The redox state of the mantle during and just after core formation

BY D. J. FROST*, U. MANN†, Y. ASAHARA‡ AND D. C. RUBIE

Bayerisches Geoinstitut, University of Bayreuth, Bayreuth 95440, Germany

Siderophile elements are depleted in the Earth’s mantle, relative to chondritic meteorites, as a result of equilibration with core-forming Fe-rich metal. Measurements of metal–silicate partition coefficients show that mantle depletions of slightly siderophile elements (e.g. Cr, V) must have occurred at more reducing conditions than those inferred from the current mantle FeO content. This implies that the oxidation state (i.e. FeO content) of the mantle increased with time as accretion proceeded. The oxygen fugacity of the present-day upper mantle is several orders of magnitude higher than the level imposed by equilibrium with core-forming Fe metal. This results from an increase in the Fe₂O₃ content of the mantle that probably occurred in the first 1 Ga of the Earth’s history. Here we explore fractionation mechanisms that could have caused mantle FeO and Fe₂O₃ contents to increase while the oxidation state of accreting material remained constant (homogeneous accretion). Using measured metal–silicate partition coefficients for O and Si, we have modelled core–mantle equilibration in a magma ocean that became progressively deeper as accretion proceeded. The model indicates that the mantle would have become gradually oxidized as a result of Si entering the core. However, the increase in mantle FeO content and oxygen fugacity is limited by the fact that O also partitions into the core at high temperatures, which lowers the FeO content of the mantle. (Mg,Fe)(Al,Si)O₃ perovskite, the dominant lower mantle mineral, has a strong affinity for Fe₂O₃ even in the presence of metallic Fe. As the upper mantle would have been poor in Fe₂O₃ during core formation, FeO would have disproportionated to produce Fe₂O₃ (in perovskite) and Fe metal. Loss of some disproportionated Fe metal to the core would have enriched the remaining mantle in Fe₂O₃ and, if the entire mantle was then homogenized, the oxygen fugacity of the upper mantle would have been raised to its present-day level.

Keywords: perovskite; oxygen fugacity; lower mantle; accretion; magma ocean; element partitioning

* Author for correspondence (dan.frost@uni-bayreuth.de).
† Present address: Institute for Mineralogy and Petrology, ETH Zurich, Clausiusstrasse 25, NW, 8092 Zurich, Switzerland.
‡ Present address: Spring 8 Material Structure Group I, Japan Synchrotron Radiation Research Institute, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan.

One contribution of 14 to a Discussion Meeting Issue ‘Origin and differentiation of the Earth: past to present’.
1. Introduction

The redox state within the proto-Earth and its constituent planetary embryos controlled the partitioning of siderophile elements between the mantle and core. The cumulative effect of this partitioning process is reflected in the present-day mantle concentrations of siderophile elements when compared with those in chondritic meteorites. It has been frequently noted that siderophile element depletions in the mantle are inconsistent with equilibration with Fe metal at a single oxygen fugacity and, in several studies, it has been proposed that oxygen fugacity evolved with time during accretion from reduced conditions at the start to more oxidized towards the end (Wänke 1981; O’Neill 1992; Wood et al. 2006). Seemingly in agreement with this evolutionary trend, the oxygen fugacity of the present-day upper mantle is several orders of magnitude higher than that imposed by equilibrium with metallic Fe during core formation (O’Neill & Wall 1987; Wood 1991). The timing and extent to which the Earth’s mantle became oxidized would have had a major impact on its evolution, and identifying the mechanisms by which this occurred should place important constraints on planetary formation processes. The redox path taken during accretion would have strongly influenced the nature of the light alloying element (or elements) in the Earth’s core (O’Neill & Palme 1998). The speciation of degassing volatiles from the mantle would have also been a function of the oxidation state of the early mantle, which may have consequently influenced the development of the hydrosphere and atmosphere (Kasting et al. 1992). Major chemical and physical differences between terrestrial planets were probably dictated by differences in their redox evolution, placing great importance on the comparative study of planetary redox states.

An important underlying question is whether mantle oxidation occurred as a result of a change in the redox state of material that was being accreted to the Earth, i.e. heterogeneous accretion (Wänke 1981; O’Neill 1992), or whether there are internal processes that could have led to an increase in mantle oxygen fugacity while retaining a single homogeneous accreting composition (Wade & Wood 2005). Integral to most ‘homogeneous’ accretion models is the concept that changes in metal–silicate partition coefficients at high pressures and temperatures may negate the necessity for changing $f_{O_2}$ during core formation (Li & Agee 1996; Chabot & Agee 2003; Wade & Wood 2005). In addition, however, several fractionation processes involving Fe, O and Si have been identified, which could have changed the oxidation state of the mantle, even if the redox state of accreting material remained essentially constant (Javoy 1995; Frost et al. 2004; Rubie et al. 2004; Galimov 2005). It is, therefore, important to determine the effectiveness of these processes and the conditions under which they may have operated.

Here we examine internal processes that could have led to changes in the redox state of the mantle during and after core formation. Throughout this analysis, we pay special attention to determining whether $f_{O_2}$ varied due to heterogeneous or homogeneous processes and how the mantle attained its present-day ferric and ferrous Fe concentrations.

2. The evolution of mantle $f_{O_2}$

Siderophile elements are generally divided into three groups based on their 1 bar metal–silicate partition coefficients (figure 1), slightly siderophile
Based on these 1 bar partition coefficients, however, the mantle depletions of these three element groups cannot be reconciled with core–mantle fractionation at a single oxygen fugacity (Ringwood 1966; Wänke 1981; O’Neill 1992). The mantle depletions of slightly siderophile elements such as V or Cr would have required core–mantle equilibration at conditions more reducing than those required for the siderophile or highly siderophile depletions. Even within the group of siderophile elements, Ni and Co 1 bar partition coefficients are inconsistent with their concentrations in the mantle. To explain these inconsistencies, homogeneous accretion models require that core–mantle equilibration occurred at high pressures and temperatures where element metal–silicate partition coefficients reached values that can explain mantle abundances (Li & Agee 1996; Righter et al. 1997), even if the Earth accreted from material with a broadly constant composition and redox state. Metal–silicate partitioning has, therefore, been envisaged to have occurred at the base of a deep silicate magma ocean. Currently, however, it is not possible to find either a set or range of pressure–temperature conditions where metal–silicate partitioning at a single $f_{O_2}$ can explain concentrations of all three groups of siderophile elements (Wood et al. 2006). Highly siderophile elements, for example, remain excessively depleted in a homogeneous accretion scenario and require the addition of a final late veneer of material that did not undergo core formation (Holzheid et al. 2000). Although it has been proposed that at high temperatures and pressures slightly siderophile (e.g. V, Cr) and siderophile element depletions could be

---

**Figure 1.** Mantle element abundances (McDonough & Sun 1995) normalized to those in CI chondrites and Ti. Siderophile elements have metal–silicate partition coefficients that are greater than 1 and were therefore depleted from the mantle during core formation. Transposed upon the effects of siderophile behaviour is an additional depletion trend resulting from volatility (circles), which is a broad function of the 50% condensation temperature. Siderophile elements can be divided into three basic groups, slightly siderophile (unfilled symbols), moderately siderophile (grey) and highly siderophile (black squares).
produced at a single $f_{O_2}$ (Gessmann & Rubie 2000; Chabot & Agee 2003; Wade & Wood 2005), the temperatures required are much higher than the liquidus of a likely magma ocean composition and therefore cannot realistically describe the conditions at the base of a magma ocean (Wade & Wood 2005). Recent data can also be used to challenge the concept that conditions exist where the mantle concentrations of Ni, Co and Fe could have been obtained simultaneously through core–mantle equilibration (Kegler et al. 2008). To overcome this problem, recent models (Wade & Wood 2005; Wood et al. 2006) have returned to the concept that $f_{O_2}$ increased during accretion from initially reducing conditions, to explain slightly siderophile element depletions, to more oxidized conditions towards the end. This would require initially FeO-poor silicate material to become FeO rich with time while silicate–metal equilibration continued. This concept is similar to the traditional heterogeneous models (Wänke 1981; O’Neill 1992), which argued for initially very reducing conditions to account for slightly siderophile element depletions, followed by accretion of more oxidized material, where either a sulphide liquid or no liquid separated to the core. It has been argued in recent studies, however, that changes in the Earth’s redox state were caused by internal fractionation processes rather than the accretion of more oxidized material (Galimov 2005; Wade & Wood 2005). Core formation models, therefore, seem to have converged on the idea that the redox state, i.e. the FeO content (or FeO/MgO ratio) of silicate material, increased with time during core formation.

In addition to an increase in FeO, the Fe$_2$O$_3$ content of the mantle must have also increased towards the end of, or just after, core formation (O’Neill 1992; O’Neill et al. 1993a,b; Delano 2001). Equilibrium with Fe-rich metal should have ensured that the oxygen fugacity of the silicate mantle remained at values below the iron–wüstite (IW) oxygen buffer during core formation. Taking into account the current concentration of FeO in the mantle, the $f_{O_2}$ is constrained during the final stages of core formation to approximately 2 log units below the IW-buffer (approx. ΔIW − 2) as shown in figure 2. The oxygen fugacity of the present-day upper mantle, as determined through oxy-thermobarometry, is between −2.5 and +1 log units relative to the fayalite–magnetite–quartz oxygen buffer (∆FMQ) or between ΔIW + 2 and +5.5 (Wood 1991). Mantle samples with closer links to the asthenosphere fall at the more reduced end of this range, i.e. ΔIW + 2 to +4.5, but this still requires that the present-day asthenospheric mantle is at an $f_{O_2}$ at least 3 log units above the level that prevailed during core formation (Wood et al. 1990; Wood 1991). Recent calibrations of V partitioning during basalt genesis have allowed the $f_{O_2}$ of the Archaean mantle to be assessed using analyses from ancient basaltic and ultramafic rocks. Such studies indicate that the $f_{O_2}$ of the mantle has remained within approximately 0.3 log units of its present-day value over the last 3.5 Gyr of the Earth’s history (Li & Lee 2004; Canil et al. 2006). Delano (2001) reached a similar conclusion by studying Cr partitioning. In fact, as will be seen, mantle $f_{O_2}$ is not constant with depth. Even if the $Fe^{3+}/\sum Fe$ or bulk oxygen content of the mantle is constant, the $f_{O_2}$ will be much lower in the deeper mantle as a result of crystal chemical effects (Ballhaus 1995; Gudmundsson & Wood 1995; Woodland & Koch 2003; Frost & McCammon 2008). The rise in the redox state of the mantle since core formation, therefore, is more accurately reflected in the $Fe^{3+}/\sum Fe$ of the upper mantle (or better still the O/Fe ratio), which is in the range of 2–3 per cent in the present-day mantle.
Canil & O'Neill 1996), but would have been much lower than this when in equilibrium with metallic Fe. In figure 2, estimates for the $f_\text{O}_2$ of the Martian mantle from SNC meteorites (Wadhwa 2001; Herd et al. 2002) and the $f_\text{O}_2$ of lunar basalts (Papike et al. 2004) are also shown. The simplest explanation would seem to be that these bodies did not undergo the same level of mantle oxidation as experienced by the Earth.

There is, therefore, evidence for two phases of mantle oxidation. The first apparently raised the FeO content of the mantle during accretion, and the second raised the Fe$_2$O$_3$ or O/Fe ratio within the first 1 Ga of the Earth’s history. To examine the possible mechanisms for these oxidation events, it is important to first study the present-day redox state of the mantle.

3. The redox state of the present-day mantle

The dominant minerals of the upper mantle, olivine and orthopyroxene, have low Fe$_2$O$_3$ solubilities, which means that in most mantle xenoliths found in alkaline basalts Fe$_2$O$_3$ is concentrated in (Mg,Fe)Al$_2$O$_4$ spinel (Canil & O’Neill 1996), a mineral of low modal abundance (2–3% in fertile peridotites). Even though the bulk Fe$^{3+}/\sum$Fe content of the mantle is relatively low (2–3%), oxygen fugacities calculated from ferric–ferrous equilibria involving spinel are high because $f_\text{O}_2$ is proportional to the activity of Fe$_2$O$_3$ in spinel (O’Neill et al. 1993b). At higher pressures, this is no longer the case and ferric Fe becomes dissolved in minerals such as garnet, which have larger modal abundances (O’Neill et al. 1993b;
Ballhaus 1995). Figure 3 shows oxygen fugacities calculated for garnet peridotite xenoliths from kimberlites by Woodland & Koch (2003) using the equilibrium (Gudmundsson & Wood 1995)

$$2\text{Fe}_3\text{Fe}^{3+}_3\text{Si}_3\text{O}_{12} = 4\text{Fe}_2\text{SiO}_4 + 2\text{FeSiO}_3 + \text{O}_2. \quad (3.1)$$

The decrease in $f_{O_2}$ with depth is mainly due to the positive volume change of equilibrium (3.1) (8.6 cm$^3$ mol$^{-1}$), which favours the stability of the $\text{Fe}_3\text{Fe}^{3+}_3\text{Si}_3\text{O}_{12}$ garnet component (skiagite) with increasing pressure. For a fixed garnet peridotite composition, pressure alone will drive $f_{O_2}$ to lower levels. Using a fertile peridotite bulk composition with a fixed Fe$_2$O$_3$ content, and accounting for interphase partitioning, the $f_{O_2}$ of a mantle assemblage can be calculated at conditions beyond the depth sampled by xenoliths, shown as the solid curve in figure 3 (Frost & McCammon 2008). The $f_{O_2}$ is predicted to decrease further due to the volume change of equation (3.1), but it cannot fall indefinitely because a level is eventually reached where NiO in silicates will be reduced to form Ni–Fe alloy (O’Neill & Wall 1987; Ballhaus 1995) via the following reactions:

$$\text{Ni}_2\text{SiO}_4 = 2\text{Ni} + \text{SiO}_2 + \text{O}_2. \quad (3.2)$$

and

$$\text{Fe}_2\text{SiO}_4 = 2\text{Fe} + \text{SiO}_2 + \text{O}_2. \quad (3.3)$$
The silica activity is determined from the coexistence of olivine and enstatite. This Ni precipitation curve occurs at an $f_{O_2}$ slightly below the IW buffer (O’Neill & Wall 1987). The $f_{O_2}$ of a garnet peridotite assemblage will cross this curve at approximately 8 GPa or a depth of 250 km, where the metal formed will contain approximately 60 mol% Ni. Although the formation of metal is instigated by the reduction of NiO, approximately 40 per cent Fe metal will also partition into the alloy. Reactions (3.2) and (3.3) are driven to the right-hand side as reaction (3.1) is driven to the left-hand side with increasing pressure. A simplified combination of reactions (3.1) and (3.3) is therefore

$$3\text{FeO}_{\text{olivine}} = \text{Fe}_{\text{metal}} + \text{Fe}_2\text{O}_3_{\text{garnet}},$$

which is effectively FeO disproportionation. The precipitation of Ni–Fe alloy raises the $\text{Fe}^{3+}/\sum\text{Fe}$ ratio of the assemblage, which will cause the $f_{O_2}$ to remain close to the Ni-precipitation curve, although the volume change of equation (3.1) will continue to lower the $f_{O_2}$ to some extent with pressure, causing more metal to precipitate and to become increasingly Fe rich. By 14 GPa, a typical upper mantle fertile peridotite should have exsolved 0.1–0.2 wt% metal and the $f_{O_2}$ will be $\sim$IW (Frost & McCammon 2008). The $f_{O_2}$ in the upper mantle will therefore drop by at least 3 log units between depths of 60 and 250 km, even if the bulk oxygen content remains constant.

A major testable implication of this calculation is that garnet with a significant $\text{Fe}_2\text{O}_3$ content should coexist with Ni–Fe alloy at high pressures and temperatures. As shown in figure 4a, garnets equilibrated in the presence of pure Fe metal at high pressure and temperature indeed have high $\text{Fe}^{3+}/\sum\text{Fe}$ ratios (O’Neill et al. 1993a; McCammon & Ross 2003; Rohrbach et al. 2007). For a given mineral FeO content, equilibrium with metallic Fe defines the lowest possible $f_{O_2}$, which means that these $\text{Fe}_2\text{O}_3$ contents are also at their lowest possible level. Lower pressure minerals such as (Mg,Fe)Al$_2$O$_4$ spinel have negligible $\text{Fe}_2\text{O}_3$ contents at conditions of IW (Ballhaus et al. 1991), which indicates a change in mineral behaviour, driven by volumetric effects that favour $\text{Fe}^{3+}$- over $\text{Fe}^{2+}$-bearing components at high pressure.

The (Mg,Fe,Al)(Al,Si)O$_3$ perovskite dominates the mineralogy of the lower mantle. As shown in figure 4b, samples of Al-free (Mg,Fe)SiO$_3$ perovskite synthesized in equilibrium with metallic Fe also have high $\text{Fe}^{3+}/\sum\text{Fe}$ ratios that increase with Fe/(Fe+Mg). In addition, however, the $\text{Fe}_2\text{O}_3$ content of perovskite increases strongly with $\text{Al}_2\text{O}_3$ concentration when in equilibrium with metallic Fe (figure 4c). At the $\text{Al}_2\text{O}_3$ content expected for lower mantle perovskite, the $\text{Fe}^{3+}/\sum\text{Fe}$ ratio is over 50 per cent. Samples synthesized at or close to the peridotite solidus (approx. 2200°C) have lower $\text{Fe}_2\text{O}_3$ contents but $\text{Fe}^{3+}/\sum\text{Fe}$ ratios are still above 20 per cent. Perovskite has an eightfold coordinated site mainly occupied by Mg and a sixfold coordinated Si site. The strong affinity for $\text{Fe}^{3+}$ in perovskite probably results from an energetically favourable coupled substitution of $\text{Fe}^{3+}$ onto the eightfold site, which charge balances Al on the sixfold site. Trace-element partitioning experiments indicate that the $\text{Al}_2\text{O}_3$ content of perovskite is also coupled to a range of trivalent trace-element concentrations (Liebske et al. 2005). Elements such as Sc, for example, which are incompatible in Al-free perovskite during partial melting, become compatible in Al-bearing perovskite.
The equilibrium between Al-bearing perovskite and metallic Fe can be described by the equilibrium

$$\text{Al}_2\text{O}_3 \text{ pv} + 3\text{FeO} \text{ Mg-wüsite \ metal} = \text{Fe} \text{ metal} + 2\text{AlFeO}_3 \text{ pv}.$$  \ (3.5)

As high concentrations of the FeAlO$_3$ component are measured in perovskite in the presence of Fe metal at 25 GPa (Frost et al. 2004), this equilibrium must lie significantly to the right-hand side within a typical lower mantle assemblage. If Fe$_2$O$_3$-poor material enters the stability field of Al-bearing silicate perovskite, equilibrium (3.5) should cause FeO to disproportionate to Fe and Fe$^{3+}$. If the Fe$^{3+}/\sum$Fe ratio, or more precisely the bulk oxygen content, of the upper mantle
is the same as that of the lower mantle, then the experimental trend in figure 4 indicates that approximately 1 wt\% Fe metal should coexist with FeAlO$_3$-bearing perovskite, at least in the top of the lower mantle (Frost et al. 2004). An indication as to whether disproportionation will occur at higher pressures can be obtained by considering the likely volume change of equation (3.5), which can be estimated by assessing the effects of Al$_2$O$_3$, Fe$^{3+}$AlO$_3$ and FeSiO$_3$ substitutions on perovskite volumes. Figure 5 shows the effects of major substitutions on perovskite molar volumes. The effects on the volume of MgSiO$_3$ perovskite from the substitution of Al$_2$O$_3$ and FeSiO$_3$ individually are quite similar. Determining the effects of Fe$^{3+}$AlO$_3$ substitution is more challenging as it requires accurate volume and Fe$^{3+}$/P$_{Fe}$ ratio measurements, the latter being possible only through electron energy loss or Mössbauer spectroscopy. The only complete measurements to date are those of Saikia et al. (submitted), although Fe$^{3+}$/P$_{Fe}$ ratios in some other samples can be estimated by assuming that Al is always charge balanced by Fe$^{3+}$ and that the remaining Fe is present as Fe$^{2+}$. The resulting data show that Fe$^{3+}$AlO$_3$ substitution causes a much larger increase in volume than either individual Al$_2$O$_3$ or FeSiO$_3$ substitutions, but the trend is complicated by the fact that most samples also contain a FeSiO$_3$ component, indicated by the number next to each symbol in figure 5. It is interesting to note, however, that the largest volumes occur for Fe$^{3+}$AlO$_3$-bearing samples with high FeSiO$_3$ concentrations, while the FeSiO$_3$-free sample of Nishio-Hamane et al. (2005) has the lowest volume for a given Fe$^{3+}$AlO$_3$ content. FeSiO$_3$ substitution apparently has a much larger effect on the volume of FeAlO$_3$-bearing perovskites than on MgSiO$_3$ perovskite. As a result of this strong effect on volume, increasing pressure should favour a low proportion of the

Figure 5. Molar volumes of perovskites synthesized along the MgSiO$_3$–FeSiO$_3$, MgSiO$_3$–Al$_2$O$_3$ and MgSiO$_3$–Fe$^{3+}$AlO$_3$ joins. Numbers next to symbols indicate the proportion of the FeSiO$_3$ component (mol%) in perovskites nominally along the MgSiO$_3$–Fe$^{3+}$AlO$_3$ join. The addition of FeSiO$_3$ to Al$_2$O$_3$-bearing perovskite has a much larger effect on the perovskite molar volume than when FeSiO$_3$ is added to Al$_2$O$_3$-free MgSiO$_3$ perovskite. Dashed line, Al$_2$O$_3$, Walter et al. (2004, 2006); dotted line, FeSiO$_3$, Yagi et al. (1979); solid line; Fe$^{3+}$AlO$_3$; circles, Saikia et al. (submitted); downtriangles, Vanpeteghem et al. (2006); uptriangles, Nishio-Hamane et al. (2005).
FeSiO₃ component in perovskite. By linearly extrapolating molar volumes along the MgSiO₃–Al₂O₃ and MgSiO₃–Fe₃CAlO₃ joins gives a volume change for equilibrium (3.5) of \( K^{2c} \text{m}^3 \text{mol}^{-1} \), indicating that pressure favours the stability of coexisting Fe metal and Fe₃CAlO₃ perovskite. The net result should be an increase in the Fe₃C/Fe²C ratio of perovskite with pressure.

4. Disproportionation during core formation and oxidation of the mantle

Silicate minerals and melts in equilibrium with core-forming Fe-rich metal at pressures less than 8 GPa contain low levels of the Fe₂O₃ component (Ballhaus et al. 1991; Jayasuriya et al. 2004). During the early stages of accretion, the silicate mantle would, therefore, have been very low in Fe₂O₃. As pressures inside the Earth increased, however, and entered the stability field first of the Fe₃Fe²Si₃O₁₂ garnet component and then the AlFe³⁺O₃ perovskite component, FeO would have been forced to disproportionate, thus creating Fe–Ni metal. Unless the mantle was completely molten throughout core formation, which seems unlikely, then the solid lower mantle, and to a lesser extent the transition zone and lower part of the upper mantle, would have contained disproportionated metallic Fe–Ni while the core was still forming. It is important to emphasize that there would, therefore, have been two types of Fe-rich liquid metal present in the mantle at this time: (i) ‘core-forming’ metal that accreted and separated to the core and (ii) ‘disproportionated’ metal that formed as a result of Fe₂O₃-bearing perovskite or garnet crystallization. If some of the disproportionated metal also separated to the core, then the remaining silicate material in the mantle would have been left...
with a greater bulk oxygen content, i.e. a higher O/Fe ratio, as can be seen in figure 6. A mantle composition that initially contains Fe as FeO only, would, in the lower mantle, be in equilibrium with Fe$_2$O$_3$-bearing perovskite and metallic Fe as a result of disproportionation. Loss of some metallic Fe to the core drives the bulk composition off the MgO–FeO tie line towards a present-day mantle composition with a higher O/Fe ratio. Homogenization of the entire mantle by convection, perhaps aided by one or more giant impacts, would have left the entire mantle with a higher O/Fe ratio. The degree to which the mantle became oxidized would have depended on the proportion of disproportionated metallic Fe that separated from the mantle. There is some uncertainty in calculating this proportion as the Fe$^{3+}/\sum$Fe ratio of perovskite in equilibrium with metallic Fe throughout the entire lower mantle during core formation is not well constrained. However, if of the order of 5–20 per cent of the disproportionated metal in the entire lower mantle separated to the core and mantle homogenization followed, then the mantle could have achieved its present-day O/Fe ratio as reflected in the Fe$^{3+}/\sum$Fe ratio and $f_{O_2}$ (Frost et al. 2004) of the sampled upper mantle.

There are a number of slightly different ways by which disproportionated metal could have been lost from the lower mantle. Many core formation models propose that core-forming metal rained down through a deep magma ocean, ponding at its base before descending through the solid lower mantle as diapirs (Li & Agee 1996; Righter et al. 1997; Rubie et al. 2003). The descending diapirs could have entrained disproportionated metal as they passed through the lower mantle (figure 7). Another possibility is that disproportionated metal, formed as perovskite crystallized from a silicate magma ocean, also ponded at the base of the ocean and separated to the core (Wood et al. 2006). As one preliminary study indicates that small degree Fe liquids can wet mineral grain boundaries at lower mantle conditions (Takafuji et al. 2004), a final possibility is that disproportionated metal separated by percolative flow to the core.

As mentioned above, towards the end of accretion, global melting during the Moon-forming giant impact (Canup & Asphang 2001) may have homogenized the mantle, mixing back the oxygen-enriched lower mantle with the upper mantle. Disproportionated metal would not have been lost as the mantle melted because Fe and Fe$_2$O$_3$ in perovskite would have recombined to produce FeO in the liquid as melting occurred. Metal would then form again and be trapped in the lower mantle as the silicate mantle crystallized.

As shown in figure 6, loss of disproportionated metal raises the O/Fe ratio of the mantle, but it does so at the expense of FeO and thus lowers the FeO/MgO ratio of the mantle. The approximate FeO/MgO ratio of the mantle must have been attained, therefore, before the O/Fe ratio was raised. It has been argued that the depletions of certain slightly siderophile elements from the mantle, such as V and Cr, required a phase of core formation to take place under very reducing conditions, compatible with a much lower mantle FeO/MgO ratio than at present (Wänke 1981; O’Neill 1992; Wade & Wood 2005). Both the FeO/MgO and O/Fe ratios of the mantle were, therefore, probably raised during or just after accretion, but these two types of oxidation are quite different and their mechanisms are unlikely to be related. Disproportionation followed by the loss of Fe to the core could not have raised the FeO/MgO ratio of the mantle through the reaction of the resulting Fe$_2$O$_3$ with additional accreting metallic Fe. This is because producing Fe$_2$O$_3$ by disproportionation consumes the same
amount of FeO as is formed when Fe$_2$O$_3$ reacts with Fe metal. While FeO disproportionation can explain the increase in the O/Fe ratio of the mantle to levels above those of equilibrium with Fe metal, it cannot explain increases in the FeO/MgO ratio of the mantle during accretion.

Loss of disproportionated Fe metal to the core followed by mantle homogenization could have raised the Fe$_2$O$_3$ content of the upper mantle. Raised upper mantle Fe$_2$O$_3$ concentrations could have only been sustained, however, once the proportion of infalling–accreting material equilibrating with the upper mantle declined, otherwise Fe$_2$O$_3$ would have been reduced by accreting Fe metal. In the final stages of accretion, however, levels of Fe$_2$O$_3$ may have been sufficient to oxidize small amounts of incoming metal, causing the mantle to retain the full compliment of siderophile elements in the accreting material. This ‘late veneer’ phase of accretion, which did not undergo metal–silicate fractionation, is required to explain the high levels of highly siderophile elements in the mantle. The higher $f_{O_2}$ of the upper mantle would have trapped a potentially reduced late veneer by oxidizing it. The redox state of the late veneer need not, therefore, have been any different from that of the bulk of the material from which the Earth formed.

*Phil. Trans. R. Soc. A* (2008)
5. Oxygen partitioning and its effect on the FeO/MgO ratio of the mantle

The partitioning of oxygen during core–mantle equilibration could have also influenced the redox state of the mantle in addition to potentially contributing at least part of the light element budget of the core (Ringwood 1977; O’Neill et al. 1998; Rubie et al. 2004). The solubility of oxygen in liquid Fe metal is relatively low at room pressure. At the 1 bar Fe–FeO eutectic, Fe metal contains only 0.16 wt% oxygen (Ringwood 1977). However, experiments have shown that solubility increases with both pressure and temperature (Kato & Ringwood 1989; Takahashi et al. 2004). The oxygen concentration of liquid metal during core formation will depend on the partitioning of oxygen between silicate melt and Fe metal, rather than its solubility in the Fe–FeO system. Although such partitioning cannot result in more oxygen in Fe metal than Fe–FeO solubility experiments would indicate, the sign of the pressure and temperature dependences of oxygen partitioning is not necessarily the same as those measured in Fe–FeO solubility measurements.

To date, the partitioning of oxygen has been studied mainly between liquid Fe alloy and magnesiowüstite (Ohtani & Ringwood 1984; O’Neill et al. 1998; Rubie et al. 2004; Asahara et al. 2007), although some data also exist for partitioning between Fe metal and silicate perovskite (Takafuji et al. 2005; Kawazoe & Ohtani 2006). Experiments on magnesiowüstite or perovskite are technically much easier to perform than those on silicate melts, which are hard to encapsulate at very high temperatures and generally react with any capsule material that does not react with liquid metal. Results can be applied to silicate melts using data on the partitioning of FeO between such melts and magnesiowüstite or perovskite. Oxygen partitioning between Fe liquid and magnesiowüstite is a function of $f_{O_2}$, but this can be accounted for by the reaction

$$\text{FeO}_{\text{magnesiowüstite}} = \text{Fe} + \text{O}_{\text{metal}} \quad (5.1)$$

and defining a distribution coefficient $K_d$

$$K_d = \frac{X_{\text{Fe}}^\text{metal} X_O^\text{metal}}{X_{\text{FeO}}^\text{magnesiowüstite}} \quad (5.2)$$

where $X_{\text{FeO}}^\text{magnesiowüstite}$, $X_{\text{Fe}}$ and $X_O$ are the mole fractions of FeO in magnesiowüstite, Fe in metal and O in metal, respectively. Experiments have shown that $K_d$ is ostensibly independent of oxygen fugacity over the range of conditions and metal oxygen contents so far studied (Asahara et al. 2007) and $K_d$ can therefore be modelled as a function of pressure and temperature alone. As a result of this simplifying assumption, inaccuracies may arise particularly when resulting models are extrapolated to high temperatures (higher than 3000 K), where metal oxygen contents become very large, and more realistic models are required, which treat oxygen partitioning as a function of oxygen fugacity.

Figure 8 shows $\ln K_d$ determined in experiments performed up to 25 GPa and 3150 K (Asahara et al. 2007). Oxygen partitioning is a strong function of temperature but a much weaker function of pressure. Oxygen contents of liquid Fe of approximately 7 wt% were observed in equilibrium with (Mg$_{0.9}$Fe$_{0.1}$)O at
the highest temperatures examined. The pressure dependence of the data is much harder to determine and an adequate fit would be obtained with no pressure dependence over the experimental pressure range examined. Asahara et al. (2007) used a thermodynamic model based on Fe–FeO solubility measurements to estimate $K_d$ at room pressure, and estimated $K_d$ at pressures up to 97 GPa using published data from diamond anvil cell experiments on the oxygen contents of liquid metal in equilibrium with (Mg,Fe)SiO$_3$ perovskite. These high-pressure data indicate that oxygen contents do increase at very high pressure and Asahara et al. (2007) consequently proposed a model in which metal–magnesiowüstit oxygen partitioning initially decreases with pressure, but reaches a minimum in the range of 20–30 GPa, above which oxygen contents in the metal start to increase. This can be explained if the partial molar volume of oxygen in Fe metal is relatively high at 1 bar but has a high compressibility. The volume change of reaction (5.1) is therefore initially negative but the high compressibility of oxygen eventually results in a sign change in the volume and oxygen starts to preferentially dissolve in Fe metal. This is in surprisingly good agreement with the predictions made by Walker et al. (2002) on the FeO content of Fe metal based on the estimates for the molar volume of O$_2$. The model of Asahara et al. (2007), however, indicates that the effect of pressure on $K_d$ over the entire range of pressure encompassed by the present-day mantle is not greater than that which would be caused by a change in temperature of 200 K. This model is in reasonable agreement with the recent experiments on partitioning between Fe liquid and magnesiowüstit performed in the diamond anvil cell up to 134 GPa (Ozawa et al. 2008). The model does, however, assume that $K_d$ remains independent of the composition over wide ranges of temperature.

\[
\ln K_d = a_0 + a_1 p + a_2 p^2 + a_3 p^3
\]

Figure 8. The oxygen exchange coefficient $K_d$ (equation (5.2)) as a function of pressure determined from experiments on magnesiowüstite and liquid Fe metal performed at various temperatures (Asahara et al. 2007). Curves are calculated at the indicated temperatures from a global fit to the experimental data.

Phil. Trans. R. Soc. A (2008)
and pressure and therefore ignores activities of the components. While Asahara et al. (2007) observed $K_d$ to be indeed independent of the composition up to 25 GPa, this is somewhat unusual given the large liquid immiscibility in the Fe–FeO system and this may not be the case at extreme pressures and temperatures. More complex models could be based on the determinations of oxygen activities in Fe metal assessed from the miscibility gap in the Fe–FeO system.

Rubie et al. (2004) proposed that the mantles of both the Earth and Mars, which have low and high FeO contents, respectively, could have been produced from material with an identical bulk composition (particularly in terms of bulk O/Fe ratio), as long as core–mantle equilibration occurred at conditions that promoted more oxygen to partition into the core of the Earth in comparison with that of Mars. Higher oxygen partitioning into the Earth’s core would have depleted the mantle of FeO, whereas if relatively little oxygen partitioned into the Martian core its mantle would have retained a higher FeO content. The results of Asahara et al. (2007) are consistent with this model and indicate that higher temperature core–mantle equilibration on the Earth than on Mars could have caused the required difference in oxygen partitioning. This implies that accretion was more energetic on Earth than on Mars, which is quite likely, given the differences in final masses and released gravitational energy during accretion.

6. Silicon and oxygen partitioning and their effects on the FeO/MgO ratio of the mantle

The partitioning of Si into the core could have also raised the FeO content of the mantle, and hence the $f_{O_2}$, during core–mantle equilibration (Javoy 1995). The partitioning of Si and Fe between liquid Fe metal and silicate melt is written as

$$\text{SiO}_2 + 2\text{Fe} = \text{Si} + 2\text{FeO},$$

where the $f_{O_2}$-independent exchange coefficient is defined as

$$K_d = \frac{X_{\text{metal}}^{\text{Si}} X_{\text{metal}}^{\text{FeO}}}{X_{\text{slicate}}^{\text{SiO}_2} X_{\text{metal}}^{\text{Fe}}^2}.$$ 

Figure 9 shows determinations of $K_d$ from analyses of silicate melt and liquid Fe metal equilibrated using a multi-anvil apparatus between 2 and 25 GPa at 1750–2400°C (Wade & Wood 2005; U. Mann, D. J. Frost & D. C. Rubie 2008, unpublished data). In addition, $K_d$ has also been calculated from the diamond anvil cell experiments of Takafuji et al. (2005) in which the Si content of Fe metal in equilibrium with (Mg,Fe)SiO$_3$ perovskite was investigated between 24 and 97 GPa. Although these experiments involved perovskite and not silicate melt, the differences in the derived $K_d$ values are likely to be small. In figure 10, all experimental data have been corrected to 2200 K and are plotted as a function of pressure. These data indicate that $K_d$ decreases with pressure up to approximately 25 GPa but is apparently almost pressure independent at higher pressures. A model has been fit to the experimental data with the temperature dependence guided by thermodynamic data on the pure oxides, as described by Wade & Wood (2005). These data indicate that, if temperatures are sufficiently

_Phil. Trans. R. Soc. A_ (2008)
Figure 9. The Si–Fe exchange coefficient $K_d$ (equation (6.2)) between liquid Fe metal and silicate melt determined as a function of pressure and temperature in a series of experiments (U. Mann, D. J. Frost & D. C. Rubie 2008, unpublished data; black symbols (triangles, 2 GPa; diamonds, 6 GPa; squares, 18–20 GPa; circles, 24–25 GPa)). Results of similar experiments by Wade & Wood (2005) are also shown (open (24–25 GPa) and grey (55 GPa) circles) in addition to data from Takafuji et al. (2005) on the Si–Fe $K_d$ between liquid Fe metal and (Mg,Fe)SiO$_3$ perovskite (crosses (93–97 GPa)). The study data of this literature are shown by black symbols. (Triangles, 2 GPa; diamonds, 6 GPa; squares, 18–20 GPa; circles, 24–25 GPa.)

Figure 10. The data shown in figure 9 normalized to 2200 K and plotted as a function of pressure (triangles, this study). Multi-anvil data are from Wade & Wood (2005) and U. Mann, D. J. Frost & D. C. Rubie 2008, unpublished data. Diamonds, Takafuji et al. (2005).
high in a magma ocean, then Si will enter the core and thus raise the FeO content of the mantle (reaction (6.1)). The effectiveness of this process, however, must be considered in conjunction with the partitioning of oxygen into Fe metal at high temperatures. Oxygen released by Si entering the core will therefore partition between the mantle and core (Javoy 1995) and this partitioning will be strongly temperature dependent.

The partitioning of Si into the core with a consequent increase in the FeO content of the mantle, as proposed by Javoy (1995), is a process that can potentially explain both the initially reducing conditions of core formation and the subsequent high (8 wt%) mantle FeO concentration. The effectiveness of this mechanism can be tested by combining mass balance calculations with high P–T partitioning models for Si and O. The core formation–accretion model of Rubie et al. (2007) adopts this approach and preliminary results are presented here in order to demonstrate its potential. The model involves continuous core formation during accretion whereby the Earth accretes through a series of collisions with planetary bodies, each of which has a mass equal to 10 per cent of the Earth’s mass at the time of impact. Following each impact, metal and silicate equilibrate in a resulting magma ocean at some specified pressure, which is a fraction of the core–mantle boundary pressure, and therefore increases during accretion. The temperature of equilibration is given by the peridotite solidus at the particular pressure (Zerr et al. 1998). Following the approach of Rubie et al. (2004), metal–silicate equilibration is modelled for a chondritic bulk composition (McDonough & Sun 1995) in which the oxygen content can be varied. The bulk composition can be varied anywhere between two extreme cases in which (i) all Fe is present as FeO (oxygen-rich composition) and (ii) all Fe is present as metal (oxygen-poor composition). The equilibrium compositions and relative proportions of coexisting silicate and metal liquids are determined at high $P$–$T$

$$\left[(\text{FeO})_x(\text{NiO})_y(\text{SiO}_2)(\text{Mg}_u\text{Al}_m\text{Ca}_n)\text{O}\right] + \left[\text{Fe}_a\text{Ni}_b\text{O}_c\text{Si}_d\right].$$

In order to solve for the seven unknown coefficients ($x$, $y$, $z$, $a$, $b$, $c$ and $d$), four mass balance equations (for Fe, Ni, Si and O, respectively) and three $K_d$ expressions that describe the partitioning of Si, Ni and FeO are used. Partitioning data described above are used together with the results of Kegler et al. (2008) for Ni. After equilibrating with the mantle at the base of the magma ocean, the metallic component of the impactor sinks to merge with the Earth’s proto-core without further equilibration.

Figure 11 shows preliminary results of calculations to determine the effect of O and Si partitioning on the evolution of the FeO content of a magma ocean during accretion. The lower curve [1] shows a model in which the Earth accretes from reduced (oxygen-poor) material. Initially, the FeO content of the magma ocean reflects that of the proto-Earth and impactors and the $f_{O_2}$ is sufficiently reducing for slightly siderophile elements, such as V, Cr and Si, to enter the core. As the magma ocean deepens and the pressure and (more importantly) the liquidus temperature increase, Si partitions increasingly into the core and the FeO content of the mantle increases. However, even with a very deep magma ocean, the FeO content of the mantle does not approach that of the present-day Earth. Curve [2] shows a model in which the bulk composition of accreting material was slightly more oxidized in an attempt to approach an Earth-like final mantle FeO

Phil. Trans. R. Soc. A (2008)
content. As the magma ocean deepens and Si enters the core, the FeO content of the mantle increases, however, at approximately 70 GPa the proportion of O entering the core increases to the point where the FeO content of the mantle starts to decrease. The back bend of the curve is controlled by not only the temperature but also the FeO content of the mantle, because more O enters the core at higher $f_{O_2}$. Curve [3] shows results for which the composition of the impactor is the same as for model [2] but the temperature of the peridotite solidus is raised by 200°. Uncertainties in the peridotite melting temperatures make this quite plausible. Here, the FeO content of the mantle also initially increases but backbends at even lower pressures as significant O starts to enter the core. Thus, although Si entering the core increases the FeO content of the mantle, the effect is limited at high temperatures by the partitioning of O into the core, which lowers the FeO content of the mantle. The largest increase in FeO content of the mantle was obtained with the first model in which $f_{O_2}$ increases from ΔIW $-4.5$ to $-2.5$ during accretion. However, although this model can adequately describe the depletion of slightly siderophile elements, it does not result in an increase in the FeO content of the mantle to the level found in the present-day Earth. The models do predict, however, that, for significant internal oxidation of the mantle to have occurred, metal–silicate equilibration in deep magma oceans that extended significantly into the Earth’s lower mantle would have been necessary (i.e. pressures far higher than 25 GPa).

Figure 11. Results of modelling calculations on the evolution of the FeO content of the mantle during accretion. The Earth grows by the accretion of a series of impactors with a constant composition and metal–silicate ratio. During each impact, the metal core of the impactor equilibrates with the entire silicate mantle of the Earth at the base of a magma ocean. The FeO content of the mantle is plotted against the pressure of equilibration, which is here taken to be 68 per cent of the pressure at the core–mantle boundary, while the temperature is determined from the silicate solidus. The initial FeO content of the mantle reflects the FeO content of the impactors with the lowest curve [1] having less FeO in the impactor mantle (i.e. more reduced) than [2] or [3]. Curve [3] is calculated for a peridotite solidus that is 200° higher than that experimentally determined. The grey shaded bar shows the FeO content of the present-day mantle.
There are, however, large uncertainties in the current model particularly at pressures above 25 GPa, where the diamond anvil cell experimental data have large temperature and compositional uncertainties. A weak element of the current model is that data for Si are taken predominantly from experiments on silicate melts, whereas the O model relies mainly on the data from experiments on magnesiowüstite and perovskite. The conclusions would be more reliable if data on O and Si were obtained in the same experimental study on silicate melts. Whether the mantle can be internally oxidized depends critically on the relative difference in partitioning between O and Si, which is currently poorly determined at the very high pressures where much of the oxidation is predicted to take place. Improved O and Si partitioning data between liquid Fe metal and silicate melts are required to conclusively exclude the possibility of complete internal oxidation of the mantle from reduced impactors, via reaction (6.1).

7. Discussion and conclusions

The depletion of slightly siderophile elements (V, Cr) from the mantle required more reducing conditions than those at which depletions of moderately siderophile elements (Fe, Ni and Co) appear to have been established (Wade & Wood 2005). A good explanation for this involves the oxygen fugacity at which core–mantle equilibration occurred increasing during accretion from initially very reducing conditions, where slightly siderophile elements (V,Cr) would have entered the core, to more oxidizing conditions where the mantle’s Fe, Ni and Co abundances were attained (Wänke 1981; O’Neill 1992; Wade & Wood 2005). Such a change could have been caused by an increase in the redox state of the material that accreted the Earth with time (Rubie et al. 2007). The variation in FeO contents of chondritic meteorites indicates that condensation processes and reactions involving H₂O could have caused very large variations in the redox state of accreting material (Krot et al. 2000). However, if accretion occurred from reduced material alone and deep magma oceans developed, the partitioning of Si into the core would have led to an increase in the FeO content of the mantle. The question then arises as to whether it is possible for the Earth to have accreted solely from reduced impactors in a homogeneous accretion scenario, with internal oxidation of the mantle occurring to the extent that the present-day upper mantle FeO content was ultimately achieved.

Current models based on existing experimental O and Si partitioning data indicate that the FeO content of the mantle could have increased from less than 1 wt% to approximately 5 wt% as Si entered the core during metal–silicate equilibration at the base of a progressively deepening magma ocean, which corresponds to an increase in \( f_{O_2} \) of approximately 2 log units. As a result of O entering the core at high temperatures, the models fail to predict conditions in which the present-day mantle FeO content is reached. However, given the current large uncertainties in the model parameters, particularly at very high pressures and temperatures, we cannot at present exclude the possibility that complete internal oxidation of the mantle is a viable mechanism. The models indicate that very high temperatures are required for this oxidation mechanism to proceed, corresponding to conditions in a magma ocean that extended deep into the present-day lower mantle. Further data on Si and O partitioning at deep lower mantle conditions are required in order to further test this hypothesis.

_Phil. Trans. R. Soc. A_ (2008)
Once a solid lower mantle formed, disproportionation of FeO to produce Fe$_2$O$_3$-bearing perovskite and Fe metal would have occurred. Loss of the disproportionated Fe to the core by entrainment in the final stages of core formation may have then raised the Fe$_2$O$_3$ content of the lower mantle. After mantle homogenization, either by convection or by a Moon-forming impact, the Fe$_2$O$_3$ content of the whole mantle could have attained its present-day level. This mechanism raises the Fe$_2$O$_3$ content of the mantle (i.e. the Fe/O ratio) but lowers the total FeO content. It therefore cannot explain increases in the FeO content of the mantle during core formation from the very low levels compatible with the loss of slightly siderophile elements (i.e. V and Cr) from the mantle because Fe$_2$O$_3$ formed by disproportionation would have reacted with accreting Fe metal to produce exactly the same amount of FeO in the mantle, which had initially disproportionated. Whole mantle oxidation by disproportionation could have operated only towards the end of core formation where levels of accreting Fe metal in the upper mantle became low and insufficient to reduce Fe$_2$O$_3$ back to FeO.

The authors are grateful to C. McCammon and T. Boffa Ballaran for their constructive discussions. U.M. acknowledges the support of the Elitenetzwerk Bayern Graduate programme. The manuscript was improved through the comments of two anonymous reviewers.

References


McCammon, C. A. 1998 The crystal chemistry of ferric iron in Mg0.96Fe0.04SiO3 perovskite as determined by Mössbauer spectroscopy in the temperature range 80–293 K. *Phys. Chem. Miner.* **25**, 292–300. (doi:10.1007/s002690050117)


Saikia, A., Boffa Ballaran, T. & Frost, D. J. Submitted. The effect of Fe and Al substitution on the compressibility of MgSiO$_3$ perovskite determined through single-crystal X-ray diffraction.


