Thermal and compositional evolution of the core

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Synopsis

This chapter examines the thermal and compositional evolution of the Earth’s core, from shortly after its formation to the present day.

The initial state and composition of the core were determined mainly by the manner in which the Earth accreted. The initial core temperature was high enough to produce lower-mantle melting and may have dissolved substantial quantities of elements (such as Mg) which later exsolved. The light element composition of the core remains uncertain; O and S are the most likely culprits, though Si, H or C might also be present.

The present-day core geodynamo is maintained primarily by compositional convection as the inner core solidifies, with exsolution as a possible additional source term. The CMB heat flux is estimated at 12 ± 5 TW and is sufficient to drive a dynamo dissipating 0.1-3.5 TW at present.

Geodynamo activity started at 3.5 Gyr B.P. at the latest, and could have been sustained without an inner core being present. Prior to inner core formation, some fraction of the lower core was probably stably stratified; a buoyant stable layer may also have gradually developed at the top of the core, whether from inner core growth, exsolution or reaction with the mantle. Our baseline model suggests inner core formation at 0.5 Gyr B.P. Uncertainty in model parameters could extend the age to 1.7 Ga, but unless a thick, insulating layer exists at the top of the core, the geodynamo must have operated long before inner core formation. The change in core temperature over 4 Gyr was 600-1600 K, implying an early lower mantle that was extensively molten. This molten layer was probably responsible for enhanced CMB heat flows which helped drive the early dynamo.

Several areas require further study. First, the extent and evolution of core stratification, and its effect on the dynamo, are unclear. Second, the evolution of the CMB heat flux over time is currently poorly understood, particularly the effect of lower-mantle melting, and yet has first-order implications for the thermal and chemical histories of both
core and mantle. And finally, future paleomagnetic measurements may help to provide further observational constraints on the evolution of the geodynamo and the onset of inner core growth.

**Keywords** Geodynamo, mantle, entropy, energy, accretion, light element, magnetic field, inner core, stable stratification.

** denotes a reference to another work in the Treatise
Table of Contents
1. Introduction
2. Present-day state of the core
   2.1 Density and Pressure
   2.2 Thermodynamic Properties
   2.3 Composition
      2.3.1 Light Elements
      2.3.2 Isotopes
   2.4 Temperature Structure
   2.5 Inner core structure
   2.6 The CMB region
   2.7 Dynamo behaviour over time
      2.7.1 Ohmic dissipation
   2.8 Summary
3. Evolution of the core
   3.1 Formation and initial state
   3.2 Thermal evolution
      3.2.1 Core cooling
      3.2.2 Maintaining the geodynamo
      3.2.3 Present-day energy budget
      3.2.4 Thermal evolution
      3.2.5 Inner core age and initial core temperature
      3.2.6 Consequences for the mantle
      3.2.7 Stable stratification
   3.3 Compositional evolution
      3.3.1 Inner core growth
      3.3.2 CMB
   3.4 Summary
4. Conclusions
1 Introduction

The evolution of the Earth’s core is important for three main reasons. First, the formation of the core was one of the central events in the ancient, but geologically rapid, period over which the Earth accreted, and generated observational constraints on this poorly-understood epoch. Second, the initial conditions, both thermal and compositional, established during this period have largely controlled the subsequent evolution of the core, and may have also significantly affected the mantle. Finally, the evolution of the Earth’s core resulted in the generation of a long-lived global magnetic field, which did not occur for the superficially similar cases of Mars or Venus. The objective of this chapter is to describe our current understanding of the evolution of the core, from shortly after its formation to the present day.

The first section of this chapter will summarize the present-day state of the core, since it is this state which is the end product of the core’s evolution. The bulk of the chapter will then examine how the core evolved from its initial thermal and compositional state. Most of the arguments will be based on physics rather than chemistry, as compositional constraints on the core’s long-term evolution are rare.

The material covered in this chapter follows on directly from the chapter by Rubie et al.**, in which the origin and formation of the core are discussed. Much of the discussion of the core’s energy and entropy budgets is derived from a more thorough treatment in Nimmo**. Other aspects of the core’s behaviour are described in chapters in this Treatise by Masters**, Jones**, Loper**, Sumita and Bergman**, Roberts**, Christensen and Wicht**, Glatzmaier and Coe** and Buffett**. The companion Treatise on Geochemistry contains useful articles on planetary accretion (Chambers 2003) and various aspects of core composition (Righter and Drake 2003, Li and Fei 2003, McDonough 2003).

This chapter differs from the original Treatise on Geophysics chapter (Nimmo 2007) in one main respect. Recent (2011-12) estimates of core thermal conductivity exceed earlier estimates by a factor $\approx 3$ (Section 2.2). As a result, the heat fluxes required to drive a dynamo are larger, the inner core is likely a young feature, and regions of the core may have been stably stratified. This article reviews our current understanding in the light of these new results; readers are warned that certain topics (especially the role of stratification) are not yet thoroughly understood, and are likely to be the subject of intensive research in the next few years.

2 Present-day state of the core

Prior to investigating the earliest history and evolution of the core, it is important to briefly describe its present-day features. More detail can be found in the chapters referred to above; here I will focus on those parameters which are most important when considering the thermal and compositional evolution of the core. In particular, the uncertainties
associated with these parameters will be assessed; doing so is important when assessing
the likely range of thermal evolution outcomes (Section 3.2). The values and uncertainties
adopted are discussed below and in more detail in Nimmo**. An important caveat to be
borne in mind is that I generally assume a fully-mixed (i.e. not stably stratified) core. A
partially-stratified core will experience different dynamo and thermal histories; the extent
to which such an eventuality is likely is briefly discussed in Section 3.2.7.

2.1 Density and Pressure

The radially-averaged density structure of the core may be derived directly from seismo-
logical observations (see Masters**, Souriau and Calvet** for reviews). The density of
the core increases monotonically with depth, due to the increasing pressure. However,
there is also a sharp density discontinuity at the inner-core boundary (ICB), which arises
because of two effects. Firstly, solid core material is inherently denser than liquid core
material at the same pressure and temperature \((P, T)\) conditions. Secondly, the outer
core contains more of one or more light elements than the inner core (e.g. Poirier 1994,
McDonough 2003), and would therefore be less dense even if there were no phase change.
This compositional density contrast \(\Delta \rho_c\) has a dominant role in driving compositional
convection in the core; unfortunately, its magnitude is uncertain by a factor \(\approx 2\).

The total density contrast across the ICB is somewhat uncertain. Seismological tech-
niques suggest a range of about 5-8.3% (Masters and Gubbins 2003, Cao and Romanowicz
2004). The density contrast between pure solid and liquid Fe at the ICB is estimated at
1.6-1.8% (Alfe et al. 1999, Laio et al. 2000). These results imply a compositional density
contrast of 3.2-6.7%, or \(\Delta \rho_c \approx 400 - 800 \text{ kg m}^{-3}\), and may in turn be used to estimate the
difference in light element(s) concentrations between inner and outer core, which helps to
sustain the dynamo (see Section 3.2.2).

For the theoretical models described later (Section 3) it is important to have a simple
description of the density variation within the Earth. One such description is given by
Labrosse et al. (2001), where the variation of density \(\rho\) with radial distance \(r\) from the
centre of the Earth is given by

\[
\rho(r) = \rho_{cen} \exp\left(-r^2/L^2\right)
\]

where \(\rho_{cen}\) is the density at the centre of the Earth and \(L\) is a lengthscale given by

\[
L = \sqrt{\frac{3K_0}{2\pi G \rho_0 \rho_{cen}}} \left(\ln \frac{\rho_{cen}}{\rho_0} + 1\right)
\]

Here \(K_0\) and \(\rho_0\) are the compressibility and density at zero pressure, respectively, \(G\) is the
universal gravitational constant and \(L=7272\) km using the parameters given in Nimmo**.
Although this expression neglects the density jump at the ICB, the error introduced is
negligible compared to other uncertainties.
The corresponding pressure is given by

\[ P(r) = P_c + \frac{4\pi G \rho_{cen}^2}{3} \left[ \left( \frac{3r^2}{10} - \frac{L^2}{5} \right) \exp\left(-\frac{r^2}{L^2}\right) \right]^R \]

where \( P_c \) is the pressure at the core-mantle boundary (CMB).

### 2.2 Thermodynamic Properties

From the point of view of the thermal evolution of the core, the most important parameters are those which determine the temperature structure and heat flux within the core, in particular the thermal conductivity \( k \) and expansivity \( \alpha \) (see Section 2.4).

As discussed in Nimmo**, recent determinations of core thermal conductivity differ significantly from the traditional estimate of about 46 W m\(^{-1}\) K\(^{-1}\) (Stacey and Anderson 2001). Two molecular dynamics calculations (De Koker et al. 2011, Pozzo et al. 2012) have been confirmed by high-pressure experimental measurements (Gomi et al. 2013) and yield thermal conductivities of 100-150 W m\(^{-1}\) K\(^{-1}\) at the core-mantle boundary (CMB), depending on the assumed temperature and composition, and up to 250 W m\(^{-1}\) K\(^{-1}\) at the centre of the core. The depth-dependence of the conductivity plays an important role in determining which regions of the core are stably stratified. For simplicity I will generally assume a constant value of \( k \) (except when considering stable stratification, Section 3.2.7) and take the baseline value to be 130 W m\(^{-1}\) K\(^{-1}\).

The thermal expansivity within the core may be obtained from seismology if the Gruneisen parameter is known. This parameter likely remains constant at roughly 1.5 throughout the core (e.g. Anderson 1998, Alfe et al. 2002b). Because the seismic parameter increases with depth, \( \alpha \) increases by a factor of 1.5-2 from the centre of the Earth to the CMB (Labrosse 2003, Roberts et al. 2003). However, little accuracy is sacrificed if a constant mean value of \( \alpha \) is adopted; furthermore, assuming that both \( k \) and \( \alpha \) are constant result in adiabatic temperature profiles that closely resemble those in which both parameters vary. I therefore adopt a range for \( \alpha \) of 0.8 – 1.9 \( \times \) 10\(^{-5}\) K\(^{-1}\). A list of estimated values for important parameters is given in Table 2; more details may be found in Nimmo**.

### 2.3 Composition

The composition of the core is important because it potentially provides constraints on its origin and mode of formation. Unfortunately, as will be seen below, the constraints provided are currently rather weak, as few elements have well-known core abundances.

#### 2.3.1 Light elements

It is clear from seismology and experiments that the outer core is 6-10% less dense than pure liquid iron would be under the estimated \( P, T \) conditions (e.g. Alfe et al. 2002a).
While the core almost certainly contains a few weight percent nickel (e.g. McDonough 2003), this metal has an almost identical density to iron and is thus not the source of the density deficit (e.g. Li and Fei 2003). The inner core also appears to be less dense than a pure iron composition would suggest (Jephcoat and Olson 1987), though here the difference is smaller. Both the outer and inner core must therefore contain some fraction of light elements, of which the most common suspects are sulphur, silicon, oxygen, carbon and hydrogen (see Poirier 1994, Hillgren et al. 2000, Li and Fei 2003 for reviews). For any particular element, or mixture of them, the inferred density deficit may be used to infer the molar fraction of the light element(s) present. Because the density deficit is larger in the outer core, it is thought that light elements are being expelled during crystallization of the inner core. This expulsion is of great importance, because it generates compositional convection which helps to drive the geodynamo (see Section 3.2.2).

Apart from their role in driving the dynamo, these light elements are important for two other reasons. Firstly, they probably reduce the melting temperature of the core by several hundred degrees kelvin (see Section 2.4). Secondly, if the actual light elements in the core could be reliably identified, they would provide a strong constraint on the conditions (e.g. oxidation state) under which the core formed. As will become clear, there is not yet a consensus on which elements are in fact present. Fortunately, from a geophysical point of view this does not matter; what matters is the density contrast across the ICB, which is known from seismology.

Table 1: Model core compositions.
MA=Morgan and Anders 1980; WD=Wanke and Dreibus 1988; A+=Allegre et al. 1995a; McD-1 and McD-2 refer to two different models given in McDonough (2003).

<table>
<thead>
<tr>
<th></th>
<th>MA</th>
<th>WD</th>
<th>A+</th>
<th>McD-1</th>
<th>McD-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe wt%</td>
<td>84.5</td>
<td>80.3</td>
<td>79.4</td>
<td>85.5</td>
<td>88.3</td>
</tr>
<tr>
<td>Ni</td>
<td>5.6</td>
<td>5.5</td>
<td>4.9</td>
<td>5.2</td>
<td>5.4</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>14.0</td>
<td>7.4</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>9.0</td>
<td>-</td>
<td>2.3</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>O</td>
<td>-</td>
<td>-</td>
<td>4.1</td>
<td>-</td>
<td>3.0</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Co</td>
<td>0.26</td>
<td>0.27</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1 gives several examples of model core compositions. All these models are derived by comparing estimates of the bulk silicate Earth elemental abundances (inferred from upper mantle nodules and crustal samples), with estimates of the initial solar nebular composition (based mainly on chondritic meteorite samples). Although there is some agreement on the abundances of Fe,Ni and Co, the relative abundances of the light elements (Si,S,O,C) vary widely. The abundance of H in the core cannot be modelled in
this way because of its extreme volatility; in practice it will be determined by the $P, T$ conditions and amount of $H$ in the Earth’s mantle prior to and during differentiation (see e.g. Abe et al. 2000, Okuchi 1997).

These cosmochemical models do not take into account the ease with which different elements partition into iron under the relevant conditions. Unfortunately, because partitioning is a strong function of pressure, temperature and oxygen fugacity, models of core composition taking partitioning into account also have to make assumptions about the conditions under which core formation happened. As a result, some calculations favour Si as the dominant element (Rubie et al. 2011, Ricolleau et al. 2011), while others prefer O (Siebert et al. 2013). Low concentrations (<2.5 wt%) of O in the outer core are also implied by comparison of experimental velocity and density determinations with seismologically-derived values (Huang et al. 2011).

On the other hand, the presence of O in the outer core is favoured, based in its inferred ability to be expelled during inner core growth. The outer core appears to contain more of the light element(s) than the inner core. This implies that one or more of the light elements must partition strongly into liquid iron during freezing, which is potentially diagnostic behaviour. Oxygen, due to its small atomic radius, tends to be expelled during freezing (Alfe et al. 2002a). Conversely, S and Si have atomic radii similar to that of iron at core pressures, and thus substitute freely for iron in the solid inner core. These results thus support the case for O being one of the light elements. Further work is needed to resolve these apparently contradictory results.

Although not traditionally viewed as a light element, Stevenson (2012) has pointed out that the apparently strong temperature-dependence of Mg solubility in iron (Nomura et al. 2012) may have important consequences for dynamo evolution. If metal-silicate equilibration happened at high temperature conditions, as for instance during the Moon-forming impact, then the core will have initially contained high concentrations of MgO. As the core cooled, this MgO will have exsolved throughout the core, and risen to form a buoyant layer at the top of the core. A similar proposal for Si was previously made by Gessmann et al. (2001). Such a stably stratified layer has previously been proposed on other grounds (see Section 3.3.1); the importance of this proposal is that exsolution provides a potent mechanism to drive the dynamo, because of the large density contrast involved. Such a scenario could potentially allow a long-lived dynamo without requiring excessively high core heat fluxes.

### 2.3.2 Isotopes

Although the bulk of the core consists of Fe, Ni and a few weight percent light elements, some trace elements are also of importance. Firstly, the radioactive isotopes of K, Th and U can potentially have a significant effect on both the age of the inner core and the maintenance of the dynamo (e.g. Labrosse et al. 2001, Buffett 2002, Nimmo et al. 2004). Unfortunately, there is as yet little agreement on whether or not such elements are really
present in the core. Longer discussions on this issue may be found in McDonough (2003) and Roberts et al. (2003); only a brief summary is given here, while the role of radioactive elements in core evolution is discussed in Section 3.2.

There is little evidence, either from cosmochemistry or partitioning experiments, to expect either U or Th to partition into the core. On the other hand, the Earth’s mantle is clearly depleted in K relative to chondrites (e.g. Lassiter 2004). However, since K is a volatile element, it is unclear whether this depletion is due to sequestration of K in the core, or simple loss of K from the Earth as a whole early in its history. Experimental investigations (Gessmann and Wood 2002, Lee et al. 2002, Murthy et al. 2003, Corgne et al. 2007, Bouhifd et al. 2007) show that partitioning of K into core materials is possible, but also depends in a complex fashion on other factors such as the amount of sulphur or oxygen present. The highest-pressure experiments to date (Nomura et al. 2012) suggest minimal quantities of potassium in the core, but at these conditions the compositional parameter space has yet not been thoroughly explored. The removal of K to the core would also likely involve the removal of other elements with similar affinities for iron, but it is not yet clear what constraints the observed abundances of these other elements place on the amount of K in the core. It currently appears that up to a few hundred ppm K in the core are permitted, but not required, by both the experiments and the geochemical observations. The detection of antineutrinos produced by radioactive decay in the Earth’s interior (Gando et al. 2011) may help to ultimately resolve this question.

Certain isotopic systems constrain the timing and $P, T$ conditions of core formation. The Hf-W (Kleine et al. 2009), U-Pb (Wood and Halliday 2005) and Pd-Ag (Schonbachler et al. 2010) systems provide constraints on core formation timescales, and are discussed in some detail in Rubie et al.**. Stable isotopes of Fe and Si may exhibit small degrees of fractionation as a result of core formation (e.g. Georg et al. 2007, Polyakov 2009), though the evidence is currently controversial.

A final set of potentially important isotopes are those of rhenium, because they may constrain the onset of inner core formation (e.g. Walker et al. 1995). As summarized in Section 3.3.1, this hypothesis has been largely rejected; nonetheless, it is mentioned here for completeness.

2.4 Temperature structure

Both the temperature structure within the core, and the shape of the melting curve, play an important role in determining the thermal evolution of the core. Assuming that the entire liquid core is convecting (i.e. no stable stratification), its mean temperature profile will be that of an adiabat, except at the very thin top and bottom boundary layers. Since the temperature at the ICB must equal the melting temperature of the core at that pressure (Figure 1), the temperature elsewhere in the core may be extrapolated from the ICB conditions by using the appropriate adiabat. Thus, determining the melting behaviour of core material is crucial to establishing the temperature structure of the core.
The adiabatic temperature $T$ within the core is given by (Labrosse et al. 2001)

$$T(r) = T_{cen} \exp(-r^2/D^2)$$

(4)

where $T_{cen}$ is the temperature at the centre of the Earth and $D$ is a lengthscale given by

$$D = \sqrt{3C_p/2\pi\alpha_{cen}G}.$$  

(5)

Here $C_p$ is the specific heat capacity, $\alpha$ is the thermal expansivity (Section 2.2) and $D=6203 \text{ km}$ using the parameters given in Table 2, model 2.

As discussed in more detail in Nimmo**, first principles calculations have been used to determine the melting curve of iron and its dependence on impurities. Alfe et al. (2003) predict a temperature at the ICB $T_i$ of $5650 \pm 600 \text{ K}$, taking into account the reduction in temperature due to the light element(s). The gradient in melting temperature is roughly $9 \text{ K/GPa}$ at the ICB. These results are broadly consistent with the low-pressure diamond anvil cell results of Shen et al. (1998) and Ma et al. (2004), though not those of Boehler (1993). Similarly, the results agree with the higher pressure shock-wave results of Brown and McQueen (1986) and Nguyen and Holmes (2004), though not those of Yoo et al. (1993). The numerical results of Belonoshko et al. (2000) and Laio et al. (2000) also give similar answers once corrections due to the different molecular dynamics techniques used have been applied. Further discussions of the differing results and the reliability of different theoretical approaches may be found in Alfe et al. (2004) and Bukowinski and Akber-Knutson (2005).

Given the ICB temperature and the relevant thermodynamic quantities, the temperature at the core side of the CMB, $T_c$, may be deduced and is here taken to be $4180 \text{ K}$. This value is actually of only secondary importance as far as the thermal evolution of the core is concerned; of much greater interest are the relative slopes of the adiabat and the melting curve (see below).

Although other approaches may be adopted (e.g. Buffett et al. 1996, Labrosse et al. 2001, Roberts et al. 2003), a reasonable approximation is that the core melting
temperature is a quadratic function of pressure. That is, the core melting temperature $T_m$ may be written as

$$T_m(P) = T_{m0} \left(1 + T_{m1} P + T_{m2} P^2\right)$$

(6)

where $T_{m0}$, $T_{m1}$ and $T_{m2}$ are constants and $T_{m0}$ incorporates the reduction in melting temperature due to the light element(s). Note that this parameterization is only intended to apply over the pressure range relevant to the core, so that $T_{m0}$ should not be taken to be the zero-pressure melting temperature.

When considering the growth history of the inner core, the crucial parameter is the difference in gradients between the melting curve and the adiabat. One way of expressing this quantity is to define $\Delta T_c$, the change in the CMB temperature since the onset of inner core solidification. As shown in Fig. 1, when the two curves are linear $\Delta T_c$ may be defined as follows

$$\Delta T_c = \frac{\Delta P}{f_{ad}} \left(\frac{dT_m}{dP} - \frac{dT}{dP}\right) = 23 K \left(\frac{\frac{dT_m}{dP} - \frac{dT}{dP}}{1 K/GPa}\right) \left(1.32 f_{ad}\right)$$

(7)

where $\Delta P$ is the pressure difference between the present ICB and the centre of the Earth, $T_a$ and $T_m$ are the adiabatic and melting temperatures, respectively, $f_{ad}$ is a factor converting the temperature at the CMB to that at the ICB and the numerical value comes from the parameters of model 2 (Table 2). By choosing values for $T_c$, $\Delta T_c$ and the adiabatic gradient, the ICB temperature $T_i$ and $dT_m/dP$ are then determined (see Table 2). In the case that the melting curve exhibits curvature (equation (??)), one also has to specify $dT_m/dP$ at the ICB in order to solve for $T_{m0}$, $T_{m1}$ and $T_{m2}$.

| Table 2: Parameter values adopted (eq. is the equation or Section in which each parameter is defined). Model 1 is an end-member case using parameter values designed to generate an ancient inner core; model 2 is a best guess at the real parameter values. Variables below the horizontal line have values derived from the initial parameter choices ($k$, $\alpha, \Delta \rho_c$, $\Delta T_c$). Other parameters not specified here are assumed constant in both models and are generally the same as those adopted in Nimmo**. In particular, $T_c=4180$ K, latent heat $L_H=750$ kJ/kg, $C_p=840$ J/kg K, $\rho_{cen}=12,500$kg m$^{-3}$ and the melting gradient at the ICB is 9.4 K/GPa. |  |
|---|---|---|---|---|---|---|---|---|---|
| model | 1 | 2 | units | eq. | model | 1 | 2 | units | eq. |
| $k$ | 90 | 130 | W/m K | 2.2 | $D$ | 7310 | 6203 | km | 5 |
| $\Delta T_c$ | 150 | 60 | K | (7) | $T_i$ | 5099 | 5509 | K | 2.4 |
| $T_{m0}$ | 8034 | 2677 | K | (6) | $T_{cen}$ | 5243 | 5726 | K | (4) |
| $T_{m1}$ | 8.37 | 69 | $\times 10^{-25}$ Pa$^{-2}$ | (6) | $T_o$ | 5431 | 5808 | K | 2.4 |
| $T_{m2}$ | 8.37 | 69 | $\times 10^{-25}$ Pa$^{-2}$ | (6) | $\tilde{E}_T$ | 3.2 | 2.0 | $\times 10^{23}$ J/K$^2$ | (10) |
| $\tilde{Q}_k$ | 7.5 | 15.0 | TW | (12) | $\tilde{Q}_T$ | 4.6 | 3.3 | $\times 10^{27}$ J/K | (8) |
Because the adiabatic and melting gradients are both uncertain and of similar sizes, the uncertainty in $\Delta T_c$ tends to be amplified. Values for $\Delta T_c$ from four studies (Buffett et al. 1996, Roberts et al. 2003, Labrosse 2003 and Pozzo et al. 2012) range from 43-146 K, with smaller values implying younger inner cores (see Nimmo**). Here I will assume a range of 50-150 K as representative of the likely uncertainties. Taking the melting gradient at the ICB to be 9.4 K/GPa, Table 2 lists the resulting quantities for a best-guess set of parameters (model 2) and a set of parameters designed to maximize inner core age (model 1).

2.5 Inner core structure

As reviewed in Souriau and Calvet** and Sumita and Bergman**, the inner core displays a surprising amount of structure. It has a depth-dependent anisotropy, and also exhibits differences in seismic properties between the eastern and western hemispheres. The causes of these observations are currently uncertain: possible explanations include magnetic stresses, inner core convection and growth/translation mediated by spatial variations in heat loss at the ICB. This inner core structure may ultimately provide a constraint on how the inner core has grown, but our present understanding is too limited to be useful.

2.6 The CMB region

The core-mantle boundary region is relevant to core evolution for two reasons. Firstly, it is the behaviour of this region, and in particular its rheology and temperature structure, which controls the rate at which heat is extracted from the core. As a consequence, the thermal evolution of the core is intimately tied to that of the mantle. This interdependence between the core and mantle is one of the reasons that theoretical investigations of core thermal evolution are subject to such large uncertainties.

Secondly, the CMB region is interesting from a compositional point of view, since it is the point at which regions containing elements with very different chemical potentials meet. The extent to which the resulting reactions have influenced the behaviour of the deepest mantle (or the outermost core) is unclear. However, because these reactions provide indications of core evolution, the question of whether core or CMB material can plausibly be entrained to the surface is of considerable interest (Section 3.3.2).

Whether or not a dynamo can be sustained ultimately depends on the CMB heat flow, that is the rate at which heat is extracted from the core (Section 3.2.2). The CMB heat flow, in turn, is determined by the ability of the mantle to remove heat. Importantly, independent estimates on this cooling rate exist, based on our understanding of mantle behaviour.

As reviewed by Tackley (2012) and Lay et al. (2008), the CMB region is complicated, because lateral variations in bulk chemistry, phase and melt fraction apparently all occur. Nonetheless, several different techniques have been used to estimate heat flux across the
CMB, with broadly similar answers.

The simplest approach is to assume conductive heat flow across the seismologically-determined bottom boundary layer (termed D”). The temperature above this boundary layer can be determined by downwards extrapolation of the mantle adiabat, while the temperature below is just \( T_c \). As discussed in Nimmo**, for likely lower mantle thermal conductivities, the resulting conductive heat flow is probably in the range 8-16 TW. This simple estimate, however, may neglect important complications, such as heat production within D”. Wu et al. (2011) used a more sophisticated statistical approach to infer a range of 13±3 TW. An alternative is to compare convection models with observations of mantle plumes to infer the CMB heat flow. For instance, Leng and Zhong (2008) found a value of ≈11 TW.

Seismological detection of the deep mantle phase transition from perovskite to post-perovskite has been used to obtain a more direct measurement of temperature gradient and thus heat flow. Two suitable regions yield extrapolated global CMB heat flows of 9-17 TW (Lay et al. 2006) and 7-15 TW (Van der Hilst et al. 2007). Nakagawa and Tackley (2010) point out that these regions have higher than average heat flux, so that the globally-averaged flow may be lower (around 9 TW).

One additional complication is that D” may contain enhanced concentrations of radioactive elements (e.g. Coltice and Ricard 1999, Tolstikhin and Hofmann 2005, Boyet and Carlson 2005). In this case, the heat flow out of the core will be less than the heat flows inferred from the estimates quoted above (Buffett 2002, Labrosse et al. 2007). Bearing this caveat in mind, a range of 12±5 TW is likely to encompass the real present-day CMB heat flow. This range of heat flows suggests a current core cooling rate \( dT_c/dt \) of 50-115 K/Gyr, using the parameters for model 2.

The compositional nature of the CMB region may also have an effect on the evolution of the core. The CMB region may be at least partially molten, an inference supported by the presence of a (laterally discontinuous) ultra-low velocity zone (e.g. Garnero et al. 1998). The presence of such a melt layer, which is probably denser than the surrounding solid material, is likely to affect heat transfer from the core to the mantle (Labrosse et al. 2007). Such a layer is also likely to have been more extensive in the past, when core temperatures were higher (see Section 3.2.5 and Rubie et al**). Another possibility is the presence of high-density, compositionally distinct material, probably subducted oceanic crust. Again, this material, especially if enriched in radioactive materials (Buffett 2002), is likely to have affected long-term core evolution (Nakagawa and Tackley 2004). Finally, the effect of CMB dynamics on the perovskite phase transition is not yet clear; for instance, if the viscosity of post-perovskite is low, the heat flow across the CMB will be increased (Nakagawa and Tackley 2011). The manner in which the CMB may have evolved with time in response to the evolution of the core is discussed further in Section 3.3.2.
2.7 Dynamo behaviour over time

One might expect that the behaviour of the Earth’s magnetic field over time would provide information on the evolution of the dynamo and core. However, despite much work on this subject (see reviews by Jacobs 1998 and Valet 2003, Tauxe and Yamazaki**), the information is limited to the following: 1) a reversing, predominantly dipolar field has existed, at least intermittently, for at least the last 3.5 Gyr; 2) the intensity of the field does not appear to have changed in a systematic fashion over time.

There are several reasons why there are so few constraints. First, the magnetic field that we can measure at the surface is different in both frequency content and amplitude from the field within the core. In particular, Ohmic heating is dominated by small-scale magnetic fields which are not observable at the surface (see below). Second, the number of observations on paleomagnetic fields decline dramatically prior to \( \approx 150 \) Myr B.P. because of the almost complete absence of unsubducted oceanic crust. Third, there is little theoretical understanding of how changes in core behaviour relate to changes in the observed magnetic field.

The first two problems are unlikely to be resolved in the foreseeable future. However, there has been some progress with the third, thanks to increasingly realistic simulations of the geodynamo (see Christensen and Wicht**). For instance, a study by Roberts and Glatzmaier (2001) found that increasing the inner core size tended to result in a less axisymmetric field and (surprisingly) greater time-variability. Thus, at least in theory, observed changes in the time-variability of the magnetic field with time could be used to place constraints on the evolution of the Earth’s core. Similarly, the degree to which the field departs from dipolarity may provide a useful metric (e.g. Pavlov and Gallet 2010, Smirnov et al. 2011). Any apparent variation in the field amplitude with time (e.g. Labrosse and Macouin 2003), however, is less likely to be useful: Bloxham (2000), Roberts and Glatzmaier (2001) and Aubert et al. (2009) all found that the magnetic field as observed at the surface of the Earth was relatively insensitive to the existence or size of an inner core. Furthermore, it seems likely that mantle behaviour may have at least as large an effect on the geodynamo as changes in core variables such as cooling rate or inner core size (Glatzmaier et al. 1999, Olson et al. 2010, Biggin et al. 2012).

In spite of the difficulties in extracting detailed information on core evolution from the paleomagnetic record, an important result is that the geodynamo appears to have persisted, without long-term interruptions, for at least 3.5 Gyr (McElhinny and Senanayake 1980, Tarduno et al. 2010). The earliest documented apparent paleomagnetic reversal is at 3.2 Gyr B.P. (Layer et al. 1996). Although the amplitude of the field has varied with time (Selkin and Tauxe 2000, Prevot et al. 1990), the maximum field intensity appears never to have exceeded the present day value by more than a factor of five (Valet 2003, Dunlop and Yu 2004), while Archean magnetic field strengths were comparable to present day values (Tarduno et al. 2010)

In summary, the fact that a reversing dynamo has apparently persisted for >3.5 Gyr
can be used to constrain the evolution of the core over time (see Section 3.2 below). Unfortunately, other observations which might potentially provide additional constraints, such as the evolution of the field intensity, are either poorly sampled or difficult to relate to the global energy budget, or both.

### 2.7.1 Ohmic dissipation

As discussed below, the power dissipated in the core by Ohmic heating is a critical parameter to determining whether a dynamo can operate: a more dissipative dynamo requires more rapid core cooling and a higher CMB heat flux. Unfortunately, this heating rate is currently very poorly constrained. The heating is likely to occur at length-scales which are sufficiently small that they can neither be observed at the surface, nor resolved in numerical models (Roberts et al. 2003). Moreover the toroidal field, which is undetectable at the surface, may dominate the heating.

The Ohmic dissipation $Q_\Phi$ may be converted to an entropy production rate $E_\Phi$ using $E_\Phi = Q_\Phi / T_D$ (Roberts et al. 2003), where the characteristic temperature $T_D$ is unknown but intermediate between $T_i$ and $T_c$ and is here assumed to be 5000 K. The entropy production rate is simply a convenient way of assessing the potential for generating a dynamo, and is discussed in more detail in Section 3.2.2 and Nimmo**. One approach to estimating the required rate is to extrapolate from numerical dynamo simulations. Roberts et al. (2003) used the results of the Glatzmaier and Roberts (1996) simulation to infer that 1-2 TW are required to power the dynamo, equivalent to an entropy production rate of 200-400 MW/K. Buffett (2002) suggested 0.1-0.5 TW and Buffett and Christensen (2007) 0.7-1 TW. Christensen and Tilgner (2004) gave a range of 0.2-0.5 TW, but this range was later updated to 1.1-15 TW (Christensen 2010) or 3-8 TW (Stelzer and Jackson, 2013). There is clearly little consensus on the dissipation rate required, but a few TW (equivalent to a few hundred MW/K) seems reasonable. Labrosse (2003) argues for a range 350-700 MW/K, and Gubbins et al. (2003) favour 500-800 MW/K. We shall regard the required Ohmic dissipation rate as currently unknown, but think it likely that entropy production rates in excess of 100 MW/K are sufficient to guarantee a geodynamo.

### 2.8 Summary

The present-day temperature structure and composition of the core establish boundary conditions which constrain both the core’s initial mode of formation, and subsequent evolution. In particular, the size of the inner core and the persistence of the geodynamo for at least 3.5 Gyr place constraints on the CMB heat flux. Light elements in the Earth’s core not only help to power the dynamo, but also constrain the conditions under which the Earth formed.

The next section will examine how the core evolved from the initial conditions established by the accretion process to its inferred present-day state.
3 Evolution of the core

3.1 Formation and initial state

The initial thermal and chemical conditions of the Earth’s core were determined by the manner in which the Earth accreted, a relatively geologically rapid process. This period of the core’s history is discussed extensively in Rubie et al.** and only a brief summary is given here.

Theoretical arguments and geochemical observations suggest that the Earth accumulated the bulk of its mass through a few, large impacts within about 100 Myr of solar system formation, and that each of these impacts generated a global, possibly transient, magma ocean. Although the impacting bodies were undoubtedly differentiated, pre-existing chemical signals appear to have been overprinted by the impact process. The impactor cores likely underwent some degree of emulsification as they traversed the magma ocean, resulting in partial chemical re-equilibration. The potential energy liberated as the metal sank resulted in high initial core temperatures, and likely extensive melting in the lowermost mantle.

After this initial period of large and geologically rapid transfers of mass and energy, the subsequent thermal and compositional evolution of the core - the focus of this section - was much less dramatic. Unfortunately, there are few observational constraints on the details of this longer-term evolution. As discussed below, present-day observations (in particular, the size of the inner core and estimates of the CMB heat flux) provide some constraints. The fact that a geodynamo has apparently operated for at least 3.5 Gyr provides a lower bound on the rate at which the core must have cooled. However, it is important to note that the long-lived field does not necessarily require a similarly ancient inner core.

The first half of this section will investigate the thermal evolution of the core. In particular, it will focus on three questions: how much has the core cooled over time?; when did the inner core start to grow?; and how was the dynamo maintained? Because of the paucity of observational constraints, this section will focus on theoretical approaches, and in particular on the uncertainties introduced by uncertainties in the relevant parameters. The second half will focus on the compositional evolution of the core, in particular the chemical effects of inner core formation, and possible reactions taking place at the core-mantle boundary.

3.2 Thermal Evolution

The thermal evolution of the Earth’s core has been the subject of considerable interest over the last decade. As outlined in Section 2, experimental uncertainties have led different groups to adopt different values for parameters of interest, such as the thermal conductivity. Accordingly, the calculations carried out in this section will make use of
two different sets of parameters (Table 2): one end-member designed to maximize the likelihood of an ancient inner core (model 1); and one using the best-guess parameter values (model 2). In this way, the uncertainties involved in the theoretical calculations will be made clear, while conclusions which are robust under both models are likely to prove durable.

### 3.2.1 Core Cooling

In one sense, the thermal evolution of the core is relatively simple. Heat is extracted out of the core at the CMB, at a rate which depends primarily on processes within the mantle. As a result, in the absence of an internal heat source, the core cools with time. At some point, the core adiabat crosses the melting curve, and inner core solidification begins (Figure 1).

The instantaneous energy balance within the core may be written (e.g. Buffett et al. 1996, Roberts et al. 2003, Gubbins et al. 2003, Nimmo**)  

\[ Q_{\text{cmb}} = Q_s + Q_g + Q_L + Q_R = \tilde{Q}_T \frac{dT_c}{dt} + Q_R \]  

(8)

Here \( Q_{\text{cmb}} \) is the heat flow across the CMB, the core contributions \( Q_s, Q_g, Q_L \) and \( Q_R \) are respectively from secular cooling, gravitational energy release, latent heat release and radioactive decay, and the outer core is assumed to be adiabatic and homogeneous. Note that the assumption that the outer core is well-mixed and convecting throughout may not be the case if a stable conductive layer (e.g. Labrosse et al. 1997, Pozzo et al. 2012, Gomi et al. 2013) or a compositionally buoyant layer (e.g. Braginsky 2006) are present at either the top or the bottom of the core. In what follows I will generally assume that the core is well-mixed and adiabatic; the potential role of a stably-stratified region will be addressed in Section 3.2.7. I will also neglect the potential role of exsolution (Section 2.3.1) since it is as yet poorly quantified.

The first three terms in equation (8) are all proportional to the core cooling rate \( dT_c/dt \), where \( T_c \) is the core temperature at the CMB and \( \tilde{Q}_T \) is a measure of the total energy released per unit change in core temperature. Both \( Q_g \) and \( Q_L \) depend on the inner core size, and are zero in the absence of an inner core. This equation allows the evolution of the core temperature to be calculated if the CMB heat flux through time is known.

This energy balance has several important consequences. Firstly, when inner core formation begins, the same CMB heat flux results in a reduced core cooling rate, because of the extra energy terms \( (Q_g, Q_L) \). Secondly, the result of radioactive heating is likewise to reduce the core cooling rate for the same CMB heat flux.

Radiogenic elements can have a strong effect on the core cooling rate, and thus the age of the inner core (e.g. Labrosse et al. 2001). Rewriting equation (8) we obtain a
core cooling rate of

\[ \frac{dT_c}{dt} = \frac{Q_{cmb} - Q_R}{Q_T} \]  

(9)

It is clear that the effect of the \( Q_R \) term is to reduce the rate of core cooling, and hence prolong the life of the inner core. This is an issue we return to below.

A major disadvantage with equation (9) is that it does not include an ohmic dissipation term, because the transformation of kinetic energy to magnetic energy to heat occurs without changing the global energy balance (see Gubbins et al. 2003). This equation is therefore not useful in determining the evolution of the geodynamo.

3.2.2 Maintaining the geodynamo


Ultimately, the geodynamo is maintained by the work done on the field by convective motions. This convection is driven partly by the extraction of heat into the overlying mantle, and partly by the fact that the resulting inner core growth (or exsolution) releases light elements into the base of the outer core. Thus, both thermal and compositional convection are important, with the relative contributions depending on the different parameter values adopted, in particular the size of the inner core.

Just as equation (9) describes the energy balance in the core, an equivalent equation can be derived for the entropy balance (e.g. Roberts et al. 2003, Labrosse 2003, Lister 2003, Gubbins et al. 2003,2004; Nimmo**). The latter equation does include ohmic dissipation (dissipation is non-reversible and is thus a source of entropy). The entropy may be thought of as the power divided by a characteristic temperature and multiplied by a thermodynamic efficiency factor. Different mechanisms (e.g. thermal and compositional convection) have different efficiency factors (e.g. Buffett et al. 1996, Lister 2003). Unfortunately, it is not currently understood how to relate the entropy production rate to global magnetic field characteristics, such as reversal frequency (Section 2.7).

The entropy rate available to drive the dynamo may be written as (e.g. Labrosse 2003, Gubbins et al. 2004)

\[ \Delta E = E_s + E_L + E_g + E_H + E_R - E_k = \tilde{E}_T \frac{dT_c}{dt} + E_R - E_k \]  

(10)

where \( E_s, E_L, E_g \) and \( E_H \) are the contributions due to cooling, latent heat and gravitational energy release and heat of reaction, respectively, \( E_R \) depends on the presence of radioactive elements in the core, and \( E_k \) depends on the adiabatic heat flux at the CMB. The first four
terms are all proportional to the core cooling rate \(dT_c/dt\), and \(\tilde{E}_T\) is simply a convenient way of lumping these terms together. This equation illustrates two important points. Firstly, as expected, a higher cooling rate or a higher rate of radioactive heat production increases the entropy rate available to drive a dynamo. Secondly, a larger adiabatic contribution (e.g. higher thermal conductivity) reduces the available entropy.

By combining equations (11) and (12), an expression may be obtained which gives the core heat flow required to sustain a dynamo characterized by a particular entropy production rate \(E_\Phi\):

\[
Q_{cmb} = Q_R \left( 1 - \frac{T_T}{T_R} \right) + T_T (E_\Phi + E_k)
\]

where \(T_R\) is the effective temperature such that \(T_R = Q_R/E_R\) and likewise \(T_T = \tilde{Q}_T/\tilde{E}_T\). This equation encapsulates the basic physics of the dynamo problem.

Equation (11) shows that larger values of adiabatic heat flow or Ohmic dissipation require a correspondingly higher CMB heat flow to drive the dynamo, as would be expected. In fact, in the absence of radiogenic heating, the CMB heat flow required is directly proportional to \(E_k + E_\Phi\). The constant of proportionality depends on the thermodynamic efficiency of the core, which increases if an inner core is present. Because the term \((1 - T_T/T_R)\) exceeds zero, a dynamo which is partially powered by radioactive decay will require a greater total CMB heat flow than the same dynamo powered without radioactivity. Alternatively, if the CMB heat flow stays constant, then an increase in the amount of radioactive heating reduces the entropy available to power the dynamo.

Equation (12) also illustrates the fact that a dissipative dynamo can exist even if the CMB heat flow is less than that conducted along the adiabat (i.e. subadiabatic) (Loper 1978). In the absence of radioactivity, the entropy production rate \(E_\Phi\) available for the dynamo is \((Q_{cmb}/T_T) - E_k\) which for the present-day core exceeds zero unless \(Q_{cmb}\) is strongly subadiabatic. Thus, a subadiabatic CMB heat flow can sustain a dynamo, as long as an inner core is present to drive compositional convection (e.g. Loper 1978, Labrosse et al. 1997). Although it is often assumed that compositional convection or lateral heat flux variations can keep the entire core well-mixed despite the subadiabatic heat flux, this situation may lead to a stably-stratified region within the core; such an eventuality is discussed further in Section 3.2.7.

In the absence of an inner core and radiogenic heating, it may be shown that

\[
Q_{cmb} = Q_k \left( 1 + \frac{E_\Phi}{E_k} \right)
\]

This equation shows that the heat flow at the CMB \(Q_{cmb}\) must exceed the adiabatic heat flow \(Q_k\) for a dynamo driven only by thermal convection to function. This result is important, because it demonstrates that there is no problem with sustaining a dynamo prior to the onset of inner core formation, as long as the core cooling rate (or CMB heat flux) is large enough. This equation also allows dynamo dissipation to be taken into
account explicitly: a more strongly dissipative core dynamo requires a more superadiabatic CMB heat flow to operate.

### 3.2.3 Present-day energy budget

Figure 2 shows how the rate of entropy production available to drive a dynamo varies as a function of the heat flow out of the core, both for a set of core parameters appropriate to the present-day Earth (with and without potassium), and for a situation in which the inner core has not yet formed. Figure 2a illustrates the case for the best-guess parameters (model 2) while Figure 2b uses parameters designed to maximize the inner core age (model 1). As expected, higher core heat fluxes generate higher rates of entropy production; also, the same cooling rate generates more excess entropy when an inner core exists than when thermal convection alone occurs.

![Figure 2: a) Net entropy production (available to drive the geodynamo) as a function of CMB heat flux, for cases without an inner core, with an inner core, and with an inner core and 300 ppm potassium. Parameters used are for model 2 in Table 2; calculation details are in Nimmo**. Labels denote inner core age in Gyr, calculated assuming a constant core cooling rate and taking \( \Delta T_c = 60 \) K. b) As for a), except using the parameters for model 1 in Table 2 (designed to maximize inner core age) with \( \Delta T_c = 150 \) K.](image)

As discussed above, when an inner core is present, positive contributions to entropy production arise from core cooling, latent heat release and gravitational energy; the adiabatic contribution is negative (equation ??). For a present-day, potassium-free core, CMB heat flows of <6.5 TW and <2.5 TW result in negative entropy contributions and, therefore, no dynamo for models 2 and 1, respectively. Higher core cooling rates generate a higher net entropy production rate; they also means that the inner core must have formed more recently.

For the present-day estimated CMB heat flow of 7-17 TW (Section 2.6), the net entropy production rate available to drive the dynamo is 50-850 MW/K, sufficient to generate roughly 0.3-4 TW of Ohmic dissipation. Since most estimates of Ohmic heating are less than 2 TW (Section 2.7.1), it is clear that there is no difficulty in driving a dynamo.
at the present day. A heat flow of 7-17 TW also implies an inner core age of 0.55-1.3 Gyr and 0.9-2.3 Gyr for models 2 and 1, respectively, assuming a constant core cooling rate. Note that in all cases an inner core significantly younger than 4.5 Gyr is obtained.

Prior to the formation of an inner core, the CMB heat flow had to exceed the adiabatic value \( Q_k \) in order to maintain a dynamo for reasons discussed above (eq. ??). For a dynamo requiring an entropy production rate of 200 MW/K, the core cooling rate had to be roughly 2.5 times as fast to maintain this rate before the onset of inner core solidification. A geodynamo prior to the onset of inner core formation is entirely possible, but implies that either CMB heat fluxes were higher in the past, or that the present-day dynamo is dissipating more heat than it did prior to inner core formation. Further discussion of these issues is given in Section 3.2.4.

Fig. 2 also shows that, as discussed above, a larger CMB heat flow is required for the same entropy production if radioactive heating is important in the present-day Earth. Prior to the existence of the inner core, the effect of radioactive decay on the entropy production is small because the thermodynamic efficiency of radioactive heat production is similar to that of secular cooling (Roberts et al. 2003, Gubbins et al. 2003, Nimmo**). Although the presence of potassium also reduces the core cooling rate, and thus increases the age of the inner core (equation (9)), this effect is quite small because the potassium heat production rate is only a small fraction of the likely CMB heat flow. This issue is discussed further in Section 3.2.5 below.

In summary, Fig. 2 shows that the estimated present-day CMB heat flow of 7-17 TW is consistent with the operation of a dynamo dissipating 0.3-4 TW of heat. Under these circumstances, an inner core could have persisted for 0.55-2.3 Gyr if the heat flux stayed constant. Radioactive heating can increase the inner core age somewhat, but the present-day radioactive heat production is likely only a small fraction of the total energy budget, and thus the effects are modest. In practice, of course, both the core heat flux and the radiogenic heat production will vary with time; investigating the time evolution of the core and mantle is the subject of the next section

### 3.2.4 Thermal evolution

There are two basic approaches to modelling the thermal evolution of the core. One approach is to start from some assumed initial conditions and evolve the core forwards in time, using equation (??) or its equivalent (Stevenson et al. 1983, Stacey and Loper 1984, Mollett 1984, Yukutake 2000, Nimmo et al. 2004, Costin and Butler 2006, Davies 2007, Nakagawa and Tackley 2010). The initial conditions can be iterated until the correct present-day core parameters (e.g. inner core size) are obtained, and the theoretical geodynamo history compared with the observations. Because the core’s evolution depends on the CMB heat flux, such models must simultaneously track the thermal evolution of the mantle. This kind of approach has two principal disadvantages: firstly, it requires the assumption of initial conditions which are poorly constrained (Rubie et al.**); and
secondly, in considering the mantle as well as the core, the number of important but uncertain parameters (e.g. mantle viscosity) greatly increases.

A second approach is to start from the present-day core conditions and evolve the core backwards in time (Buffett et al. 1996, Buffett 2002, Labrosse 2003, Gomi et al. 2012). This approach has the advantage of automatically satisfying the present-day observations. However, because diffusion equations are unstable if run backwards in time, the evolution of the CMB heat flux cannot be calculated in the same way as it can in the forward models. A common choice is to specify the time-evolution of the entropy production in the core, which then specifies both the core cooling rate and the evolution of the CMB heat flux (equation ??). This approach has the virtue of not requiring any knowledge of the mantle to do the calculations; however, it makes a major assumption in assuming a specific entropy production history for the core. Nonetheless, this approach is both simpler and subject to fewer uncertainties than the alternative, and will be focused on here. A major caveat is that the core is assumed to be well-mixed throughout; if regions of the core are stably stratified, that will have major (but currently rather unclear) consequences for core thermal evolution. This issue is addressed briefly in Section 3.2.7 below.

Partly because of geochemical arguments suggesting that the inner core was old (Section 3.3.1), many of the investigations cited above have focused on the age of the inner core. While there is a general tendency to find relatively young (~1 Gyr) inner cores, the robustness of these results is often unclear because of the large number of poorly-constrained parameters which have to be chosen. Another aim of this section is to tabulate the most important parameters, and to investigate the robustness of the thermal evolution results to likely parameter variations. The conclusion that the inner core is young (<2 Ga) is found to be robust, mainly because of the recent increase in estimates of core thermal conductivity \( k \) (Section 2.2). An additional conclusion is that the early lower mantle was extensively molten.

**Parameters**

Of the various parameters discussed in Section 2, we may identify those which will have the largest influence on whether a dynamo can be maintained while producing an ancient core. They are as follows:

1) Thermal conductivity \( k \) and thermal expansivity \( \alpha \). A low thermal conductivity or expansivity reduces \( E_k \), and thus allows the same rate of entropy production for a lower CMB heat flux (equation 11).

2) Gradient of the melting curve. The quantity \( \Delta T_c \) (equation 7) is the change in \( T_c \) since the inner core started solidifying, and is determined by the relative slopes of the adiabat and the melting curve. A larger \( \Delta T_c \) results in an older inner core for the same CMB heat flux (or alternatively a higher entropy production rate for an inner core of the same age).

3) The compositional density contrast \( \Delta \rho_c \). The larger the value of \( \Delta \rho_c \), the higher the entropy production rate for the same rate of cooling.

4) The rate of entropy production required to drive the dynamo. As discussed in
Section 2.7.1, this value must exceed 0 MW/K, and is more likely closer to 100 MW/K.

5) Radioactive heating within the core. Internal heat production reduces the core cooling rate (Figure 2 and equation 9).

6) The extent of stable stratification of the core. A stable layer is likely to reduce the surface field strength, and may affect long-term thermal evolution. Below I generally assume the entire outer core is well-mixed (but see Section 3.2.7).

Other factors, such as latent heat, specific heat capacity, heat of reaction and so on are either better known than the factors listed above, or have only a small effect.

Factors 1-3 are known with some uncertainty, while factors 4-6 are less well known. We have therefore adopted two models (Table 2) designed to result in maximum and best-guess inner core ages, respectively. In this way, a conservative assessment may be made of the model variability arising from uncertainties in parameter values.

The calculations shown below take a similar approach to those of Buffett (2002) and Labrosse (2003) and assume a specified rate of entropy production with time. The core temperature is evolved backwards from the present-day conditions. The entropy production rate prior to inner core formation is assumed constant, which allows the CMB heat flux and core cooling rate to be determined. The CMB heat flux during inner core solidification is assumed to stay constant at the value immediately prior to solidification. The justification for making this assumption is that the CMB heat flux is determined primarily by conditions in the mantle, and is thus unlikely to be significantly affected by changing core conditions. This assumption is less reliable for inner cores of greater ages or having larger values of $\Delta T_c$. A result of the assumption is that the entropy production increases significantly when inner core solidification starts, because of the extra contributions (e.g. latent heat release) to the entropy budget.

Other assumptions could be made. For instance, Labrosse (2003) assume that the present-day entropy production is some constant factor times the entropy production immediately prior to core formation. It will be shown below that different assumptions of this kind do not significantly affect the results. In theory, one would like to use observations of the Earth’s magnetic field to constrain the entropy evolution. For instance, one might anticipate that a higher field strength would lead to greater dissipation and thus higher entropy production. Unfortunately, as discussed in Section 2.7, neither the observations, nor our theoretical understanding of geodynamos, are currently good enough to infer how the entropy production has changed. The assumption of constant entropy production prior to inner core formation at least has the virtue of simplicity; furthermore, since if anything entropy production is likely to have declined with time, this assumption will result in conservatively old inner core ages.

Figure 3 shows the evolution of various parameters of interest for models 1 and 2 when the net entropy production rate prior to inner core formation is 100 MW/K, probably a reasonable value (see Section 2.7.1). This entropy production rate determines the core cooling rate, and thus the heat flux. The present-day heat fluxes are in the range 13-18 TW, in line with expectations (Section 2.6). The change in CMB heat flow over 4 Gyr
is modest, a factor 35% or less. Whether such a small change is dynamically plausible is currently unclear, and will be discussed further below.

As expected, the heat flux required for model 1 (Fig 3b) is lower than for model 2 (Fig 3a), because model 1 uses parameter values chosen to favour a long-lived geodynamo. A consequence of this lower heat flux is that the temperature change of the core over 4.5 Gyr is smaller than for model 2. The lower heat flux also results in an inner core of greater age, 1.1-1.4 Gyr. The present-day rates of entropy production for models 1 and 2 are comparable, because the lower core growth rate in model 1 is offset by a large compositional density contrast. The total energy released since inner core formation due to secular cooling, gravity and latent heat is in the ratio 51:19:30 for model 2, and 70:14:16 for model 1, illustrating the greater relative importance of compositional convection in model 1.

The solid lines and dashed lines in Fig 3 represent cases without and with 300 ppm potassium, respectively. Because of the large present-day CMB heat fluxes involved, adding potassium has little effect on the age of the inner core; however, it does substantially decrease the total change in core temperature (equation 9). In fact, in model 1 the core temperature actually initially increases slightly, a probably unphysical result.

Figure 3: a) Evolution of core heat flux and core temperature $T_c$ with time for model 2 (Table 2). Heat flux prior to inner core formation is calculated by fixing entropy production rate at 100 MW/K. Heat flux after the onset of inner core formation is kept at the same level as it was immediately prior to solidification. Equations are integrated backwards in time from the present-day and $C_r=-10,100$ m K$^{-1}$ (see Nimmo**). Dashed lines represent cases with 300 ppm in core; dotted blue line is heat produced by $^{40}K$ decay. Green line is model heat flow evolution from Labrosse et al. (2007). b) Evolution of the entropy production rate and dimensionless inner core radius $R_i/R$ as a function of time. Note that the entropy production increases when inner core formation occurs. c) As for a), except using parameters for model 1 with $C_r=-4,900$ m K$^{-1}$. d) As for b).

Figure 4 shows the same situation as the preceding figure, but now with a net entropy production rate prior to inner core formation of 0 MW/K, a lower bound. The lower
entropy production results in a reduction in the heat flux required (8-15 TW at the present day), and also a reduction in the amount by which the core has cooled over 4.5 Gyr. As a consequence of this reduction in cooling rate, the inner core can persist further back in time. Nonetheless, even adding 300 ppm of potassium, the conservative model 1 still only yields an inner core age of 1.7 Gyr, much less than the age of the Earth.

Figure 4: Similar to Fig 3, but here with an entropy production rate prior to inner core formation fixed at 0 MW/K (i.e. a marginal dynamo).

3.2.5 Inner Core Age and Initial Core Temperature

Figure 5 summarizes the outcomes of several similar models by plotting inner core age and the initial core temperature against present-day CMB heat flux. As expected, a higher $Q_{\text{cmb}}$ results in a younger inner core and a higher initial core temperature. For the same current heat flux, model 1 results in an older inner core than model 2, and also generates a higher rate of entropy production. Models 1 and 2 have very similar initial core temperatures for the same present-day heat flux (as expected), but adding potassium significantly reduces the initial core temperature. Figure 5b marks the likely range of lower mantle solidus and liquidus temperatures, indicating that irrespective of the model details, the lower mantle will have initially been partially molten.

A baseline model, with an entropy production rate prior to inner core formation of 50 MW/K yields a present-day CMB heat flow of 17 TW, an initial core temperature of 5600 K and an inner core age of 0.5 Gyr. The present-day entropy production rate is 700 MW/K, more than enough to drive a dynamo, and the present-day CMB heat flow is marginally compatible with the observational constraints (Section 2.6).

The two key conclusions from Figure 5 are as follows:
1) The inner core is always young (<1.7 Gyr);
2) The initial core temperature significantly exceeded the mantle solidus, so the base of the mantle was initially molten.

Figure 5 also plot comparable results from two recent studies (Pozzo et al. 2012, Gomi et al. 2013). The Gomi et al. (2013) results assume a marginally adiabatic core,
permitting somewhat lower CMB heat flows and lower initial core temperatures than our baseline results (model 2). The Pozzo et al. (2012) results are very similar to our baseline model; their present-day entropy production rate of 865 MW/K is larger than our value of 630 MW/K because they neglect the heat of reaction term. In any event, Figure 5 shows that the two main conclusions listed above are robust, despite these differences in detail.

Figure 5: a) Inner core age as a function of present-day CMB heat flow; circles are based on a suite of models like those shown in Figs 3 and 4. The shaded region indicates the likely present-day heat flow (Section 2.6). Parameters for models 1 and 2 are given in Table 2. Labels on individual circles give the fixed entropy production rate (in MW/K) prior to the onset of inner core formation. Squares are from Gomi et al. (2013, Fig 4) taking conductivities of 90 and 130 W m$^{-1}$ K$^{-1}$; cross is from Pozzo et al. (2012, Table 2 case 5). b) As for a), but plotting initial core temperature against present-day CMB heat flow. The lowermost mantle solidus and liquidus ranges are from Andrault et al. (2011).

It is striking that, at least for the baseline case (model 2), even very modest entropy production rates prior to inner core formation imply present-day CMB heat flows at the upper end of the likely range. Going further back in time, CMB heat flows increase further (Figs 3,4) even with the conservative assumption of constant entropy production. This creates two potential problems. First, are such high heat flows compatible with our understanding of mantle behaviour? Second, how can such low entropy production rates be reconciled with an ancient dynamo? The first question will be discussed further below (Section 3.2.6). The answer to the second question might simply be that our estimates of the entropy production rates required to drive a dynamo are too high, or that the estimated CMB heat flows are too low. Alternatively, additional sources of entropy production (such as exsolution) may have been available.

An apparently young inner core seems inescapable. Although Os isotopic measurements have been advanced in favour of an old inner core, these observations can be explained by non-core processes (Section 3.3.1). The onset of inner core growth might be associated with a change in magnetic behaviour, but it is not clear that such a difference would really be detectable in the paleomagnetic record (Aubert et al. 2009 and
The initial temperature of the core raises further issues. Here “initial” refers not to the temperature of the core during accretion (which may have been as high as 10,000 K - see Rubie et al**), but to the temperature once accretion had finished and the density structure of the Earth resembled the present-day arrangement. Because we are assuming a fixed entropy production rate prior to inner core growth, we are effectively minimizing the CMB heat flux, and thus minimizing the core temperature drop. Hence, the points plotted in Fig 5b are lower bounds. Thus, it also appears inescapable that the early mantle was extensively molten (Gomi et al., 2013).

The consequences of this molten state for the CMB heat flux are unclear, and in particular depend on whether the melt is more or less dense than the solid. Current thinking favours a dense melt layer (Stixrude et al. 2009, Nomura et al. 2011), although agreement is not universal (Andrault et al. 2012). Assuming a dense melt, the CMB heat flux will ultimately be controlled by the ability of the solid mantle above the melt layer to remove heat. Labrosse et al. (2007) estimate an initial heat flow of 30 TW from the melt layer, declining to 15 TW at the present day. Their present-day flow is shown in Fig 3a and resembles our model result; their initial flow is somewhat higher than our value, suggesting that the entropy production rate (and perhaps field intensity?) decreased with time.

3.2.6 Consequences for the mantle

The above discussion illustrates an important point: the thermal evolution of the core cannot really be considered separately from the thermal evolution of the mantle. In particular, the evolution of the CMB heat flux controls the thermal evolution of the core, and yet is to a large extent determined by mantle processes. Conversely, the early state of the core implies that the lowermost mantle was probably extensively molten, with potentially important consequences for mantle chemistry and dynamics.

A consequence of the requirement of constant entropy production prior to inner core formation is that the core heat flux does not change very much with time (Figs 3,4). Whether a roughly constant heat flux is dynamically plausible remains to be seen, as it depends on the poorly-understood details of how the mantle extracts heat from the core. Nonetheless, if the core heat flux has remained roughly constant, there are interesting consequences for the evolution of the mantle.

The evolution of the mantle temperature depends on three factors: internal heat generation; heat added from the core; and the rate of heat loss to the surface. Some petrological constraints on the evolution of mantle temperatures exist (e.g. Herzberg et al. 2010) and suggest that the mantle potential temperature has changed by perhaps 100 – 300 K in the last 3.5 Gyr (an average secular heat flow of 9 ± 4.5 TW). Given this temperature change, an approximately constant heat flux from the core into the bottom of the mantle, and an assumed mantle heat production rate, the average rate of heat lost
by the mantle can be calculated. Assuming a depleted mantle (Davies**), the present-day heat production rate is $2.45 \times 10^{-12}$ W kg and the average flow over 3.5 Gyr is 16 TW. Taking an average CMB heat flow of 20 TW (Fig 3a), the mean mantle heat loss rate is $45 \pm 4.5$ TW. This is roughly 25% higher than the present-day mantle heat loss rate of 36 TW (Davies**), and suggests that (for either linear or exponential decay) the rate of heat loss at 3.5 Ga was roughly 50% higher than the present-day value.

Of course, this calculation is very crude. Nonetheless, it illustrates two important points. First, the secular cooling contribution is small compared to the internal heat production, so whether the depleted upper mantle reflects the overall mantle composition is the key uncertainty. For instance, a deep enriched layer (Boyet and Carlson 2005) would require much higher mean mantle loss rates. Second, taken at face value it is surprising that the mantle heat loss rate should change by only a factor of 1.5 over 3.5 Gyr. A mantle temperature reduction of 200 K would cause a viscosity increase of about two orders of magnitude. Convective heat flow scales as $(viscosity)^{\beta}$, where $\beta \approx 1/3$ in the absence of complicating factors (Davies**). So the predicted change in heat flow is more like a factor of 6 than a factor 1.5.

There are at least three possible explanations. One is that the average (bulk) mantle is more enriched in heat producing elements than the estimate above. The second is that the mantle temperature change over 3.5 Gyr has been at the lower end of the estimated range, $\approx 100$ K. The third is that mantle heat loss, which is controlled by plate tectonics, is less sensitive to temperature than the usual $\beta \approx 1/3$ scaling would suggest. This is not an outlandish hypothesis: Korenaga (2003) has speculated that higher temperatures can even lead to lower heat fluxes.

A related question is whether the mantle is truly capable of removing roughly 20 TW from the core. Based on current estimates of mantle thermal conductivity and D” thickness, it seems improbable that purely conductive heat transport would suffice. However, if the post-perovskite layer is weak (Nakagawa and Tackley 2010) or there is a deep molten layer (Labrosse et al. 2007), heat fluxes in excess of 20 TW appear permissible. This problem is likely to be an area of vigorous future work.

### 3.2.7 Stable Stratification

There are two ways in which the core might become stably stratified. First, a buoyant compositional layer could accumulate immediately beneath the CMB, formed either by accumulation of light elements expelled from the inner core, from exsolution, or by transfer of light material from the mantle above (see Section 3.3.1). Such a layer is likely to be stable against penetrative convection from the material beneath (Buffett and Seagle 2010) and will grow at a rate determined by the supply rate of light elements; however, it may be disrupted by lateral variations in CMB heat flow.

Second, regions of the core in which the heat flux is subadiabatic may also become stably stratified (Loper 1978), unless disrupted by compositional convection. The location
of such a layer depends strongly on the calculation details. For instance, Gubbins et al. (1982), Labrosse et al. (1997) and Lister and Buffett (1998) concluded that a subadiabatic, stratified layer would be found at the top of the core. In the presence of light elements, this situation is a double-diffusion problem: the effects of compositional and thermal buoyancy are competing against each other (Buffett and Seagle 2010). As a result, whether such a layer would be stable or not is quite unclear.

Prior to inner core formation and light element release, the situation is clearer. As shown in Gomi et al. (2013) and Nimmo**, the strong variation in thermal conductivity with depth results in a stably stratified layer at the bottom of the core. Penetrative convection from material above is unlikely to disrupt it (although exsolution within might), and its thickness depends primarily on the CMB heat flow.

Figure 6: a) Evolution of stably stratified layer as a function of time for a specified constant CMB heat flow of 20 TW. The location of the top of the stable layer is calculated using equations (81)-(83) of Nimmo** and taking the thermal conductivity to vary as $k(r) = k_c (1 - \frac{r^2}{D_k^2})/(1 - \frac{r^2}{D_k^2})$ with $k_c=130$ W m$^{-1}$ K$^{-1}$, $D_k=5900$ km and $r_c=3480$ km. The evolution of the CMB temperature $T_c$ is also plotted. b) As for a), but CMB heat flow varies exponentially with time. c) As for a), but with 300 ppm potassium in the core. d) As for b), but with 300 ppm potassium in the core.

Stably stratified layers at the top and bottom of the core are likely to affect thermal and dynamo evolution in different ways. A stagnant conductive layer on top of an active dynamo will screen out short-timescale and short-wavelength fluctuations (e.g. Nakagawa 2011). A stagnant layer below a dynamo will behave essentially like the solid inner core. A stable bottom layer will not greatly affect the overall thermal evolution of the core, but
a stable top layer can potentially act as an insulator (Gubbins et al. 1982, Labrosse et al. 1997), reducing the rate at which the core cools and reducing the entropy available to drive a dynamo.

Figure 6 presents some simplified calculations in which the evolution of a deep stable layer is tracked. The CMB heat flow as a function of time is specified; given this value and the CMB temperature \( T_c \), the location of the top of the stable layer can be calculated using equations (69) and (81)-(83) of Nimmo**. The calculations are truncated at 0.5 Gyr B.P., since inner core growth renders them invalid, and the thermal conductivity at the CMB \( k_c = 130 \text{ W m}^{-1} \text{ K}^{-1} \). Figs 6a and 6c show how the stable layer thickness and core temperature evolve when the CMB heat flow is fixed at 20 TW. In this scenario, the unstable layer gets thinner further back in time, and in a case without potassium results in a completely stable core prior to 3 Gyr B.P. Radiogenic heating helps destabilize the core, and allows a thin unstable layer to persist over the entire history of the Earth. Figs 6b and 6d show similar plots but with a time-variable heat flow similar to that obtained by Labrosse et al. (2007). In this case the unstable layer gets thicker further back in time, owing to the higher heat flow. Potassium has only a minor effect in this case.

These results are quite sensitive to both the heat flow history and the value of \( k_c \) assumed. For instance, taking \( k_c = 90 \text{ W m}^{-1} \text{ K}^{-1} \) (the value adopted by Gomi et al. 2013) greatly reduces the temporal and radial extent of the stably-stratified region. Furthermore, stratified layers can potentially be destabilized by lateral heat flux variations at their boundaries, an effect not included in Fig 6. Nonetheless, these calculations raise the possibility that a significant fraction of the lower core was stably stratified prior to inner core formation. The dynamo was therefore likely operating only in an outer shell, similar to the situation which pertains today.

### 3.3 Compositional Evolution

The compositional evolution of the core since its formation has been a relatively neglected field of study, perhaps because of the paucity of observational constraints. There are two main ways in which the core composition evolves: through solidification of the inner core; and through reaction with the mantle at the CMB. Each of these is dealt with briefly in turn; consequences of inner core growth and core-mantle interactions are discussed in more detail in Sumita and Bergman** and Buffett**, respectively.

#### 3.3.1 Inner core growth

One potentially observable consequence of inner core growth is its effect on Os isotope systematics. The basic hypothesis is relatively simple (Walker et al. 1995): both Re and Pt are presumed to partition preferentially into the outer core relative to Os as solidification proceeds. Since \(^{187}\text{Re} \) and \(^{190}\text{Pt} \) decay to \(^{187}\text{Os} \) and \(^{186}\text{Os} \), respectively, the outer core will become progressively enriched in these Os isotopes relative to stable \(^{188}\text{Os} \).
The amount of enrichment depends on the time since inner core crystallization, and the relative partitioning of Re and Pt into the outer core compared to Os. Furthermore, the enrichments in $^{186}$Os and $^{187}$Os are expected to be coupled if core crystallization occurs (since both are occurring due to the same process). Assuming values for the partition coefficients of Pt, Re and Os, it has been argued (Brandon et al. 2003, Puchtel et al. 2005) that the onset of inner core crystallization must have been prior to 3.5 Ga to explain the komatiite Os-isotope ratios.

These results, if correct, are of great significance; unfortunately, they are probably not correct (Meibom 2008). Other studies have ascribed the osmium anomalies to mantle heterogeneities rather than a core contribution (Hauri and Hart 1993, Baker and Jensen 2004, Schersten et al. 2004, Luguet et al. 2008). Moreover, a corresponding signal should also be observed in tungsten and lead isotope anomalies; such signals appear to be lacking in Hawaiian lavas (Schersten et al. 2004, Lassiter 2006) and Afar plume basalts (Rogers et al. 2010). Finally, measurements of Pt, Re and Os partition coefficients at intermediate pressures and temperatures give values which are too small to explain the observed isotopic anomalies (Van Orman et al. 2008, Hayashi et al. 2009). Thus, the isotopic argument that the inner core formed prior to 3.5 Ga is not widely accepted and (as seen above) is in serious conflict with the geophysical results.

Another consequence of inner core growth is that it involves the expulsion of one or more light elements into the outer core. Unless they are efficiently mixed into the outer core by convective stirring, these elements will rise to the CMB and generate a stably stratified layer (see Braginsky 2006 and references therein). A similar situation may arise if exsolution of light elements occurs. Rather than the light elements segregating to form a separate layer, it has instead been argued (Buffett et al. 2000, Buffett and Seagle 2010) that the addition of elements (specifically Si and O) to the outer core from the mantle drives a chemical reaction, resulting in a silicate-rich layer of light sediments at the top of the core.

The growth of an inner core and associated light element release would presumably disrupt any pre-existing stably-stratified layer in the lower core (Fig 6). In this context, it is perhaps surprising that there is some seismological evidence (see Gubbins et al. 2008 and Souriau and Calvet** for reviews) for a stratified layer immediately above the ICB. There is also some evidence for a stably-stratified layer at the top of the core. Helffrich and Kaneshima (2010) used seismological observations to infer a 300 km thick subadiabatic layer, though this is not yet generally accepted. Gubbins (2007) used geomagnetic observations to limit the thickness of such a layer to <100 km, while Buffett (2010) used Earth nutations to argue that such a layer exists. Future observational constraints on the location and extent of stably-stratified layers would be very valuable.
3.3.2 CMB

The bulk compositions of the core and mantle are strongly out of equilibrium with each other, so the CMB is certainly a region at which reactions will occur (Knittle and Jeanloz 1991). Oxygen and silicon will be transferred to the outermost core, providing another potential mechanism for stable stratification there (Buffett and Seagle 2010). Conversely, the lowermost mantle will tend to become enhanced in iron. The thickness of this iron-enriched layer, however, is currently unclear. Solid-state diffusion is too slow to be of interest, while because of the strong negative density contrast, layers generated by capillary action or mantle deviatoric stresses are unlikely to exceed 100 m (Poirier et al. 1998, Kanda and Stevenson 2006). One possibility is that a so-called morphological instability between Fe and (Mg,Fe)O can result in an Fe-rich layer tens of km thick (Otsuka and Karato 2012). The layer thickness is of interest because observations based on Earth nutations suggest that the CMB region must include a relatively electrically conductive layer (e.g. Buffett et al. 2002). If this layer were iron-rich it would presumably also have a higher thermal conductivity, thus potentially increasing the heat flux across the CMB; further speculation at this point is premature.

3.4 Summary

Neither the thermal nor the compositional evolution of the core are currently very well understood, because of a lack of observational data (Section 2.7) and considerable uncertainties in the relevant parameter values and the extent of stable stratification. Nonetheless, by assuming that Ohmic dissipation was constant prior to inner core formation, and by using models spanning the likely range of parameter values, the thermal history of the core can be investigated, with results summarized in Fig 5. Several important points are evident, all of which are robust to likely variations in model parameters.

First, there is no difficulty in maintaining a moderately dissipative dynamo prior to inner core formation as long as the core is cooling fast enough (c.f. Figs. 2-4); an inner core is not required to drive the early geodynamo.

Second, a higher CMB heat flux implies a more dissipative dynamo and a younger inner core, although the addition of potassium can make the inner core slightly older (Fig. 5a). An estimated present-day CMB heat flux of 7-17 TW yields a present-day entropy production rate of 30-700 MW/K and an inner core age of 0.45-1.7 Gyr. Prior to inner core formation, the entropy production rate was probably significantly lower (<100 MW/K).

Third, a dynamo operating for 4 Gyr implies initial core temperatures 600-1600 K hotter than the present day (Fig. 5b). These temperatures imply that the early lower mantle was probably extensively molten, likely leading to enhanced CMB heat fluxes (Labrosse et al. 2007).

There are several ways in which future progress in the study of the long-term evolution
of the core are likely to be made.

1) Perhaps the most outstanding question is the extent to which regions of the core were stably stratified. The results in Fig 6 and Gomi et al. (2013) raise the possibility that a significant fraction of the lower core was stably stratified prior to inner core formation. The consequences of such a layer for the thermal and magnetic evolution of the core have yet to be thoroughly explored. Inner core formation (or other processes) may have led to the development of a buoyant layer at the top of the core. Neither the fluid dynamics of this layer, nor its implications for the dynamo are thoroughly understood. Observational constraints on stably stratified regions would be very valuable.

2) The likelihood that the lower mantle was initially extensively molten seems inescapable. Although some preliminary work has been carried out (Labrosse et al. 2007, Ulvrova et al. 2012), the consequences for the chemical and thermal evolution of both mantle and core have not yet been explored in detail.

3) More generally, the evolution of the CMB heat flux is not well constrained, while being absolutely central to the evolution of the core and geodynamo (c.f. Nimmo et al. 2004, Davies 2007). Complicating factors such as possible melting, the post-perovskite phase transition, and perhaps chemical layering, render dynamical models uncertain. The models shown in Figs 3-4 (which do not include any dynamics) suggest a CMB heat flux which does not vary greatly over 4 Gyr; it is not yet clear whether such results are dynamically plausible. So far, few models have included the available observational constraints on mantle cooling rates, which may help to reduce the possible parameter space (Section 3.2.7).

4) The potential for exsolution of MgO or other species to help drive the dynamo has scarcely been explored, but potentially represents an important way of providing enough entropy without requiring excessively high CMB heat flows (Section 2.3.1).

5) Whether or not the core contains any potassium is still an unresolved issue, though the best currently-available partitioning experiments argue against it (Nomura et al. 2012). However, the high CMB heat fluxes now preferred mean that the significance of this question has been reduced: potassium has only a small effect on inner core age (Fig 5a), though it can still contribute to reducing initial core temperatures (Fig 5b).

6) Finally, one would expect the changing CMB heat flux, the extent of stable stratification and the growth of the inner core all to have observable effects on the behaviour of the geodynamo. Thus, at least in principle, the paleomagnetic record ought to provide observational constraints on core thermal evolution. The strength of the paleofield is predicted to be insensitive to inner core formation (Aubert et al. 2009). On the other hand, the time-variability of the magnetic field and perhaps the degree of dipolarity are likely to be affected by the inner core; thus, good enough paleomagnetic data may help to tie down when the inner core formed (Coe and Glatzmaier 2006).
4 Conclusions

This chapter set out to examine the thermal and compositional evolution of the core, from shortly after its formation to the present day. This period probably involved only two events of importance: the initiation of the geodynamo; and the onset of inner core formation. Prior to inner core formation, some fraction of the lower core was probably stably stratified; a buoyant stable layer may also have gradually developed at the top of the core, whether from inner core growth, exsolution or reaction with the mantle.

Geodynamo activity started at 3.5 Gyr B.P. at the latest; however, it is important to understand that this dynamo could easily have been sustained without an inner core being present. Our baseline model suggests inner core formation at 0.5 Gyr B.P. Uncertainty in model parameters could extend the age to 1.7 Gyr, but unless a thick, insulating layer exists at the top of the core, the geodynamo must have operated long before inner core formation.

The change in core temperature over 4 Gyr was probably 600-1600 K, implying an early lower mantle that was likely extensively molten. This molten layer was probably responsible for enhanced CMB heat flows which helped drive the early dynamo.

The present-day core geodynamo is maintained primarily by compositional convection as the inner core solidifies, with exsolution as a possible additional source term. The CMB heat flux is estimated at $12 \pm 5$ TW and is sufficient to drive a dynamo dissipating 0.1-3.5 TW.

As should be clear, there are several areas which require further study. Firstly, the extent and evolution of core stratification, and its effect on the dynamo, are unclear. Second, the evolution of the CMB heat flux over time is currently poorly understood, particularly the effect of lower-mantle melting, and yet has first-order implications for the thermal and chemical histories of both core and mantle. And finally, future paleomagnetic measurements may help to provide further observational constraints on the evolution of the geodynamo, and thus of the core.

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