Physics of the Earth and Planetary Interiors 215 (2013) 21–28

Contents lists available at SciVerse ScienceDirect

Physics of the Earth and Planetary Interiors

journal homepage: www.elsevier.com/locate/pepi

# The stratified layer at the core–mantle boundary caused by barodiffusion of oxygen, sulphur and silicon

D. Gubbins [a,b,c], C.J. Davies [a,b,*]

[a] School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK
[b] Institute of Geophysics and Planetary Physics, Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA 92092-0225, USA
[c] Miller Institute, Department of Earth & Planetary Science, University of California Berkeley, CA 94720-4767, USA

ARTICLE INFO

*Article history:*
Received 17 February 2012
Received in revised form 6 August 2012
Accepted 13 November 2012
Available online 22 November 2012
Edited by C. Jones

*Keywords:*
Barodiffusion
Stratified layer
Earth's core

ABSTRACT

Barodiffusion is the tendency of light elements to migrate down a pressure gradient. In the Earth's outer core, this effect can lead to the development of a chemically stable layer beneath the core–mantle boundary (CMB). Barodiffusion has so far been considered unimportant relative to other effects, but here we show that it dominates at the CMB and leads to an order-100 km-thick layer that is rich in light elements and stably stratified. Barodiffusion changes not only the equations governing molecular diffusion of light elements in the core but also the boundary condition at the CMB to a non-zero compositional gradient, a point missed by previous studies. The mathematical problem has the same form as the recently-proposed migration of light elements passing from the mantle into the core; the effect of barodiffusion is comparable provided all light elements in the outer core are included, not just the light element driving the convection as in previous studies. We therefore conclude that a substantial stable layer can exist at the top of the core independent of any mass flux across the CMB. We solve the relevant diffusion equations in a thin layer beneath the CMB for barodiffusion of oxygen, sulphur and silicon over the whole history of the core using diffusion constants obtained from first principles calculations. The lower boundary of the layer is defined to be the neutrally stable level where the stabilising barodiffusive gradient is equal and opposite to the destabilising gradients associated with buoyancy sources in the well-mixed bulk of the core. We assume no mass flux across the CMB, and find the compositional gradient imposed by barodiffusion to be so large that its stable density gradient could not be overcome by any destabilising gradient at any time. The light layer therefore develops at the top of the core immediately after core formation; solving the diffusion equations shows it to grow to a thickness of order 100 km. The final thickness is remarkably insensitive to the model of core cooling used to specify the destabilising gradients in the well-mixed region of the core. We consider a variety of instability mechanisms and argue that the stratification is strong enough to inhibit virtually all radial motion within the layer, although conclusive evidence for the existence of stratification can only come from observations. The variation in composition is sufficiently strong to produce geomagnetic effects and seismic velocity anomalies of a fraction of a percent that could be, and may already have been, detected. Differences in the diffusion parameters for the three light elements cause differences in their relative concentrations in the layer, leaving the layer oxygen-rich relative to sulphur or silicon.



## 1. Introduction

Barodiffusion is usually negligible in the laboratory but may be significant in the Earth's core, as originally suggested by Braginsky (1963). Any diffusion of light elements towards the core–mantle boundary (CMB) detracts from the buoyancy force driving chemical convection in the core in the same way that heat conducted down the adiabatic gradient detracts from the buoyancy force driving thermal convection. Barodiffusion is, however, a weaker effect than adiabatic conduction because chemical diffusivity is generally smaller than thermal diffusivity. Estimates of the entropy gain by barodiffusion show it to be about an order of magnitude smaller than the entropy gain from thermal conduction (Gubbins et al., 1979, 2004) and it is usually neglected from estimates of the power available to drive the geodynamo (e.g., Loper, 1978; Labrosse et al., 1997).

Another effect of barodiffusion is to accumulate light elements at the top of the core over time, which would create a chemically stratified layer there. Fearn and Loper (1981) concluded that such a layer would be limited in thickness to a few tens of kilometres, if

* Corresponding author at: School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK. Tel.: +44 (0) 113 3435543.
*E-mail address:* c.davies@earth.leeds.ac.uk (C.J. Davies).

0031-9201/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.pepi.2012.11.001

indeed it existed at all and was not destroyed by the convective processes. Braginsky (1993, 1999) has developed a theory for the dynamics of a "hidden ocean of the core" that could form from such a barodiffusive layer. Lister and Buffett (1998) considered the disruption of a stratified layer by thermochemical convection and concluded that such a layer would survive, although they did not include the effects of barodiffusion. The possibility of a chemically stratified layer at the top of the core has been the subject of recent interest following the suggestion of Asahara et al. (2007) and Frost et al. (2010) that oxygen may be dissolving slowly into the core from the mantle over time. This would also lead to a stratified upper layer in the outer core, which has been studied by Buffett and Seagle (2010). Their study includes barodiffusion, but they only include the light element expelled from the inner core, the one driving core convection, and omit the remaining light elements, thereby underestimating the effect.

The main bulk of the core convects in response to an underlying destabilising density gradient caused by cooling, freezing, and release of light elements at the inner core boundary (ICB). We assume the stratification caused by barodiffusion is strong enough to resist significant penetration by the underlying convection and that double-diffusive effects are restricted to negligibly thin interfaces; the stratified layer grows by diffusion, relatively unhindered by the weaker underlying destabilising gradients. These assumptions are assessed subsequently in terms of the calculated destabilising and stabilising density gradients.

Diffusive flux of a light component of a two-component liquid mixture is usually assumed to depend linearly on the gradients of the three state variables: pressure $P$, temperature $T$, and light element concentration $c$. Temperature effects are negligible in the Earth's core but the hydrostatic pressure gradient modifies Fick's law of mass diffusion [Eq. (2) below]. If we adopt an upper boundary condition of zero mass flux at the CMB, the appropriate boundary condition on the concentration gradient there is a non-zero gradient fixed by the barodiffusion term. The diffusion problem to be solved is therefore mathematically identical to one where light elements diffuse in from above at a fixed rate, the same situation proposed by Asahara et al. (2007) (if movement of oxygen within the mantle is unrestricted the boundary condition is constant $c$ instead of constant gradient, but this makes little qualitative difference). The magnitude of the concentration gradient applied to the boundary is given by the known hydrostatic pressure gradient times the barodiffusion constant, which has been estimated from first principles calculations (Alfè et al., 2002a,b) for two-component mixtures of O, S, and Si in Fe under core conditions [see also Gubbins et al., 2004].

The paper is organised as follows. In Section 2 we solve the time-dependent diffusion equation that governs the growth of a stable layer. We compute the stabilising barodiffusive gradient using estimates of the diffusion constants for each of the three elements and combine them into a single layer, assuming the multi-component mixture acts as three independent two-component mixtures. In Section 3 we calculate the stable layer thicknesses due to barodiffusion. In Section 4 we assess the dynamical stability of the barodiffusive layers. Discussion and conclusions are presented in Section 5 and Section 6.

## 2. Time-dependent evolution of the stratified layer caused by barodiffusion

The diffusion equation is

$$\rho \frac{\partial c}{\partial t} + \nabla \cdot \boldsymbol{i} = 0. \tag{1}$$

The mass flux, $\boldsymbol{i}$, in the presence of a pressure gradient is

$$\boldsymbol{i} = -\rho D \nabla c + \alpha_c \alpha_D g_0 r, \tag{2}$$

where $\rho$ is the density, $D$ is the molecular diffusivity, $c$ is the mass concentration, $\alpha_c = -\rho^{-1}(\partial\rho/\partial c)_{P,T}$ is the compositional expansion coefficient, $g_0$ is acceleration due to gravity at the CMB, and $r$ is radius. The barodiffusion constant, $\alpha_D$, is defined in terms of the gradient of the chemical potential $\mu$ (Landau and Lifshitz, 1959)

$$\alpha_D = \frac{\rho D}{(\partial\mu/\partial c)_{P,T}}, \tag{3}$$

$$(\partial\mu/\partial c)_{P,T} = \frac{k_B \overline{T}}{\bar{c}} + \lambda \quad \text{eV/atom}, \tag{4}$$

where $k_B$ is Boltzmann's constant, $\bar{c}$ is the molar concentration, and $\lambda$ is a correction to the first term, the ideal solution theory approximation (Gubbins et al., 2004). $\overline{T} = (T_i + T_o)/2$ is the average outer core temperature, where $T_i$ is the ICB temperature and $T_o$ the CMB temperature.

The barodiffusion profile is obtained by solving Eq. (1) for $c(r,t)$ with initial condition $c(r,0) = c_0$, a constant, and zero mass flux at the outer boundary $r = r_o$,

$$\left.\frac{\partial c}{\partial r}\right|_{r=r_o} = \frac{\alpha_c \alpha_D g_0 r_o}{\rho D} = b, \tag{5}$$

which results from (2) with $\boldsymbol{i} = 0$. A second boundary condition is needed to determine the average concentration. This could be obtained by matching the concentration at the base of the layer to the value in the well-mixed core below, but that would require an unnecessarily complicated calculation. Instead we assume the layer remains thin throughout Earth's history, an approximation that is fully justified later by the results. The skin depth is $\sqrt{Dt}$ for age $t$, or about 38 km in 4.5 Ga. This allows us to neglect spherical geometry and solve the problem in Cartesian geometry. The spherical diffusion equation for $c(r,t)$ becomes a one-dimensional Cartesian diffusion equation for $c(x,t)$ with $x = r_o - r \geqslant 0$ and flux boundary condition (5) applied at $x = 0$. A second, related, approximation is that the concentration at the base of the layer remains close to the well-mixed value $c_0$ for all elements and all time. The results confirm this: concentrations fall to within 0.1% of the well-mixed value for all calculations. This allows us to ignore any implied changes in the well-mixed concentration and to apply the bottom boundary condition at $x = \infty$. The problem reduces to solving

$$\begin{aligned}
&\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial x^2} = 0; \quad x \geqslant 0 \\
&c(x,0) = c(\infty,t) = c_0; \\
&\left.\frac{\partial c}{\partial x}\right|_{x=0} = -b.
\end{aligned} \tag{6}$$

The solution is standard (Carslaw and Jaeger, 1959) and is given by

$$c(x,t) = b\sqrt{\frac{D}{\pi}} \int_0^t \frac{1}{\sqrt{t'}} \boldsymbol{e}^{-x^2/4Dt'} dt' + c_0. \tag{7}$$

The concentration at the CMB, $c(0,t)$, increases with the square root of time, reaching a value

$$c(0,t) = \frac{2\alpha_c \alpha_D g_0 r_o}{\rho} \sqrt{\frac{t}{\pi D}} + c_0. \tag{8}$$

This formula, with $t = 4.5$ Ga, was used to calculate the increase in concentration, $\delta c$, at the CMB in Tables 1 and 2.

Simplifying (7) by putting $y = x/2\sqrt{Dt}$ and $h = \sqrt{Dt}$ gives

$$c(x,t) = \frac{b}{\sqrt{\pi}} \int_{x/2h}^{\infty} \frac{x}{y^2} \boldsymbol{e}^{-y^2} dy + c_0. \tag{9}$$

Setting $\xi = x/2h$ and integrating by parts gives