann's constant. The quantity σ is the interfacial energy between liquid and solid; for iron, we may take $\sigma \approx 0.204 \text{ J} \cdot \text{m}^{-2}$.

$\Delta G_f = \Delta S_f \Delta T$ is the difference in free energy between crystal and liquid phases (free energy of fusion), where ΔS_f is the entropy of fusion, respectively and ΔT is the supercooling. Taking $\Delta S_f = 6.5 \text{ J/mol} \cdot \text{K} = 1.485 \times 10^6 \text{ J/m}^3 \cdot \text{K}$ for ϵ -Fe (Poirier and Shankland, 1993), we obtain $\Delta G_f = 1.485 \cdot 10^6 \Delta T \text{ J/m}^3$.

Taking the temperature at ICB equal to 5500 K, we obtain

$$N = 10^{39} \exp \left[- \frac{8.4 \times 10^5}{\Delta T^2} \right] \text{ s}^{-1} \text{ m}^{-3} \quad (\text{B.2})$$

For values of supercooling of the order of a few degrees, the number of nuclei formed by homogeneous nucleation is essentially zero.

Heterogeneous nucleation remains therefore the only possibility. For the sake of simplicity, we may reasonably assume that there is a uniform distribution of nucleant particles in the zone of constitutional supercooling and we will take the number N of nuclei formed per unit volume and unit time as a free parameter.

The growth rate of crystals is given by Kirkpatrick (1975) (and also, Loper (1992) : see the note below eq.(B.7)). It depends on the degree of supercooling $\Delta T(x) = \Theta(x) - T(x)$, which, in turn, depends on the distance x to the interface.

The linear growth rate of a crystal is given, in m/s, (Kirkpatrick, 1975) by :

$$\Gamma = \frac{D_{Fe}}{a_0} \left[1 - \exp\left(-\frac{\Delta G_f}{RT}\right) \right] \quad (\text{B.3})$$

where D_{Fe} is the self-diffusion coefficient of the melt, a_0 is an average interatomic distance in the liquid, taken equal to 0.3 nm, and ΔG_f is the free energy of fusion, which can be written, as above, $\Delta G_f = \Delta S_f \Delta T$, and as $\Delta S_f \Delta T \ll RT$, we can write

$$\Gamma \approx \frac{D_{Fe}}{a_0} \frac{\Delta S_f \Delta T}{RT} \quad (\text{B.4})$$

or

$$\Gamma \approx 2 \times 10^{-3} \Delta T \quad \text{m/s} \quad (\text{B.5})$$

A nucleus can grow when the free energy ΔG_f lost by increasing the volume of a grain becomes greater than the surface energy gained by increasing its area. This happens for a critical radius $r_c = 2\sigma/\Delta G_f \approx 2 \times 10^{-9}$ m.

Let us assume, for the sake of simplicity, that in 1 second, N nuclei per m^3 grow, and fall toward the ICB as they grow.

The Stokes velocity (assumed to be reached rapidly) is

$$V_s = \frac{2\Delta\rho g r^2}{9\eta}. \quad (\text{B.6})$$

$\Delta\rho \approx 600 \text{ kg/m}^3$ is the difference in density between solid and liquid core, $g = 4.4 \text{ ms}^{-2}$ is the gravity at ICB, $\eta = 6 \times 10^{-3} \text{ Pa.s}$ is the viscosity of the liquid core near ICB and r is the radius of an iron grain assumed spherical, varying linearly with time, according to (B.6). With these values, the Stokes velocity can be written :

$$V_S \approx 10^5 \Gamma^2 t^2. \quad (\text{B.7})$$

The growth rate Γ and the Stokes velocity (B.7) will be used in the analysis given in Appendix C.

Although it is not employed in this paper for simplicity, note here that nonequilibrium theory of slurry is studied by Loper (1992), and growth rate of the crystal in supercooled zone is evaluated. The growth rate is evaluated to the dominant order as

$$\frac{dr}{dt} = \frac{\Psi_\infty}{\rho \bar{\mu}_0 C_0^L r} \quad (\text{B.8})$$

where Ψ_∞ is the measure of departure from liquidus equilibrium far from the particle written as

$$\Psi_\infty = -\delta_0 p + L + (\bar{\mu} C^L)_0 C_0^L, \quad (\text{B.9})$$

$\bar{\mu}_0$ is change of chemical potential of liquid with liquid composition, C_0^L is the concentration of light material far from the crystal, and δ_0 is volume expansion upon melting. By employing $\bar{\mu}_0 = 4.4 \times 10^7 \text{ J/kg}$, $\delta_0 = 1.0 \times 10^{-6} \text{ m}^3/\text{kg}$ (Loper and Roberts, 1981), and $C_0^L = 0.1$, we obtain

$$r = \sqrt{2.6 \times 10^{-6} t + r_0} \quad (\text{B.10})$$

and

$$V_S \approx 2.5 \times 10^{-1} t. \quad (\text{B.11})$$

APPENDIX C: A one-dimensional quasi-steady state model of a slurry layer

$$(m_c = -0.2 \text{ K})$$

We now use the considerations outlined in section 3 to construct a simple model of a slurry layer in order to examine the amount of supercooling and profile of concentration in the layer. The results will provide some information if such layer may actually exist in nature. Let us sum up the simplifying assumptions:

i) The main body of the liquid core is well mixed by convection, so that the temperature gradient is adiabatic: $dT/dx|_{ad}$ and the concentration of light element is uniform and equal to C_∞ .

ii) Due to solidification at the interface and precipitation of crystals from the supercooled layer, the solid-liquid interface ($x=0$, the top of the crystal pile) moves with velocity v . The ratio of the amount of iron crystallized at the ICB to the total amount crystallized is equal to $f < 1$. (The assumption of a smooth solid-liquid interface needs some more justification. This depends on the rate at which the crystals raining onto the surface are incorporated into the inner core by sintering.)

iii) Close to the ICB, there exists a boundary layer of thickness $\delta = D/v \approx 100 \text{ m}$, where diffusion of light element is dominant. We assume that the temperature gradient is adiabatic beyond δ , and that the temperature profile in the layer of thickness δ is solution of the diffusion equation.

iv) Even though the supercooled layer extends beyond δ into the outer core, we assume that most of the crystallization occurs in the layer of thickness δ . Hence, we take δ as the thickness of the slurry layer.

v) Crystallization in the slurry layer releases heat and light element, thus creating a source term proportional to the crystallized volume in the diffusion equations for temperature and concentration.

vi) The volume rate of solidification per unit volume and unit time in the slurry layer is

$$\phi(x) = A\Delta T(x) \quad (C.1)$$

where $\Delta T(x) = \Theta(x) - T(x)$ is the value of supercooling at distance x from the ICB.

The value of $\phi(x)$ is constrained by the relation:

$$\int_0^\delta \phi(x) dx = (1-f)v \quad (C.2)$$

A is a constant whose value will be found as part of the solution.

In the diffusive boundary layer (slurry layer) of thickness δ , the equations governing the temperature T and concentration C of light element are:

$$\kappa \frac{d^2 T}{dx^2} + v \frac{dT}{dx} = -\frac{L}{c_p} \phi(x) \equiv Q_T(x) \quad (C.3)$$

$$D \frac{d^2 C}{dx^2} + v \frac{dC}{dx} = -[C(x) - C_s] \phi(x) \equiv Q_C(x) \quad (C.4)$$

where κ is the thermal diffusivity, D is the diffusion coefficient of the light element, c_p is the specific heat at constant pressure, L is the latent heat of crystallization and C_s is the concentration of light element in the inner core.

The liquidus temperature Θ is a function of concentration and pressure. Assuming hydrostatic equilibrium, we have:

$$\frac{d\Theta}{dx} = m_c \frac{dC}{dx} - \rho g m_p \quad (C.5)$$

where $m_c = \frac{\partial \Theta}{\partial C}$ and $m_p = \frac{\partial \Theta}{\partial P}$ at the ICB. Integrating eq. (C.5), we obtain

$$\Theta = m_c [C(x) - C_0] - \rho g m_p x + \Theta_0. \quad (C.6)$$

The boundary conditions for integration of eqs (C.3) and (C.4) are the following at the solid-liquid interface (ICB):

$$T=\Theta_0 \quad (C.7)$$

$$fv = \frac{k}{\rho L} \left[\left. \frac{dT}{dx} \right|_s - \left. \frac{dT}{dx} \right|_L \right] \quad (C.8)$$

where k is the thermal conductivity (taken equal in the solid and liquid) and $\left. \frac{dT}{dx} \right|_s$ and

$\left. \frac{dT}{dx} \right|_L$ are the temperature gradients in the solid and liquid, respectively. Note that

eq.(C.7) may not be exactly true because $x=0$ is the top of the crystal pile that might have temperature slightly different from the liquidus temperature. However, the deviation is expected to be very small and we employ the condition (C.7) as first order approximation.

From eq. 4 (with v replaced by fv), we see that the concentration gradient at the ICB ($x=0$) must satisfy

$$fv = \frac{D}{C_s - C_0} \frac{dC}{dx} \quad (C.9)$$

where C_0 is the concentration at the interface ($x=0$), which will be determined as part of the solution.

At the edge of the diffusive layer ($x=\delta$), we must have

$$C=C_\infty \quad (C.10)$$

Eqs.(C.3) and (C.4) are solved iteratively.

Initial profiles for temperature and concentration are first specified in a layer of thickness λ . Using eq.(C.9), λ is given by:

$$\lambda = \frac{C_\infty - C_0}{\left. \frac{dC}{dx} \right|_{x=0}} = \frac{C_\infty - C_0}{C_s - C_0} \frac{D}{fv} \quad (C.11)$$

For concentration, we take

$$C(x) = \begin{cases} C_0 + x \left. \frac{dC}{dx} \right|_{x=0} & \text{for } 0 \leq x \leq \lambda \\ C_\infty & \text{for } \lambda < x \end{cases} \quad (\text{C.12})$$

and for temperature,

$$T(x) = \begin{cases} \Theta_0 + x \left. \frac{dT}{dx} \right|_{x=0} & \text{for } 0 \leq x \leq \lambda \\ \Theta_0 + \lambda \left. \frac{dT}{dx} \right|_{x=0} + (x - \lambda) \left. \frac{dT}{dx} \right|_{ad} & \text{for } x > \lambda \end{cases} \quad (\text{C.13})$$

where $\left. \frac{dT}{dx} \right|_{ad}$ is the adiabatic gradient in the outer core near the ICB.

The liquidus temperature is taken as

$$\Theta(x) = \begin{cases} m_c \left. \frac{dC}{dx} \right|_{x=0} - \rho g m_p x + \Theta_0 & \text{for } 0 \leq x \leq \lambda \\ m_c (C_\infty - C_0) - \rho g m_p x + \Theta_0 & \text{for } x > \lambda \end{cases} \quad (\text{C.14})$$

From eqs (C.13) and (C.14), we obtain the supercooling ΔT

$$\Delta T = \begin{cases} \left[m_c \left. \frac{dC}{dx} \right|_{x=0} - \rho g m_p - \left. \frac{dT}{dx} \right|_{x=0} \right] x & \text{for } 0 \leq x \leq \lambda \\ \left[-\rho g m_p - \left. \frac{dT}{dx} \right|_{ad} \right] x + m_c (C_\infty - C_0) - \left[\left. \frac{dT}{dx} \right|_{x=0} + \left. \frac{dT}{dx} \right|_{ad} \right] \lambda & \text{for } x > \lambda \end{cases} \quad (\text{C.15})$$

Note that supercooling is possible only if

$$m_c \left. \frac{dC}{dx} \right|_{x=0} - \rho g m_p - \left. \frac{dT}{dx} \right|_{x=0} > 0 \quad (\text{C.16})$$

Starting with the initial profiles of temperature and concentration, and a given value of f , we calculate the value of $\Delta T(x)$ and of $\phi(x)$ and A from eqs (C.15) and (C.1), and therefore the values of the source terms $Q_T(x)$ and $Q_C(x)$ in eqs (C.4) and (C.5).

The diffusion eqs.(C.3) and (C.4) are then solved with the boundary conditions (C.7), (C.8) and (C.9), (C.10) at $x=0$ and $x=\delta$.

Values of A and C_0 are found, as well as new profiles $T'(x)$ and $C'(x)$ which are used to solve again the diffusion equations, and so on until a satisfactory convergence is obtained. Convergence is obtained after about 3 iterations.

We find the steady-state profiles as shown in Fig. 3 for $f=0.3$ (in the region of interface stability and supercooling) and $f=0.5$ (in the region of interface instability, but very small relative growth rate: 10^{-13} s^{-1}).

The values of A and the concentration C_0 at the ICB are:

$$\begin{array}{lll} \text{For } f=0.3 & A \approx 1.47 \times 10^{-11} & C_0 \approx 0.125 \\ \text{For } f=0.5 & A \approx 2.87 \times 10^{-11} & C_0 \approx 0.136 \end{array}$$

From the values of A , we can estimate the number N_{nc} of nuclei necessary for satisfying the constraint that the total volume of crystallized iron par square meter is equal to the growth rate v of the inner core.

By definition of $\phi(x)$, we have

$$\phi(x) = N_{nc} \cdot 4\pi \langle r^2 \rangle \frac{dr}{dt} \quad (\text{C.17})$$

where $\langle r^2 \rangle$ is an average of the square of the radii of the crystals (assumed spherical for simplicity), representative of the population, and dr/dt is the linear growth rate Γ , given by eq.(B.5): $\Gamma \approx 2 \times 10^{-3} \Delta T$ m/s.

We can therefore write

$$\phi(x) = 8 \times 10^{-3} \pi \langle r^2 \rangle N_{nc} \Delta T \quad (\text{C.18})$$

and by comparison with eq.(C.1), we have

$$A = 8 \times 10^{-3} \pi \langle r^2 \rangle N_{nc} \quad (\text{C.19})$$

We see, from Fig.3, that the maximum supercooling at about 100 m from the ICB is of the order of 0.1 K. Crystals starting to form on nuclei at this height would grow and fall rapidly, hitting the boundary in times of the order of one minute, with radii of the order of one centimeter (eqs B.5 & B.7). However the distribution of nuclei is assumed to be uniform in the slurry layer and the crystals formed closer to the boundary would grow much more slowly, as the supercooling goes to zero near the ICB.

The number of nuclei, per unit volume and unit time, necessary for the crystals growing ahead of the ICB to provide a fraction ($1-f$) of the total increase of volume of the inner core, can be found, as a function of the final radius, by eq. (C.19). As an example, for $f=0.3$, $A \approx 10^{-11}$ and $N_{nc} \approx 10^{-4}$ nuclei/ m³, if the average final radius (square root of $\langle r^2 \rangle$) is equal to 10^{-3} m. The existence of a distribution of radii makes a rigorous calculation difficult. However, the estimate gives a rather reasonable value of the average radius and provides a rough idea of the population of the slurry layer in steady state, leading to the qualitative conclusion that the layer is not densely crowded with crystals. As a consequence, the effective viscosity of the slurry layer should not be very different from the viscosity of entirely liquid iron.

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TABLES

Table 1. The values of the parameters used in this study.

Growth rate of the inner core	v	10^{-11} m/s
Viscosity of the outer core	η	$6 \cdot 10^{-3}$ Pa.s
Melting temperature at ICB	Θ_0	5500 K
Coefficient of self-diffusion of liquid Fe	D_{Fe}	$4.5 \cdot 10^{-9}$ m ² /s
Coefficient of heterodiffusion of light element	D	10^{-9} m ² /s
Latent heat of crystallisation at ICB	L	570 kJ/kg
Thermal conductivity of inner & outer core	k	60 W/m.K
Thermal diffusivity of outer core	κ	$6 \cdot 10^{-6}$ m ² /s
Specific heat at constant pressure	c_P	860 J/kg.K
Density of outer core	ρ	12000 kg/m ³
Concentration of light element in outer core	C_∞	0.1
Concentration of light element in inner core	C_S	0.05
Slope of the liquidus $\Theta(C)$ at ICB	m_C	$-0.2 - 1.1 \times 10^4$ K
Slope of the liquidus $\Theta(P)$ at ICB	m_P	$9 \cdot 10^{-9}$ K/Pa
Temperature gradient in the inner core	$dT/dx _S$	$-1.7 \cdot 10^{-4}$ K/m
Adiabat in the outer core	$dT/dx _{ad}$	$-3.7 \cdot 10^{-4}$ K/m

Table 2

Maximum growth rate of linear instability

m_c (K)	growth rate (sec ⁻¹)	wavelength (m)
-1.0×10^2	3.08×10^{-10}	0.68
-1.3×10^3	1.12×10^{-9}	0.19
-1.1×10^4	3.25×10^{-9}	0.065

FIGURE CAPTIONS

Figure1. The region of stability and supercooling, see equations 1 and 7 for the criteria of supercooling and stability. . The values of physical quantities listed in Table1 are used. (a) $m_c = -0.2 \text{ K}$, (b) $m_c = -1.0 \times 10^2 \text{ K}$, (c) $m_c = -1.3 \times 10^3 \text{ K}$, and (d) $m_c = -1.1 \times 10^4 \text{ K}$. Note that f is the fraction of the total crystallized mass onto the ICB.

Figure2. Growth rate of the perturbation normalized to its amplitude ε for various f with respect to wave length of perturbation. The values of physical quantities listed in Table1 are used. (a) $m_c = -0.2 \text{ K}$, (b) $m_c = -1.0 \times 10^2 \text{ K}$, (c) $m_c = -1.3 \times 10^3 \text{ K}$, and (d) $m_c = -1.1 \times 10^4 \text{ K}$

Figure3. Steady state profiles of fluid and liquidus temperatures (upper panels) and concentration (lower panels) for $f=0.3$ and 0.5 .