REVIEWS

Accretion of the Earth and segregation of its core

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The Earth took 30–40 million years to accrete from smaller 'planetesimals'. Many of these planetesimals had metallic iron cores and during growth of the Earth this metal re-equilibrated with the Earth's silicate mantle, extracting siderophile ('iron-loving') elements into the Earth's iron-rich core. The current composition of the mantle indicates that much of the re-equilibration took place in a deep (>400 km) molten silicate layer, or 'magma ocean', and that conditions became more oxidizing with time as the Earth grew. The high-pressure nature of the core-forming process led to the Earth's core being richer in low-atomic-number elements, notably silicon and possibly oxygen, than the cores of the smaller planetesimal building blocks.

From observations of newly formed stars it appears that the Sun's planetary system formed from a flattened disk of dust and gas which accreted rapidly ($\sim 10^4$ yr) into 'planetesimals' ~ 10 km in diameter[1]. Gravitational interactions and collisions between these bodies generated Moon-to-Mars-sized planetary embryos in 10^5–10^6 yr and planetary bodies on a timescale of 10–100 million years (Myr)[1]. Tungsten isotope anomalies in meteorites[2] demonstrate that their asteroidal parents segregated cores within a few million years of the origin of the Solar System. Applied to the Earth, the same techniques point to protracted (30–40 Myr) metal re-equilibration during planetary growth. Comparison of the composition of the Earth's mantle with that of presumed protoplanetary material[3] indicates high-pressure, high-temperature conditions of core segregation[4–6], consistent with the existence of a deep silicate 'magma ocean' during much of the Earth's growth. Once the Earth had attained the size of Mars, however, crystallization of silicate perovskite in the lower mantle led to increasingly oxidized conditions[6,7], which ultimately halted the segregation of metal and may have led to a latest phase of sulphide addition to the core[8,9]. This drawn-out process generated a core containing, in addition to the major components Fe ($\sim 85\%$) and Ni (5%), 1.9% S, 4–5% Si and possibly >1% O.

Accretion and core formation in planetary objects

The planets of the Solar System originated as dust and gas in the young Sun's protoplanetary disk. The mechanisms of initial growth towards large bodies are poorly understood, but whether by gravitational instability or simple 'sticking together' of aggregates, the process must have formed a large number of 10-km-sized objects rapidly if the condensed materials were to avoid being dragged into the Sun[10–12]. Once bodies reached this critical size, gravitational perturbation became the dominant mechanism for further accretion through collision. Although some planetesimals were destroyed in collisions, others would have continued to accrete, provided impact velocities were low enough, or impact angles shallow enough, for gravity to recombine impact fragments and ejecta[1,13–15]. Models show that once a population of larger planetary embryos emerged, they accreted rapidly at the expense of smaller objects in a period of 'runaway growth' driven by dynamical friction and gravitational focusing[1]. Accretion eventually became self-regulated by gravitational interactions among planetary embryos and surviving planetesimals in a period of oligarchic growth[16]. The few tens of planetary embryos that survived this accretionary phase of about one million years were Moon-to-Mars-sized objects, with masses of the order of 0.01–0.1 times the mass of the Earth[17].

The evidence for early core formation in planetary embryos and planetesimals (radius > 30 km) is substantial. Many meteorites are samples from the asteroid belt between Mars and Jupiter, and are probably a remnant of the early days of accretion. The occurrence of distinct populations of iron and achondritic silicate meteorites attests to early differentiation in planetesimals that were subsequently destroyed during collisions[18]. Tungsten (W) isotopes confirm early core formation and place strict time limits on the timing of segregation of metal from silicate[19]. ^{182}Hf decays to ^{182}W with a half-life of about nine million years. Hafnium (Hf) is lithophile, having a pronounced preference for silicate phases over metal, whereas W is siderophile, preferring the metal phase. So when a metal core segregates from silicate, the Hf/W ratio becomes elevated in the silicate but is near zero in the metal. If metal segregation occurred while ^{182}Hf was 'alive' (<45 Myr after the origin of the Solar System), then silicate reservoirs exhibit positive ^{182}W anomalies and metal reservoirs exhibit negative anomalies relative to undifferentiated proto-nebular material such as the chondritic meteorites. The 'depleted' ^{182}W isotopic composition of iron meteorites relative to the chondrite standard constrains metal segregation in precursor objects to within a few million years (<5 Myr) of the origin of the Solar System[2,19]. This time frame is consistent with statistical models in terms of how long it takes to grow objects large enough (>30 km) to retain their heat[15]. Heat retention is important because metal does not segregate from silicate unless it is molten and efficient segregation also requires melting of the silicate[20,21].

Several heat sources contributed to melting of protoplanets in the young Solar System. Decay of the short-lived radionuclides ^{26}Al (half-life $t_{1/2} \approx 7 \times 10^5$ yr) and ^{60}Fe ($t_{1/2} \approx 3 \times 10^5$ yr) could have supplied sufficient heat to completely melt an early formed planetesimal[21–24]. Even in the absence of radioactive decay, the kinetic energy supplied by impact among small, porous planetesimals, and especially from collisions involving larger objects, would have

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caused substantial melting. Surviving undifferentiated bodies must, therefore, have grown relatively slowly, enabling heat to be radiated away and after substantial decay of the most important radio-nuclides. In small, differentiated bodies, the pressure at which metal and silicate material equilibrated during core segregation would generally have been less than 2 GPa. Equilibration temperature is more difficult to define because young objects can reach very high temperatures from the heating processes discussed above and from potential energy released during settling of metal[21]. Metal–silicate equilibration in early-formed objects may therefore have occurred at a wide range of high temperatures (for example, 1,500 to >3,000 K).

By the end of the oligarchic growth stage the tens of surviving planetary embryos were no longer constrained in well-regulated orbits and began to interact gravitationally, setting up a final, cataclysmic stage of accretion by collision which lasted ~10^7 years[1,25]. Many of these objects had proto-cores of iron alloy. A large terrestrial planet like the Earth probably sustained a number of big collisions during accretion, and a late-stage giant impact between a Mars-sized object (~10^{26} g), sometimes referred to as 'Theia', and the proto-Earth (~10^{27} g) is the prevailing theory for the formation of the Moon. This would have provided sufficient energy to melt the proto-Earth completely.

In summary, the Earth accreted over a period of at least 10^7 years from smaller bodies, most of which had already-segregated metallic cores. The energies of impact and metal separation provided sufficient heat to induce substantial melting episodically throughout the accretion and core-formation process. It is in the context of accretion, melting and metal segregation that the process of core formation needs to be viewed.

Chemical signature of core formation

Growth of the Earth from planetary embryos and planetesimals resulted in the substantial partitioning of siderophile elements into the metallic core, leaving lithophile elements behind in the silicate mantle. Observed metal–silicate partitioning behaviour can, in principle, be used to understand the core separation process provided chemical compositions of the bulk silicate Earth (otherwise known as the primitive mantle), the core and the bulk Earth are

known. Primitive mantle is estimated from analyses of mantle peridotites[3,26], bulk Earth from the compositions of undifferentiated protoplanetary material, represented by the CI carbonaceous chondrite meteorites and the core is obtained by calculating the difference.

Figure 1 shows a plot of the ratios of elemental concentrations in the bulk silicate Earth divided by those in CI chondrites, normalized to $\frac{[Mg]_{Earth}}{[Mg]_{CI}} = 1.0$ to correct for the high volatile contents of the meteorites. The elemental ratios are plotted as a function of the temperature by which 50% of the element of interest would have condensed during cooling of a gas of solar composition[27]. The most important point is that, although the bulk Earth does not have an exactly CI composition[28], refractory lithophile elements such as Ca, Sc, Ti and the rare earths are present in the silicate Earth in the same relative proportions as in the carbonaceous chondrites[3,26,29]. Carbonaceous chondrites represent undifferentiated protoplanetary material, so the implication is that the bulk Earth contains the same relative proportions of all refractory elements as carbonaceous chondrites. This is the basis of the chondritic reference model.

As can be seen on the left-hand side of the diagram, there is a decreasing relative abundance of elements in the silicate Earth with decreasing condensation temperature or increasing volatility. This demonstrates that the Earth is depleted in volatile elements with respect to the chondritic reference, although the correlation with increasing volatility is purely qualitative. Depletions of the silicate Earth in refractory siderophile elements such as W, Mo, Re and Os are due to partial extraction of these elements into the core. The extent of extraction can be estimated by comparing silicate Earth concentrations (ratioed to CI chondrites) to those of refractory lithophile elements such as the rare-earth elements. This enables us to calculate, for each element, a core–mantle partition coefficient D_i defined as follows:

$$D_i = \frac{[i]_{core}}{[i]_{silicate\ Earth}}$$

where [i] is the concentration of element i. Lithophile elements have D values close to zero. Table 1 shows that siderophile elements exhibit a very wide range of core–mantle partitioning behaviour, reflecting their different chemical properties and the conditions under which core segregation took place.

Core–mantle partitioning is best defined for those refractory elements that are weakly or moderately siderophile and which, like Ni and Co, are compatible in solid mantle silicates. The concentrations of these elements vary little in mantle samples, which means that D_i values based on the chondrite model have small uncertainties. Highly siderophile refractory elements such as the Pt group (Fig. 1) are slightly less well-constrained. The abundances of these elements in mantle samples are very low and, since they enter minor sulphide
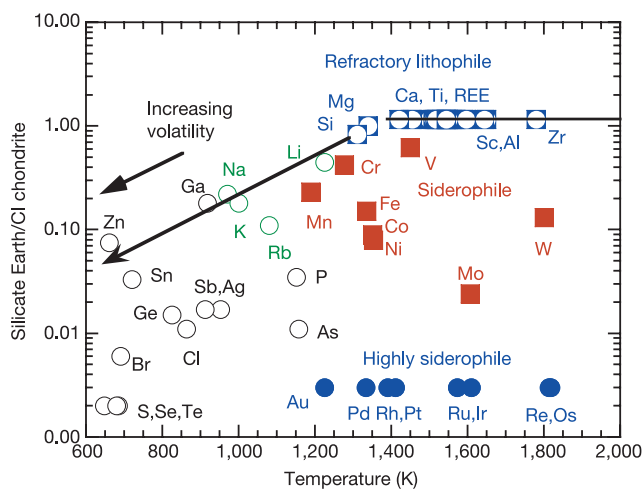

Figure 1 | Elemental abundance in the silicate Earth versus temperature of 50% condensation. Elemental abundances in the silicate Earth are ratioed to those in CI carbonaceous chondrites[3] and normalized to $\frac{[Mg]_{Earth}}{[Mg]_{CI}} = 1.0$. The abundances are plotted against the temperature by which 50% of the element would have condensed from a gas of solar composition at a total pressure of 10^{-4} bar (ref. 27). We note that depletions of the silicate Earth in refractory 'Siderophile' and 'Highly siderophile' elements relative to 'Refractory lithophile' elements are due to sequestration in the core. Core contents of volatile elements that condense at low temperatures are more difficult to constrain. REE, rare-earth elements.

Table 1 | Core–mantle partition coefficients

Element	Refs 3 and 29	Ref. 26	Likely range	Low-pressure experimental D_i (refs 30 and 31)
D_{Fe}	13.66	13.65	13.65	13.65
D_{Ni}	26.5	24.4	23–27	4,900
D_{Co}	23.8	24.7	23–27	680
D_V	1.83	NE	1.5–2.2	0.02
D_W	16	NE	15–22	3
D_{Pd}	800	NE	600–1,000	7×10^5
D_{Ir}	800	NE	600–1,000	10^{11}
D_{Pt}	800	NE	600–1,000	4×10^6
D_{Nb}	NE	NE	0.2–0.8	NE
D_{Cr}	3.4	2.9	0.5–3.5*	0.2
D_{Mn}	0.29	5	0.2–2.0*	0.006
D_{Si}	0.29	0.34	0.1–0.35*	10^{-5}
D_S	76	NE	50–100*	50
D_{Ga}	NE	NE	0–1.5*	15
D_P	22	45	20–50*	30

NE, not estimated.
*Value uncertain due to volatility.

minerals, rather variable. It is generally accepted, however, that their ratios to one another in the silicate Earth are, as shown in Fig. 1, approximately chondritic.

Core concentrations of volatile siderophile elements such as Si, S and P are difficult to estimate because their bulk Earth contents are not well constrained. This means, for example that depletions in Si and Cr (Fig. 1) could be due to volatility or to sequestration in the core or both. The lack of constraint means that the uncertainties in D_i are large (Table 1).

Segregation of the reduced core from the oxidized mantle took place at high temperatures as shown above, and element partitioning between the two depended on oxygen fugacity, as can be seen from the redox reaction:

$$MO_{n/2} = M + \frac{n}{4}O_2 \qquad (1)$$

This reaction represents reduction of the element as it transfers from its normal oxidation state (n) in the silicate to oxidation state zero in the metal. Given a concentration of FeO in the mantle of about 8 weight per cent (wt%) and of Fe in the core of 85 wt% (refs 3, 26, 29), reaction (1) implies that the core separated from the mantle at an oxygen fugacity approximately 2 log f_{O_2} units below Fe–FeO (iron–wüstite, IW) equilibrium.

Table 1 shows a comparison of the calculated core (metal)–mantle (silicate) partition coefficients and those obtained experimentally at low pressures (0–2 GPa), high temperatures (~1,800 K) and oxygen fugacity corresponding to 8 wt% FeO in the mantle[30,31]. As can be seen, the observed core–mantle partition coefficients are, for many of the siderophile elements, much (orders of magnitude) smaller than those determined experimentally. This manifests itself in the concentrations of many elements of concern (such as Ni, Co, Pd) being much greater in the mantle than would be predicted from the experimental data[32], the so-called 'excess siderophile problem'. Of equal importance are the weakly siderophile elements such as V and Cr for which the mantle concentrations are lower than predicted from the experimental data. Clearly, the mantle concentrations of these two groups of elements cannot be explained by an equilibrium with the metallic core at the fixed pressure, temperature and oxygen fugacity conditions of Table 1. We would expect, however, that early core segregation in small planetesimals and planetary embryos, including the proto-Earth, would have resulted in siderophile element abundances generally consistent with the D values given in Table 1. The Earth has apparently inherited little of the geochemistry of these earlier events.

Explanations for the 'excess siderophile problem'

The W-isotopic anomalies of iron and silicate meteorites show that asteroidal bodies segregated metallic cores very rapidly, within about 5 Myr (ref. 2) after the beginning of the Solar System. The Earth, on the other hand, appears to have undergone more protracted core formation, the W-isotopic composition of the mantle implying single-stage separation of the core about 30 Myr (refs 2 and 19) after the beginning of the Solar System or, using an exponential accretion model[33], a mean-life of accretion and core-separation of 12 Myr. The implications of the W-isotopic data are that the asteroidal cores re-equilibrated with the silicate Earth during accretion. If re-equilibration had not occurred, the silicate Earth would have inherited the low-pressure core–mantle partitioning of the small bodies and also their large positive W-isotopic anomalies. Given that the 'excess siderophile problem' was not inherited, but arose from the manner of core formation on the Earth, several possible explanations have been proposed:

(1) Inefficient core formation[34,35]. This is a disequilibrium model in which incomplete core separation left some fraction of core material mixed with the mantle. Later re-oxidation and re-mixing of this metal led to the observed elevated mantle concentrations of siderophile elements. Although this model can fit many of the elemental abundances, it cannot explain those of the weak side-

rophiles V and Cr[30]. A further objection is the enormous amount of water, about 15 times the current mass of the hydrosphere, which would be required to re-oxidize the 'retained' metal[8].

(2) Heterogeneous accretion[8,36,37]. This model proposes that the conditions of core segregation changed from reducing at the beginning of accretion to more oxidized towards the end. During the earliest, reduced, phase, highly and moderately siderophile elements (Ni, Co and the Pt group, for example) would have been completely extracted to the core, together with some fraction of the weak siderophiles such as Si, V and Cr. As conditions became more oxidizing, core extraction of siderophile elements would have ceased progressively, beginning with the weakest siderophiles and ending with more strongly metallic elements. The final phase, after core formation had ceased, was the addition of a 'late veneer' of about 0.5% of chondritic material. The latter raised the concentrations of highly siderophile elements in the mantle and, because core formation had ceased, ensured their approximate chondritic proportions to one another (Fig. 1). This model solves the 'excess siderophile problem', but, being a disequilibrium model with multiple steps, is very difficult to test.

(3) High-pressure core formation. Extension of metal–silicate partitioning experiments to pressures above 3 GPa (refs 4, 5, 38–41) demonstrated that the partition coefficients of some siderophile elements (most notably Ni and Co; Fig. 2) change with increasing pressure such that their mantle abundances may be explained by metal–silicate equilibrium at very high pressures and temperatures (see refs 4 and 42 for example). These observations led to the 'deep magma ocean' hypothesis to explain the 'excess siderophile' problem. As the Earth grew, it is argued (see ref. 43 for example), droplets of metallic liquid descended through a 700–1,200-km-deep (28–40 GPa) magma ocean, equilibrating with the silicate liquid as they fell[44]. The liquid metal ponded at the base of the magma ocean and subsequently descended in large diapirs to the growing core without further equilibration with the surrounding silicate (Fig. 3). High-pressure core formation can explain, by metal–silicate equilibrium, the partitioning of many elements between core and mantle without recourse to *ad hoc* assumptions about the oxidation state of the growing Earth. The 'late veneer' of chondrite-like material is, however, still required to explain the concentrations of the highly siderophile elements in the silicate Earth.

The 'deep magma ocean' model of core formation

As the Earth grew, the gravitational energy deposited by accreting planetesimals increased and at about 10% of its current size[45] was sufficient for significant melting to occur. After this point the
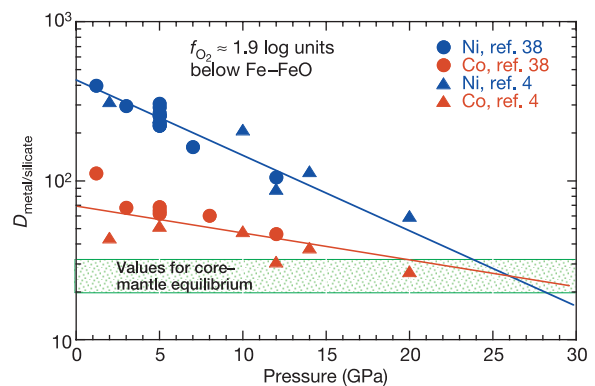

Figure 2 | The effect of pressure on Ni and Co partitioning. The liquid metal–liquid silicate partition coefficients ($D_i = \frac{[i]_{metal}}{[i]_{silicate}}$) for Ni and Co are those at 2,123–2,750 K and oxygen fugacity corresponding to current FeO content of the mantle. Data are from ref. 4 and ref. 38. Note that values approach those required for core–mantle equilibrium at the current FeO content of the mantle when pressure is ~28 GPa.

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Earth would have periodically had an extensively molten outer layer (a magma ocean) of variable thickness. In some cases the impact energy would have been sufficient to melt both the impactor and the proto-Earth[46,47]. The fates of pre-existing cores depended on the sizes of the Earth and impactor at the times of impact. Large impacts may have allowed the accreting core to combine directly with that of the proto-Earth. This cannot have been common, however, because of the evidence of metal–silicate re-equilibration on the Earth. Most impactors disaggregated and metallic iron sank though the molten silicate layer in droplets which, because of Rayleigh–Taylor instabilities[44], would have been about 1 cm in diameter. Droplets of this small size would have re-equilibrated with silicate melt as they fell through depths of only 60 m (ref. 44). Liquid metal and silicate therefore continued to re-equilibrate until the former either reached the core–mantle boundary (if the mantle were completely molten) or collected at a level above a solid, high-viscosity lower layer (Fig. 3). In the latter case the metal layer would cease re-equilibrating after it had reached about 5 km in thickness[44] and because of the high viscosity of the lower layer would segregate as large diapirs to the core[48].

Numerical simulations[49,50] indicate that a magma ocean extending to the core–mantle boundary would be short-lived and that the lower mantle would crystallize in a few thousand years. A shallower, partially molten layer would crystallize much more slowly, however, and could remain as a mixture of crystals and melt for 100 Myr (refs 49, 50). Considering these results and the energetics of impact and core segregation leads to a dynamic view of the growing Earth in which the outer molten part deepened and shallowed many times after episodic impact. The pressures and temperatures recorded by core–mantle partitioning are therefore values averaged over numerous cycles of metal accumulation and segregation such as that depicted in Fig. 3.

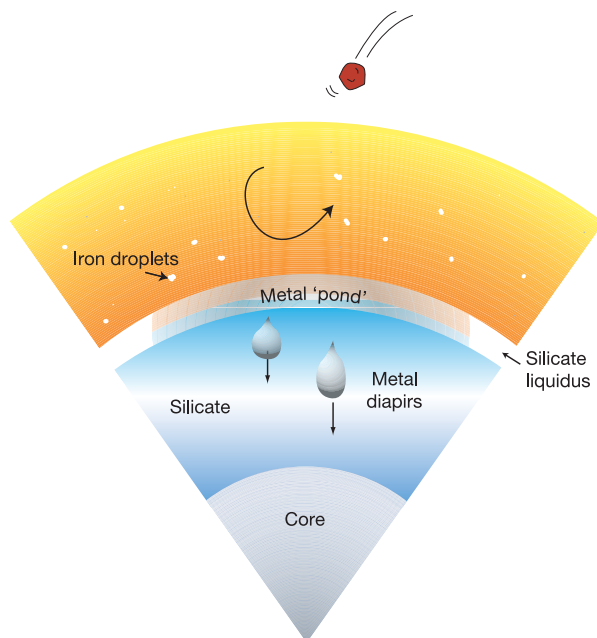Inspection of Fig. 3 and consideration of pressures within a growing planet lead to several conclusions about the conditions of core segregation. First, accumulation at the base of a completely or partially molten layer implies temperatures close to or slightly below the liquidus of mantle peridotite. Second, average pressure should have increased as the planet grew. Third, because the liquidus has a positive pressure–temperature slope, the average temperature of core segregation should also have increased as the planet grew. Having accepted these principles, we can use the dependences of D_i on pressure and temperature[6,39,40,51] to develop constraints on the core-segregation process. As shown in Fig. 2, the metal–silicate partitioning behaviour of both Ni and Co is strongly dependent on pressure, with temperature effects being subordinate[6,52] while partitioning of V and Si, for example, depends predominantly on temperature[6]. Therefore, by simultaneous consideration of a number of elements of differing chemical behaviour, it is possible to test potential pressure–temperature paths of the accretion and core-segregation process.

Accretion and core-segregation processes

For the simplest end-member case of single-stage equilibration of mantle and core, current partitioning data for Ni and Co yield pressures close to 40 GPa while temperature sensitive elements such as V and Cr yield temperatures of about 3,750 K (ref. 6). These conditions result in a core with about 10.5 wt% Si as the dominant light element[6] but, as illustrated in Fig. 4, correspond to temperatures about 650 K above the liquidus of the mantle. Such temperatures are physically implausible, however, because the base of the magma ocean must be close to the mantle liquidus (Fig. 3). If the FeO content of the mantle (and hence the oxygen fugacity) is fixed, then forcing core–mantle equilibration to remain on the peridotite liquidus results in an overall vanadium (V) core–mantle partition coefficient of about 0.4, a factor of four lower than that required. Because V partitioning is insensitive to pressure[6,51], this is purely a temperature effect—peridotite liquidus temperatures are too low to partition the requisite amount of V into the core. V partitioning into the metal can be enhanced by assuming that the silicate is a crystal–liquid mixture but the effect is small. Furthermore, crystal–liquid mixtures tend to partition too much Nb and W into the core. The
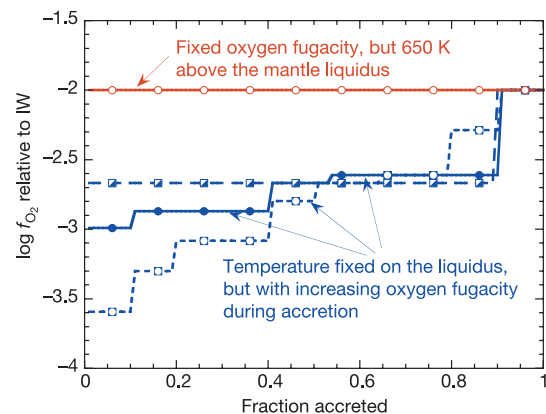

Figure 3 | **The deep magma ocean model.** Impacting planetesimals disaggregate and their metallic cores break up into small droplets in the liquid silicate owing to Rayleigh–Taylor instabilities. These droplets descend slowly, re-equilibrating with the silicate until they reach a region of high viscosity (solid), where they pond in a layer. The growing dense metal layer eventually becomes unstable and breaks into large blobs (diapirs), which descend rapidly to the core without further interaction with the silicate. Note that the liquidus temperature of the silicate mantle should correspond to pressure and temperature conditions at a depth above the lower solid layer and plausibly within the metal layer as indicated.

Figure 4 | **Conditions yielding correct core–mantle partitioning of siderophile elements during accretion.** Oxygen fugacity (relative to IW or Fe–FeO) is plotted as a function of fraction accreted, for Earth accretion models that yield the expected D values of Table 1 for Fe, Ni, Co, V, W, Nb, Cr, Mn, Ga, Si and P. Accreting metal was assumed to equilibrate with the silicate mantle at the base of the magma ocean, which deepens as the Earth grows. Note that at fixed oxygen fugacity (or FeO content of the mantle) during accretion, a temperature about 650 K above the silicate liquidus is required. Metal–silicate equilibration models fixed at the silicate liquidus temperature during accretion require pressures (from Ni and Co partitioning) corresponding to 30–40% of the depth to the core–mantle boundary in the growing planet and also that oxygen fugacity increases as the planet grows.

simplest solution[6], as illustrated in Fig. 4, is to allow oxygen fugacity (as represented by the FeO content of the mantle) to increase as accretion and core-segregation progress.

Figure 4 illustrates a continuous process of accretion and core segregation in 1% intervals. New material added to the Earth was assumed to be mixed with the pre-existing mantle, but isolated from the proto-core. The core was segregated in 1% steps, each aliquot being in equilibrium with the entire mantle at the time of segregation at pressures constrained by Ni and Co partitioning and temperatures on the peridotite liquidus[6]. The latter were found to be consistent with magma oceans extending to 30–40% of the depth of the growing mantle. A large number of oxygen fugacity paths (of which three are illustrated) yield the partitioning of V, W, Nb, Ni, Co, Mn, Cr, Ga, P and Si, consistent with the estimates of Table 1. All require, however, that most of the Earth formed under conditions more reducing than those implied by the current FeO content of the mantle and that the Earth became more oxidized towards the end of accretion.

Additionally, although this is an area of continuing debate[53], these accretion models require addition of 0.5% of chondritic material after cessation of core formation to generate the chondritic ratios of the highly siderophile elements such as Pd, Ir and Pt in the silicate Earth (Fig. 1). The current 'best explanation' is therefore an amalgam of 'deep magma ocean' and 'heterogeneous accretion' hypotheses, that is, core segregation at the base of a deepening magma ocean under progressively more oxidizing conditions[6]. The important questions then are: what was the mechanism of oxidation and when did it operate? That oxidation has occurred is demonstrated by the current high oxygen fugacity of the mantle[54].

Oxidation of the Earth during and after accretion

The oxidation state of the Earth would have increased during accretion if late-arriving planetesimals had higher FeO/Fe ratios than the early ones[8], thus increasing the oxidized iron content of the mantle and generating a concomitant increase in oxygen fugacity. This idea, although impossible to quantify, is broadly consistent with planetesimal theory, which states that during the period of oligarchic
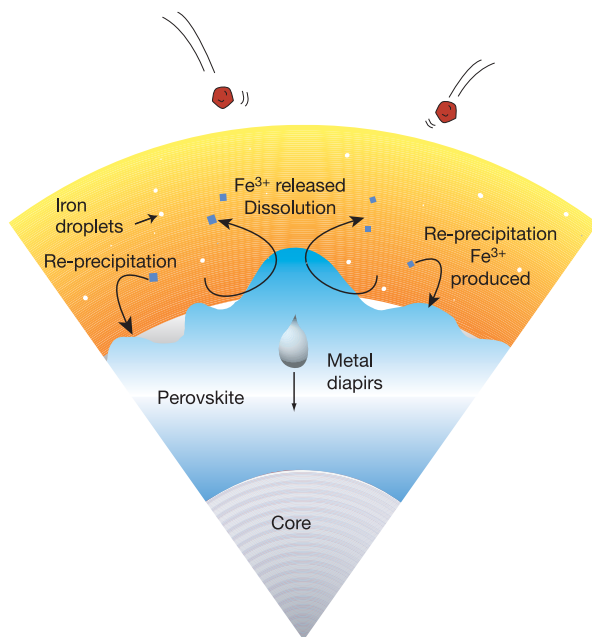

Figure 5 | Sketch of a possible mechanism by which the mantle may have self-oxidized via perovskite crystallization. Lower-mantle perovskite (Pv) generates Fe^{3+} and Fe^0 (metal) from disproportionation of Fe^{2+}. Fe metal is swept to the core by descending metal diapirs while the vigour of accretion and core segregation causes dissolution and recrystallization of perovskite with release of Fe^{3+} to the overlying magma ocean.

growth the proto-Earth consumed bodies in a narrow feeding zone (0.01 astronomical units, AU) but that the source of accreting bodies dramatically widened in the later stages of planetary growth[1]. It is thus conceivable that late accretion added more oxidized materials from the current position of the asteroid belt[1].

Dissociation of H_2O and escape of H_2 from the Earth's atmosphere[55] may also have caused oxidation. If this is an important oxidation mechanism, however, it is difficult to see why the mantle of Mars, a more volatile-rich planet than the Earth, with a higher FeO content[37], appears to be more reduced than the Earth's mantle[56]. Finally, a recent hypothesis[6,7] (elaborated below) is that the Earth simply self-oxidized through crystallization of magnesium silicate perovskite.
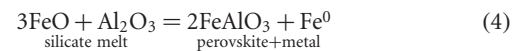
At depths below 660 km in the present-day Earth, the stable phases are, assuming peridotitic composition, $(Mg,Fe)SiO_3$, magnesium silicate perovskite (79% by volume, vol.%; ref. 57), $(Mg,Fe)O$ magnesiowüstite (16 vol.%) and $CaSiO_3$ perovskite (5 vol.%). An important property of magnesium silicate perovskite is that it dissolves the 4% Al_2O_3 present in peridotite by a coupled substitution with Fe^{3+} (refs 58 and 59) as follows:

$$Mg^{2+}Si^{4+} \leftrightarrow Fe^{3+}Al^{3+} \tag{2}$$
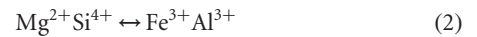
It has recently been discovered that this substitution mechanism is so stable that it forces ferrous iron to disproportionate to ferric iron plus iron metal[7]:

$$3Fe^{2+} \leftrightarrow 2Fe^{3+} + Fe^0 \tag{3}$$

Or, in terms of oxide components:

$$\underset{\text{silicate melt}}{3FeO + Al_2O_3} = \underset{\text{perovskite+metal}}{2FeAlO_3 + Fe^0} \tag{4}$$

This means that, as perovskite began to crystallize in the extensively molten Earth, it dissolved ferric iron as $FeAlO_3$ component and produced Fe metal. The perovskite is stable above 23 GPa, so this process took place over a substantial part of the history of the Earth's accretion and core formation. The implications are that metal sinking through the lower mantle to the core would inevitably have dissolved some of this internally produced Fe, resulting in a perovskitic layer which was relatively oxidized. Given the gravitational instability of any metal layer (Fig. 3), accretional energies and heat-loss, the depth of the magma ocean must have fluctuated continuously, thereby generating fronts of dissolution and precipitation at the lower boundary, as depicted in Fig. 5.

Perovskite dissolution and re-precipitation acted as a ferric or oxygen 'pump', releasing ferric iron to the magma ocean during dissolution and producing more during precipitation. As the Earth grew, ferric iron released to the magma ocean would have been consumed by reduced species such as CH_4. Droplets of Fe metal falling through the magma ocean would also have reacted with ferric iron, driving reaction (3) to the left and producing more Fe^{2+} to dissolve in the silicate melt. Hence the oxygen fugacity and the content of oxidized iron in the mantle (magma ocean) increased naturally as a consequence of perovskite crystallization and dissolution. In the very final stages of earth accretion this mechanism may have caused sufficient oxidation to halt metal segregation, setting the stage for the 'late veneer' of chondritic or similar material to add the highly siderophile elements exclusively to the mantle. The importance of this self-oxidation mechanism is that it is experimentally observed to take place when magnesium silicate perovskite crystallizes[7].

The self-oxidation mechanism removes the need to make *ad hoc* assumptions about the compositions of the materials added to the Earth during accretion. The oxidation-state changes required by partitioning data are a simple consequence of the size of the Earth. Any planet in which magnesium silicate perovskite is an important crystallizing phase should undergo the same process. It could explain why the Earth's mantle is more oxidized than that of Mars[56], a planet in which perovskite is either absent or only stable very close to the

core–mantle boundary. Because of its small size, Mars cannot have undergone the same period of extensive perovskite crystallization during accretion as did the Earth.

Consequences of 'self-oxidation' and the age of the core

The timing of core segregation can, in principle, be determined from a radioactive decay system in which either the parent or the daughter isotope is siderophile, so that core formation established the current parent/daughter ratio in the silicate Earth. The systems ^{182}Hf–^{182}W and $^{238,235}U$–$^{206,207}Pb$ are potential core chronometers. The daughters, W and Pb, are siderophile and their current isotopic constitutions yield model-dependent 'ages' of core formation. Ages are obtained by assuming, for example, instantaneous core segregation at a fixed time or, more realistically, continuous core segregation as the Earth grew.

If it is assumed that all accreting material mixed isotopically with the silicate Earth, that accretion rate decreased exponentially with increasingly larger impacts, as predicted from the planetesimal theory and that the core segregated continuously with fixed parent and daughter partitioning, a time constant for core formation can be obtained (Fig. 6):

$$F_t = 1 - e^{-\lambda \Delta t} \qquad (5)$$

where F_t is the cumulative fractional mass of the Earth at time t relative to the present day, λ is the time constant for core formation ($= 1/\tau$, where τ = the mean life) and $\Delta t = t_0 - t$ (where t_0 is the age of the Solar System). On this basis, both Hf–W and U–Pb timescales should be the same, but as can be seen from Fig. 6, the mean-life of core formation is about 12 Myr using the Hf–W system and 28 Myr using U–Pb. Changing the model (for example, to single-stage equilibration) alters both timescales, but the discrepancy between them remains. The U–Pb timescale is always more protracted than that of Hf–W.

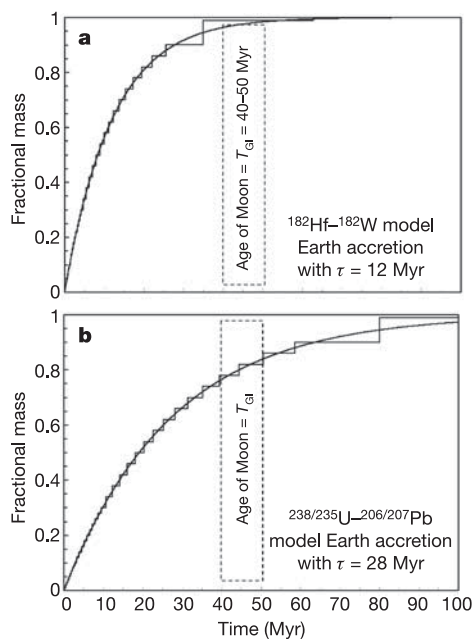The only way in which both Hf–W and U–Pb timescales could be

correct is if Pb entered the core at a later stage than W, after the formation of the Moon[9]. The giant impact believed to have formed the Moon[46,60] defined the last major growth stage of the Earth, adding about 10% of its mass. The timing of the impact is given by the Hf–W age of the Moon which appears to lie between 40 and 50 Myr (Fig. 6)[61]. Under the reducing conditions of early accretion (Fig. 4) W would be a siderophile element while Pb partitioning into the metal phase would be weak[9,62]. Conditions appear to have become more oxidizing during accretion, however, so that, as found in modern MORB[63], an Fe–Ni sulphide became the only stable 'metallic' phase (Fig. 7). Figure 7 shows the effect when ferric iron produced from perovskite crystallization is recycled back into a melt of peridotitic composition under upper mantle conditions. Oxygen fugacity increases by about three log units and sulphur-rich liquids are the only metallic phases which can coexist with the putative magma ocean.

The giant Moon-forming impact should have completely melted the Earth[60], dramatically increasing the solubility of sulphur and chalcophile elements in the liquid silicate[9]. As the Earth cooled, however, an FeS-rich liquid would have 'rained out' of the liquid mantle, extracting chalcophile elements. Importantly, Pb is chalcophile, partitioning strongly into iron sulphide liquid[64]. Segregation of <1% of late sulphide liquid, the 'Hadean Matte'[8], would therefore have fractionated U from Pb, re-setting the U–Pb age without affecting the Hf–W age because the ^{182}Hf parent was already extinct[9]. Thus the U–Pb age of the Earth (65–85 Myr after the beginning of the Solar System) plausibly represents the very last stages of core segregation at the end of accretion, while the W age represents the major phase of core segregation before the Moon-forming impact.

The 'light' element in the core

Although the Earth's core is, in Birch's[65] words, an 'uncertain mixture of all the elements', we are able through geochemical and geophysical arguments to constrain its composition quite well. The chondritic reference model (Fig. 1), when combined with the compositions of carbonaceous chondrites[66] and the primitive mantle[3,26], leads to a core which is about 85% Fe and 5% Ni by weight. All of the other refractory elements discussed here should be present at very low concentration in the core, with the exceptions of Cr (≤0.9%) and Co

Figure 6 | **Two estimates of the timing of accretion and core formation on the Earth.** Both estimates assume an exponential growth model (equation (5) with progressively increasing masses of impactors). **a**, The result that satisfies the W isotopic composition of the bulk silicate Earth[9]. **b**, A result that satisfies recent estimates of the Pb isotopic composition of the bulk silicate Earth[9]. The Hf–W age of the Moon corresponding to the Moon-forming giant impact (T_{GI}) appears to lie in the range 40 to 50 Myr (ref. 61). As discussed in the text, the W result dates the principal phase of core formation, while the Pb result plausibly dates a late-stage segregation of sulphide after the giant impact.
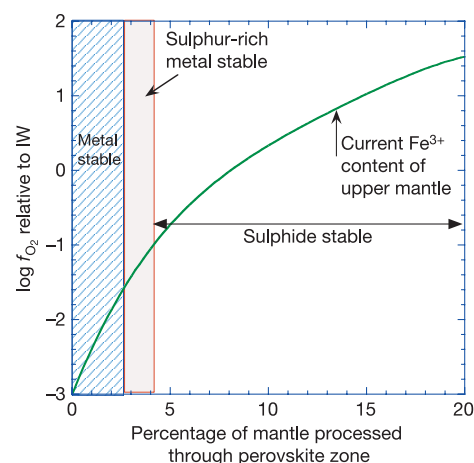

Figure 7 | **Calculated effect of perovskite crystallization on the Fe^{3+} content and hence oxygen fugacity of a magma ocean of peridotite composition.** The calculation began by assuming peridotitic mantle of current composition, containing 8% FeO. Perovskite crystallized from a melt of this composition contains about 3.5% 'FeO' but rather than being entirely ferrous, half of the iron is actually ferric[7,77]. The Fe^{3+} content of the molten mantle increases as perovskite crystallizes, then dissolves, releasing Fe^{3+}, and finally recrystallizes at the base of the magma ocean. This 'processing' of the mantle was converted from Fe^{3+} content to oxygen fugacity using experimental data on silicate melts[78]. Oxygen fugacities are expressed relative to the iron-wüstite (Fe–FeO) buffer.

(0.25%). This means that the core contains about 8 wt% of non-refractory elements and this 8% also corresponds reasonably well to the density deficit of the core compared to pure Fe–Ni alloy under core conditions[45,67].

Because only elements of low atomic number can significantly lower the density of an Fe-rich core, the 'missing' 8% of core mass is generally referred to as the 'light' element. The most likely candidates are low-atomic-number elements that are soluble in Fe and that are cosmically abundant. This leads us to H, O, C, S, P and Si as possible 'light' substituents in the core[68]. Of these, the clearest case can be made for sulphur, which is a strongly siderophile element. Sulphur is moderately volatile (Fig. 1), but is almost two orders of magnitude more depleted in the silicate Earth than an element of similar volatility, zinc (Zn) (Fig. 1). Making the reasonable assumption that this depletion of S relative to Zn in the silicate Earth is due to core formation gives us a core concentration of 1.9 wt% S (refs 26, 29, 69). The same procedure applied to phosphorus leads to about 0.2% of this element in the core[29]. Hydrogen and carbon are two cosmically abundant siderophile elements which are also highly volatile and hence strongly depleted in the Earth. A rough estimate of their core concentrations based on an extrapolation of the volatility trend of Fig. 1 leads to 0.1% and 0.2%, respectively[29]. This leaves the most controversial of the candidates, oxygen and silicon to make up the balance.

The depletion of Si in the silicate Earth relative to the chondritic reference (Fig. 1) is due to an unknown combination of volatility (incomplete accretion) and dissolution in the core. If dissolution in the core were the principal reason then the latter would contain 6–7 wt% Si (refs 26 and 29) and Si would be the major 'light' component. Low-pressure core segregation cannot achieve such high Si concentrations without conditions being much too reducing for the current FeO content of the mantle[70]. Si solubility in liquid Fe increases with both pressure and temperature[6,71], however, such that significant amounts would dissolve at pressures above 20 GPa, even at the current FeO content of the mantle. If we assume that, as discussed earlier (Fig. 4), most of the core formed under slightly more reducing conditions, then the continuous growth and segregation models (Fig. 4) lead to 4–5 wt% Si in the core, which implies that, without making any explicit assumptions about volatility, Si is an important constituent. The oxygen content of the core is more difficult to constrain because the available experimental data conflict with one another. At low pressures and temperatures, oxygen solubility in liquid iron is negligible[72]. All studies show that the effect of temperature is to increase solubility dramatically, however[72,73], so that at low pressures and 2,800 K iron liquid in equilibrium with liquid mantle would contain about 4 wt% oxygen[73].

The main controversy concerns the effect of pressure. Ohtani et al.[74] suggested that the effect of pressure is to increase oxygen solubility in Fe, whereas most recent studies[73,75] have found the opposite effect. If we take the combined effects of temperature and pressure as found by Rubie et al.[73], and apply them to metal–silicate equilibration on the peridotite liquidus, we find oxygen concentrations of up to about 1 wt% in the metal. Lowering of oxygen fugacity during most of accretion decreases the oxygen content of the metal. Thus, if we accept the data indicating that pressure reduces the solubility of oxygen in metallic iron, then the oxygen content of the core should be <1%. This is an area of vigorous current debate, however, and a recent study in the diamond anvil cell[76] found the opposite effect of pressure on oxygen solubility. Furthermore, at approximately the appropriate oxygen fugacity for core–mantle equilibrium, Takafuji et al.[76] found oxygen concentrations in the metal to be about 1.5 times the Si concentrations. Clearly Si is likely to be present at moderate concentrations in the core and oxygen may also be a significant substituent.

Conclusions

Chemical and isotopic measurements on the silicate part of the Earth combined with astronomical observations of young stars and physical models of planetary development lead to a coherent view of the early history of the Earth. The energetics of accretion[45] imply continuous core segregation from a partially molten mantle under conditions that generated the core–mantle partition coefficients of Table 1. The siderophile elements Ni and Co have strongly pressure-dependent partitioning and point towards a mean pressure of core segregation greater than 30 GPa. Partitioning of more highly charged weak siderophiles such as V, Cr, Si and Nb provide better constraints on mean temperature and oxygen fugacity of core formation. Thus, at pressures constrained principally by Ni and Co, these elements point to temperatures 650 K above the peridotite liquidus (Fig. 4). To reduce the required temperature to the liquidus, consistent with the deep magma ocean model (Fig. 3), some part of core formation must have taken place under conditions more reducing than those implied by the current FeO content of the mantle[6] (Fig. 4). Thus, current best estimates of metal–silicate partitioning are consistent with an important component of the 'heterogeneous accretion' model, that oxygen fugacity increased during accretion. The constraints provided by the partitioning data would, however, be stronger if there were more experimental data at pressures above 15 GPa, particularly for the weakly siderophile elements.

Following the demonstration that lower-mantle perovskite forces disproportionation of Fe^{2+} to Fe^{3+} plus iron[7], it has become clear that the Earth's mantle probably 'self-oxidized' during core formation[6]. This means that the increase in oxygen fugacity implied by the metal–silicate partitioning data could be explained as a natural consequence of the Earth having reached a size large enough to stabilize substantial amounts of perovskite in the lower mantle (Fig. 5). The same mechanism could have operated on Venus, to a limited extent on Mars and not at all on the Moon, or any of the asteroids.

Self-oxidation during accretion has also been invoked as the reason for the difference between Hf–W and U–Pb ages of the core[9]. In this hypothesis (Fig. 6), W was partitioned into the core during the early 'reduced' phase of metal segregation while Pb largely remained behind in the mantle. Progressive oxidation means, it is argued[9], that the compositions of liquid metals extracted during the last stages of core formation were sulphur-rich and Pb should partition strongly into such metals. Thus, the Hf–W age of the Earth could reasonably refer to the earliest phases of core formation and the U–Pb age to the last. To test this hypothesis properly it will be necessary to obtain experimental data on the partitioning of Pb between silicates and metals as a function of oxygen fugacity, pressure, temperature and sulphur content.

The density of the liquid outer core is about 8% lower than pure Fe alloy under core conditions, implying the presence of low-atomic-number alloying elements. Cosmochemical arguments suggest that S, H and C are present at concentrations of 1.9, 0.1 and 0.2 wt% respectively. Si is a cosmochemically abundant element which dissolves readily in iron under reducing conditions and at high pressures and temperatures. The accretion model discussed earlier, in which increases in oxygen fugacity accompany core segregation, leads (given a mantle Si content of 21 wt%; refs 3, 26) to 4–5% Si in the core. The remaining potentially important component, oxygen, is more difficult to constrain because the available experimental data conflict with one another. Estimates based on some recently published data[73] lead, under the conditions of core segregation implied by siderophile element partitioning, to <1 wt% oxygen in the core. Other recent data[76] imply that the core should be richer in oxygen than in silicon. Clearly, more experimental data are needed to resolve the question of the oxygen content of the core.

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