



A two-stage scenario for the formation of the Earth's mantle and core

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ABSTRACT

Various geophysical constraints on the deep Earth point to a chemically heterogeneous mantle. Based on such constraints, Bulk Earth compositions inferred from Enstatite chondrites (E-Earth composition) predict that, whereas the Primitive Upper mantle (PUM) had a pyrolitic composition, the Primitive Lower mantle (PLOW) was enriched in Fe and Si. In E-Earth formalism, this chemical heterogeneity is related to the formation and differentiation of the Early Earth, and mantle Si and Fe variations reflect variations in the efficiency of Si and FeO dissolution in the metal phase during core formation. In the simplest scenario of homogeneous accretion, we calculate by mass balance the composition and the mass fraction of the metallic extract in equilibrium with a pyrolite. The O, Si and Ni contents of this metal extract correspond to a silicate-metal equilibrium at high pressure (50 ± 5 GPa) and high temperature (3500 ± 500 °C), in line with a giant impact scenario. Mass balance calculations then yield the composition of the proto-core and the proto-mantle prior to the giant impact. We obtain that the core of the proto-Earth was almost devoid of oxygen, hence formed under lower pressure and temperature conditions, in agreement with an early differentiation of planetesimals in the early solar system. In such a two-stage scenario of Earth's core formation, no massive silicate differentiation is required to create a pristine mantle heterogeneity. The concentration of lithophile elements in the Primitive Lower mantle can then be constrained using RLE ratios in E-chondrites and in the upper mantle.

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1. Introduction

The bulk composition of the Earth, which is related to the conditions of its accretion and differentiation, bears major consequences for its early and present dynamics (e.g., Tackley, 2012). In particular, the existence of a primitive chemical heterogeneity between the upper and lower mantle will exert a strong control on the thermal evolution of the planet and the efficiency of reservoir-mixing through thermo-chemical convection (e.g., Davaille, 1999; McNamara and van Keken, 2000; Tan and Gurnis, 2007; Deschamps et al., 2011).

The composition of the Primitive Upper mantle (PUM) can be inferred solely from the composition of basalts and peridotites (Ringwood, 1975), and eventually be improved by the use of constraints brought by primitive chondrites, such as the ratio of refractory lithophile elements (RLE) (e.g., Jagoutz et al., 1979; Hart and Zindler, 1986; McDonough and Sun, 1995; Lyubetskaya and Korenaga, 2007). The resulting composition defines a theoretical rock, the pyrolite, which allows a reasonable fit of the geophysical constraints of PREM (Preliminary Reference Earth

Model, Dziewonski and Anderson, 1981) to a maximum depth of about 400 km (Cammarano and Romanowicz, 2007). Seismic properties of the pyrolite at higher pressure and temperature would match the PREM velocity profiles only for a *super*-adiabatic geotherm (Matas et al., 2007). However, a chemically homogeneous convective system heated from within has a slightly *sub*-adiabatic thermal profile (Parmentier et al., 1994; Sotin and Labrosse, 1999). Since density and sound velocity experimentally determined in pyrolite at high pressure and high temperature do not match PREM, the composition of the mantle at depth may be significantly different from a pyrolite (Ricolleau et al., 2009; Murakami et al., 2012).

Geophysical methods, particularly seismic tomography, can be used to confirm the existence of chemical heterogeneities in the mantle, and even to give their gross repartition (e.g., Li and Romanowicz, 1996; Ishii and Tromp, 1999; Trampert et al., 2004; Lekic et al., 2012). Recycled MORB (Mid-Oceanic Ridge Basalts) can form stable reservoirs at the base of the mantle (e.g., Samuel and Farnetani, 2003; Xie and Tackley, 2004), but the recent modeling of Deschamps et al. (2012) indicates that they cannot explain low shear-wave velocity provinces. Furthermore, Samuel and Tosi (2012) have shown that the presence of “weak” post-perovskite (ppv) significantly increases mixing efficiency in thermo-chemical convection. Since ppv may appear only in the cold lithospheric plates in

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the D'' layer (Grocholski et al., 2012) and not in the surrounding mantle, this effect may render the MORB reservoir less stable. Noble gases also confirm the presence of an undegassed primitive reservoir at depth (e.g., Moreira et al., 2001; Marty, 2012; Mukhopadhyay, 2012). The existence of a primitive reservoir, enriched in Fe and SiO₂, is then a good way to consistently account for the present day seismic characteristics of the lower mantle (e.g., Kaminsky, 2012; Deschamps et al., 2012; Murakami et al., 2012). However, geophysical methods by themselves are not sufficient to quantify thoroughly the composition of the lower mantle, because of the entangled influence of temperature and composition (Fe, Si content) on seismic properties (Deschamps and Trampert, 2004; Deschamps et al., 2007), or the limited impact on them of some elements (Al, Ca) (Matas et al., 2007).

The “E-Earth” geochemical model of Earth composition of Javoy (1995) and Javoy et al. (2010) proposes that the Earth composition is similar to the bulk composition of a sulfur-free Enstatite chondrite (E-chondrite), based on the isotopic similarities between E-chondrites and the Earth's mantle (e.g., Regelous et al., 2008; Trinquier et al., 2009; Moynier et al., 2010; Gannoun et al., 2011; Warren, 2011). This model uses a pyrolitic composition for the Primitive Upper mantle (PUM) only, and includes additional geophysical constraints on the amount of light elements in the core as well as the results of the ab initio calculations of Alfè et al. (2002). It provides, by mass balance, the composition of the Primitive Lower mantle (PLoM). The composition of the PLoM is characterized by an increase of Fe and Si at depth, as required by seismic data (Deschamps et al., 2012), together with a decrease of Mg, Ca and Al. The resulting decrease of the Mg/Si ratio in the lower mantle is consistent with the PREM inversion performed by Matas et al. (2007).

E-Earth models provide a stringent framework to model the formation and differentiation of the Earth. Javoy (1995) described a simple way to generate the Primitive Upper/Lower mantle differentiation from a single bulk composition, and established the equation governing that differentiation. However, the lack of reliable experimental data at that time on the solubility of key light elements (Si, O, S) in Fe–Ni alloys at very high temperature and pressure did not allow then a definitive test of the model predictions in terms of accretion and differentiation scenarios for the Earth. Such data are now available (Asahara et al., 2007; Corgne et al., 2008; Bouhifd and Jephcoat, 2011; Siebert et al., 2012) and can be incorporated into a complete model of E-Earth formation (e.g., Wade and Wood, 2005). The output of the model can then be confronted to various scenarios which have been proposed for the differentiation of the Earth, such as a chemical evolution of the accreting material in the course of accretion (e.g., Wänke and Dreibus, 1988), or some petrological differentiation between the upper and lower mantle (e.g., Liebske et al., 2005). The aim of this paper is to show that, within the framework of E-chondrite model, it is possible to form the Earth with an accreted material of constant composition, while producing a chemical contrast between the lower and upper mantles through a variation of P,T conditions of metal extraction during the formation of the core. A two-stage scenario, first with a proto-core formed at relatively low pressure and temperature, then a pyrolitic upper mantle resulting from a HP–HT giant impact episode, is shown to be able to account for all the chemical characteristics of the E-Earth.

2. Formation of a pyrolitic upper mantle from an “E-chondrite” bulk Earth

2.1. A model for metal–silicate separation in the E-Earth

The baseline of the E-Earth model is that the bulk composition of its building material corresponds to the composition of a sulfur-free Enstatite chondrite. This means in particular that there

is no (or little) oxidized Fe in the material falling on Earth during accretion, and that an internal iron-oxidation mechanism is required to produce the present day iron content of the Bulk Silicate Earth (Javoy, 1995).

A sulfur-free Earth material composition can be derived from E-chondrite composition by a moderate temperature increase, leading to reactions such as (Javoy et al., 2010)

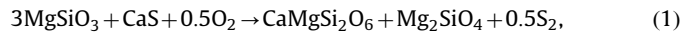


Table 1 gives the sulfur-free bulk composition of the Earth's Building Blocks (EBB) obtained from Javoy et al. (2010), as well as their metal and silicate fractions compared to those of the Primitive Upper mantle (PUM). As noted in Javoy et al. (2010), the model composition of the sulfur-free E-chondrite corresponding to the Earth composition is intermediate between EH chondrites (high Fe content) and EL chondrites (relatively high Mg content). The composition of the EBB silicate phase is different from both the primitive upper (PUM) and lower (PLoM) mantles of Javoy et al. (2010), notably because it is devoid of FeO and too rich in Silica. Hence, the pyrolitic Primitive Upper mantle shall result from the FeO enrichment of the EBB silicate phase through silica reduction by metal Fe and dissolution of the resulting Si into the metal (hereafter metal extract).

Following the approach of Javoy (1995), we consider that the differentiation of the E-Earth can be modeled as the fractionation of the different elements between a silicate phase and a sinking metal extract. An incoming mass flow rate of EBB $(1+f) \, \text{dm}/\text{dt}$ splits into a fraction $f \, \text{dm}/\text{dt}$ of sinking metal and a fraction dm/dt of “floating” silicate. The equation of Javoy is written as

$$\frac{d(mC)}{dt} = C_0(1+f) \frac{dm}{dt} - KCf \frac{dm}{dt}, \quad (3)$$

where C is the concentration of an element in the silicate, C_0 its concentration in the EBB, and K the “effective” silicate/metal partition coefficient of the element. For lithophile elements (Mg, Ca, Al) $K=0$, whereas, for the elements partitioned between metal and silicate (Fe, Ni, Si, O), K will reflect the P,T conditions of metal extraction.

The simplest solution of that differential “filtration” equation is the time-independent steady state solution written as

$$C_\infty = \frac{C_0(1+f)}{1+Kf}, \quad (4)$$

where C_∞ is the concentration of the element in the silicate phase at steady state. In the following, we make the hypothesis that the Primitive Upper mantle results from such a steady state metal extraction, hence, that the concentration C_∞ is the concentration of the element in the pyrolite. Because we do not want to fix a priori the P,T conditions that prevailed during this stage, we apply the minimum a priori constraints on K for Fe, Ni, Si and O: for Ni, Si and Fe, we consider about twice the range of variation allowed

Table 1

Composition (wt%) of the Primitive Upper mantle (PUM) and of the Earth's Building Blocks (EBB) and their metal and silicate phases (from Javoy et al., 2010). The metal phase represents $34.8 \pm 0.51\%$ of the Bulk Earth.

Element	PUM	EBB bulk	EBB silicate	EBB metal
Mg	23.8 ± 0.68	14.7 ± 0.32	23.0 ± 0.54	–
Al	1.90 ± 0.32	0.87 ± 0.19	1.33 ± 0.30	–
Si	21.4 ± 0.51	18.2 ± 0.30	26.5 ± 0.49	1.91 ± 0.83
Ca	2.03 ± 0.34	0.92 ± 0.20	1.42 ± 0.30	–
Fe	6.31 ± 0.41	32.5 ± 0.36	0.44 ± 0.45	92.7 ± 1.08
Ni	0.20 ± 0.02	1.87 ± 0.26	–	5.39 ± 0.74
O	44.4 ± 0.20	30.82 ± 0.24	47.3 ± 0.21	1.99 ± 0.46

in Wade and Wood (2005), i.e., $0 \leq K_{Si} \leq 0.7$, $14 \leq K_{Ni} \leq 40$, and $10 \leq K_{Fe} \leq 15$. We use the same range of variation for O as for Si, i.e., $0 \leq K_O \leq 0.7$. Since the compositions of the pyrolite and EBB are known within error bars, we use a Monte Carlo method to find the steady state solution. Using a uniform probability density function, an EBB composition is randomly chosen within the range of Table 1, and K is randomly chosen in the a priori range for elements that may enter the metal extract (Fe, Si, Ni and O). Combinations yielding element concentrations C_∞ in the silicate phase inconsistent with the PUM composition given in Table 1 are rejected. We randomly sampled one million sets of (K , EBB compositions) among which 7.4% led to a suitable PUM composition.

The resulting composition of the metal extract, as well as its mass fraction, is shown in Fig. 1. The average mass fraction of the metal extract is $38 \pm 2\%$ (i.e., $f \approx 0.61$), whereas the metal represented about 34% of the EBB (Table 1). That increase is due to the metal uptake of Si and O by dissolution at HP–HT. A mass increase of 4% implies a very significant dissolution of Si and O in the metal (as this is in part counter-balanced by the oxidation of metallic Fe which goes into the silicate phase): 12 ± 1.5 wt% of Si and 8.5 ± 2.2 wt% of O (Fig. 1). From these concentrations, it is now possible to constrain the P,T conditions that prevailed during the formation of the pyrolite, using experimentally determined partition coefficients between silicates and metal in the likely hypothesis of metal–silicate equilibration in the magma ocean (e.g., Deguen et al., 2011; Samuel, 2012).

2.2. P,T conditions during the formation of the pyrolitic upper mantle

The partition of Si, Ni and O between silicate and metal is described by a set of three equations

$$\text{SiO}_2^{\text{silicate}} + 2\text{Fe}^{\text{metal}} = 2\text{FeO}^{\text{silicate}} + \text{Si}^{\text{metal}}, \quad (5)$$

$$\text{NiO}^{\text{silicate}} + \text{Fe}^{\text{metal}} = \text{FeO}^{\text{silicate}} + \text{Ni}^{\text{metal}}, \quad (6)$$

$$\text{FeO}^{\text{silicate}} = \text{Fe}^{\text{metal}} + \text{O}^{\text{metal}}, \quad (7)$$

which introduce three distribution coefficients

$$K_d^{\text{Si}} = \frac{X_{\text{Si}}X_{\text{FeO}}^2}{X_{\text{SiO}_2}X_{\text{Fe}}^2}, \quad (8)$$

$$K_d^{\text{Ni}} = \frac{X_{\text{Ni}}X_{\text{FeO}}}{X_{\text{NiO}}X_{\text{Fe}}}, \quad (9)$$

$$K_d^{\text{O}} = \frac{X_{\text{Fe}}X_{\text{O}}}{X_{\text{FeO}}}, \quad (10)$$

where X stands for the mole fractions. As K_d^{Si} and K_d^{Ni} are normalized to iron partitioning, they can be used to compare our results to the experimental data obtained at different oxygen fugacities (e.g., Siebert et al., 2012). Oxygen fugacity may however become important for the comparison of K_d^{O} between various experiments when the metal oxygen content becomes large relative to the IW buffer (e.g., Frost et al., 2008). To allow such a comparison, we estimate the oxygen fugacity as

$$\Delta\text{IW} = 2 \log \left(\frac{X_{\text{FeO}}}{X_{\text{Fe}}} \right), \quad (11)$$

which is a common ideal approximation in the experimental literature (e.g., Chabot et al., 2005).

The f_{O_2} is quite different in the highly reduced E-chondritic material falling on Earth, which contains less than 1 wt% of oxidized Fe (e.g., Rubin, 1983), i.e., $\approx \text{IW}-4$, and in the pyrolite which contains more than 6 wt% of oxidized Fe, i.e., $\text{IW} \approx -2.2$. That difference results from the progressive dissolution of Si in the metal phase through Eq. (5): at first the dissolution of Si in the metal is very efficient (because f_{O_2} is low, which favors Si dissolution, Malavergne et al., 2004), increasing silicate's f_{O_2} until a final equilibrium is reached. The previous calculation corresponds to that final equilibrium.

As shown in Fig. 2, the final f_{O_2} varies between IW-3 and IW-2.5. If the Earth's Building Blocks have the same f_{O_2} as E-chondrite ($\approx \text{IW}-5/\text{IW}-4$), then the f_{O_2} change during the differentiation process is about two log units, in line with the conclusion reached

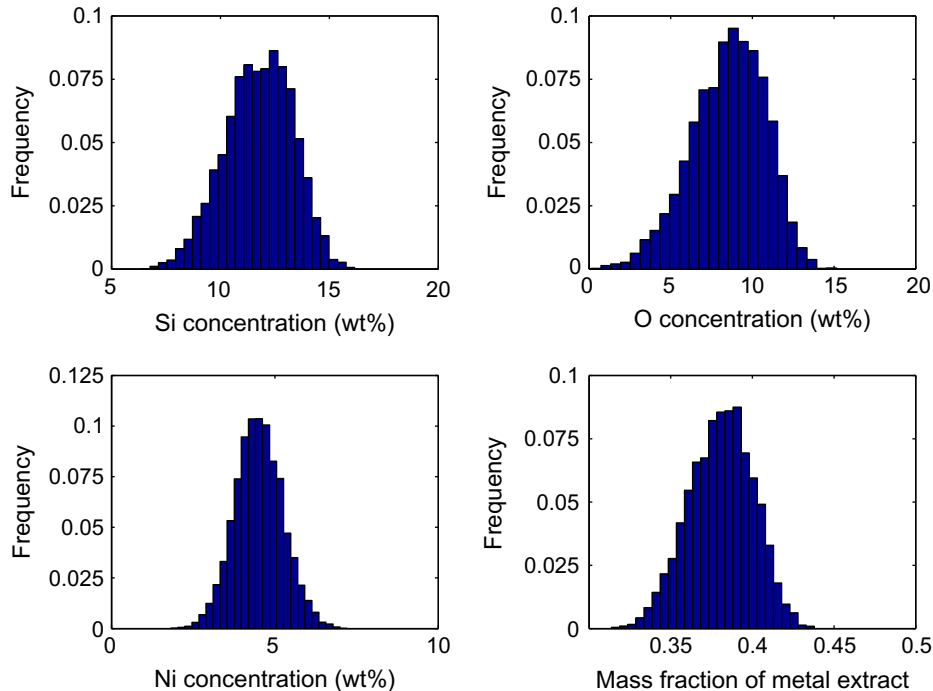


Fig. 1. Composition (in wt%) and mass fraction of the metal extract resulting from the formation of a pyrolite from the E-Earth building material.

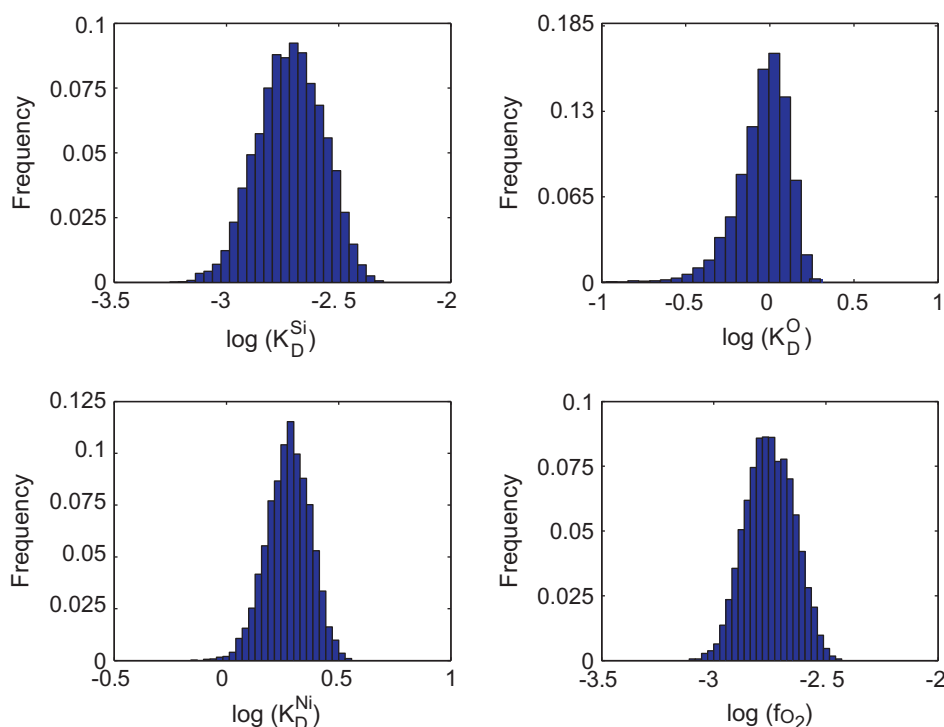


Fig. 2. Repartition coefficients and oxygen fugacity (ΔIW) corresponding to the metal compositions of Fig. 1 and a pyrolitic mantle.

Table 2

Pressure and temperature conditions for the formation of the pyrolitic upper mantle in the framework of the E-chondrite Earth, as inferred from experimental results of Asahara et al. (2007), Corgne et al. (2008), Bouhifd and Jephcoat (2011) and Siebert et al. (2012).

Element	$\log K_d$	Pressure range (GPa)	Temperature range (°C)
O	-0.04 ± 0.15	30–74	2700–4000
Si	-2.71 ± 0.14	40–62	2900–4000
Ni	0.28 ± 0.10	50–60	3000–4000

by Wade and Wood (2005). Furthermore, the final f_{O_2} is either within the range of usual experimental conditions, or close enough to allow the comparison between our predictions and experimental results (Frost et al., 2008). The results of the comparison between the model predictions for O, Si and Ni, shown in Fig. 2, and various HP–HT experiments are summarized in Table 2. They indicate that the equilibrium between the pyrolite and the metal phase occurred at $P=55 \pm 5$ GPa (i.e., at a depth of $\approx 1350 \pm 100$ km) and at $T=3500 \pm 500$ °C which lies within the range of estimates for the liquidus at these depths (Fiquet et al., 2010; Andraut et al., 2011). These conditions are consistent with a deep magma ocean, related itself to the formation of the Moon by a giant impact that induced a large – but not complete – melting of the Earth's mantle (e.g., Cuk and Stewart, 2012). They are also consistent with the most recent estimates of P,T conditions of metal–silicate equilibration in the deep magma ocean based on the experimental data on molybdenum (Burkemper et al., 2012).

The composition of the Primitive Upper mantle formed during the magma ocean episode slightly differs from the composition of the Bulk Silicate Earth in the E-Earth model (Javoy et al., 2010). Similarly, the metal extracted from the Earth-building material during that episode is different from the composition inferred for the present day core in Javoy et al. (2010). This implies that the proto-Earth was already differentiated when the Great Impact and the correlative extraction of the pyrolite occurred, an

hypothesis consistent with the modeling of planetesimal differentiation of Ricard et al. (2009). Since the bulk E-Earth composition is known, it is possible to obtain by mass balance the composition of the proto-core and of the proto-mantle, hence to characterize the first stage of core formation.

3. The first stage of core formation in the proto-Earth

3.1. Composition of the proto-core and of the proto-mantle

For the description of the earlier stage of differentiation (i.e., prior to the magma ocean), we shall consider again the simplest hypothesis, which is that of homogeneous accretion. The difference in composition between the proto-core and the present day core is then simply related to variable P,T conditions for Si and O dissolution in the metal.

To obtain the composition of the proto-core, we first need to know the metal mass extracted during the magma ocean episode. We have seen above that the pyrolitic upper mantle was extended down to ≈ 1350 km. Hence, it represented $\approx 44\%$ of the volume of the present-day mantle, that is $\approx 30\%$ of the mass of the Earth. Knowing the mass fraction of the metal extract and its composition (Fig. 1), it is straightforward to deduce the composition of the proto-core by mass balance between the present-day core as given in Javoy et al. (2010) and the metal extract. Rejecting cases giving negative concentrations in the proto-core, we obtain the results shown in Fig. 3.

The proto-core, a little less than 50% of the mass of the present day core, contained about half as much Si as the metal extracted at high pressure and temperature during the magma ocean episode, and much less Oxygen. This indicates a formation at lower temperature and pressure. To determine more precisely these conditions, one needs to calculate the metal–silicate partition coefficients for Si, O and Ni as in the previous section, hence to determine first the composition of the proto-mantle.

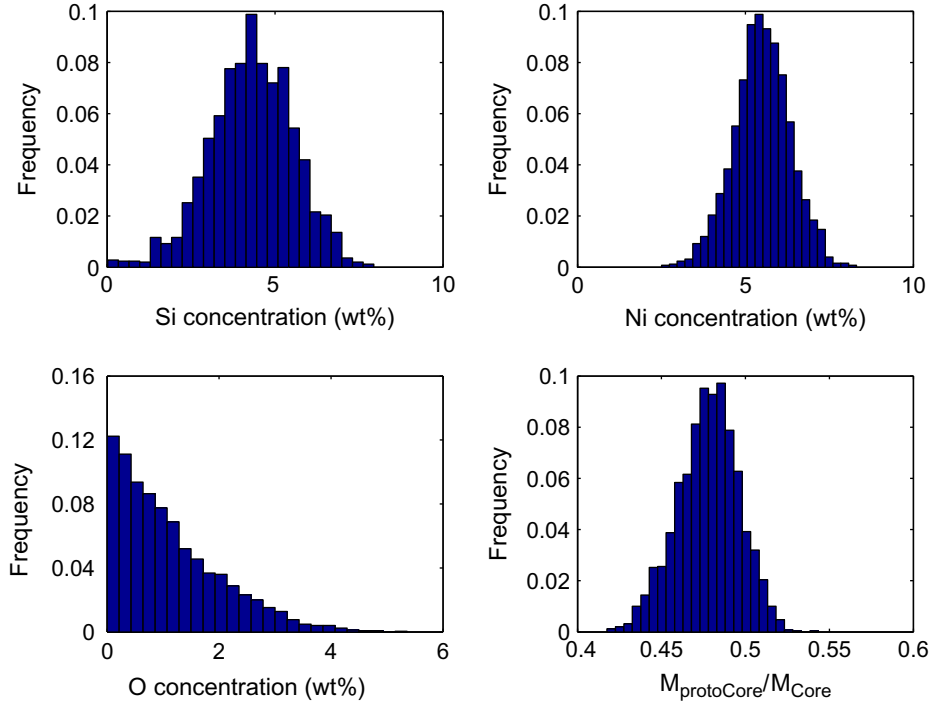


Fig. 3. Composition (in wt%) and mass (as fraction of the present day core) of the Earth's proto-core. The concentrations of Si and O in the proto-core are much smaller than in the metal extracted during the magma ocean episode.

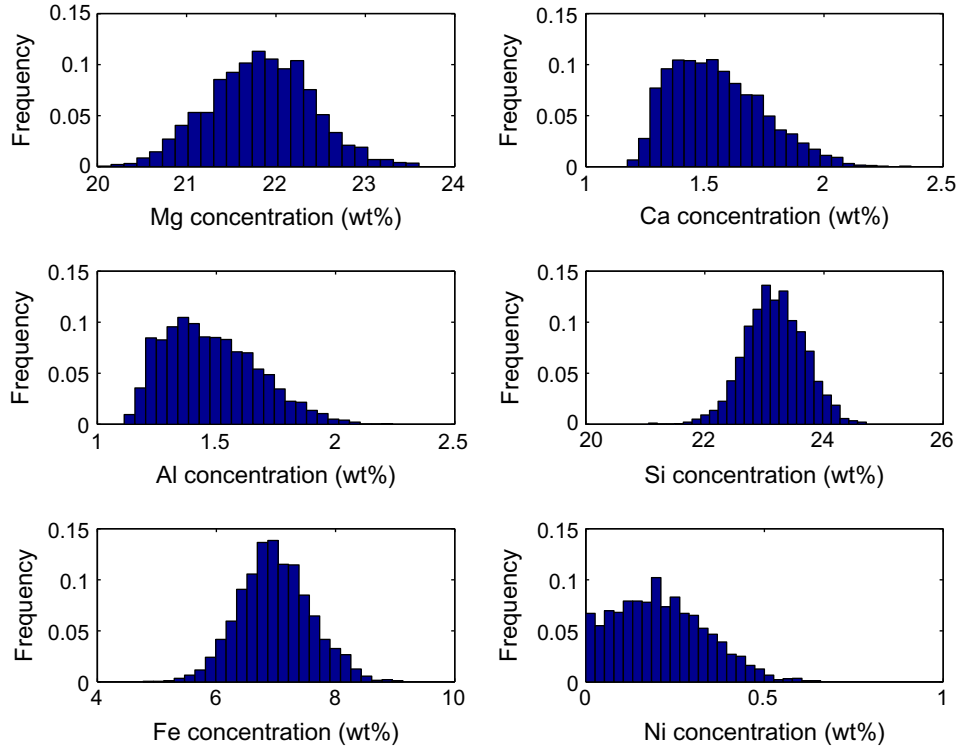


Fig. 4. Composition (in wt%) of the Earth's proto-mantle obtained by mass balance. The proto-mantle is enriched in Si and Fe relative to a pyrolitic composition, and is Mg poor, as predicted by the E-Earth formalism.

The composition of the proto-mantle is calculated by mass balance between the pyrolitic upper mantle and the Bulk Silicate Earth of Javoy et al. (2010), using the previously inferred vertical extent of the pyrolitic upper mantle (≈ 1350 km). This yields the compositions shown in Fig. 4. The proto-mantle is enriched in Si and Fe relative to the pyrolite, and poorer in Mg, and is consistent

with the chemical composition of the Primitive Lower mantle (PLoM) of Javoy et al. (2010). This result demonstrates that the present day chemical heterogeneity of the mantle can be related to the variation of thermodynamic conditions during Earth differentiation, and does not require an evolution of the chemical composition of the accreting material.

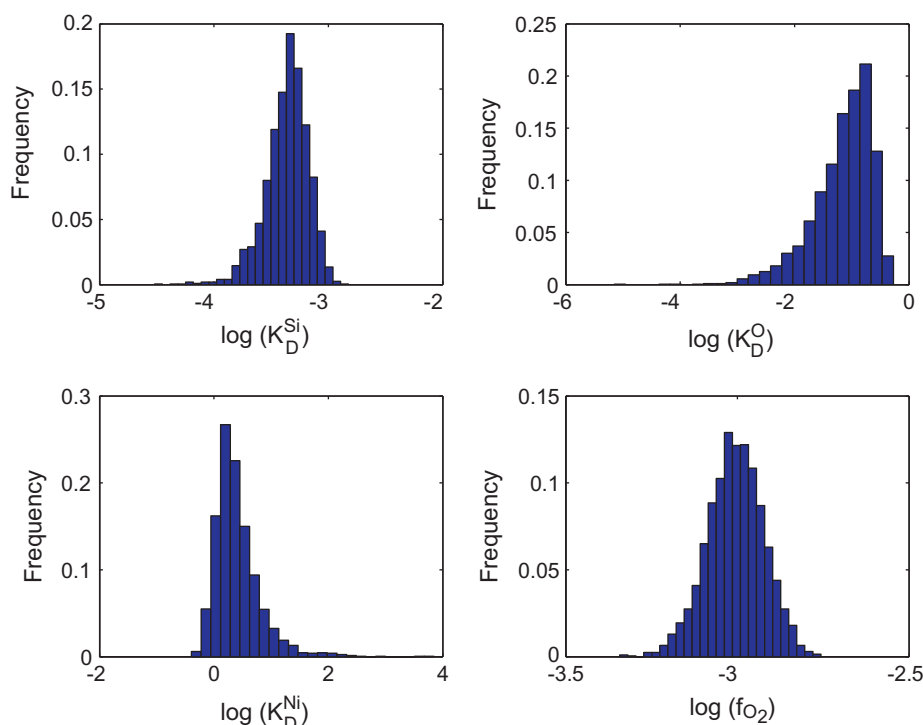


Fig. 5. Repartition coefficients and oxygen fugacity (ΔIW) corresponding to the equilibrium between the proto-core and the proto-mantle of the E-Earth.

Table 3

Pressure and temperature conditions for the formation of the proto-core in the framework of the E-chondrite Earth, as inferred from experimental results of Mann et al. (2009) and Bouhifd and Jephcoat (2011).

Element	$\log K_d$	Pressure range (GPa)	Temperature range (°C)
O	-1.16 ± 0.53	≤ 20	≤ 2600
Si	-3.36 ± 0.19	15–30	2500–2700
Ni	0.41 ± 0.40	≥ 20	≥ 2500

3.2. Pressure and temperature conditions during the formation of the proto-core

Once the compositions of the proto-core and of the proto-mantle are known, it is possible to calculate the repartition coefficients K_d^{Si} , K_d^{Ni} and K_d^{O} , as well as the oxygen fugacity relative to IW, using the formulae given in Section 2.2. The results given in Fig. 5 can be used in turn to infer the pressure and temperature during the formation of the proto-core by comparison with the experimental data. The comparison, summarized in Table 3, allows a tight determination: $P \approx 20$ GPa and $T \approx 2550$ °C. This result is consistent with a first stage of differentiation in small planetesimals, occurring at relatively low pressure and temperature (Ricard et al., 2009).

4. Discussion

4.1. A refined composition for the E-Earth

The two-stage scenario of core formation described in the previous sections is summarized in Fig. 6. In this scenario of homogeneous accretion, the chemical difference between the Primitive Upper mantle (PUM) and the Primitive Lower mantle (PLOM) is linked to the change in P,T conditions of metal extraction after the giant impact. This pristine heterogeneity can

still be detected today by geophysical methods because of the relatively low efficiency of reservoir mixing in thermo-chemical convection (Deschamps et al., 2011). The consistency between the two-stage scenario for core formation and the main chemical characteristics of the E-Earth can be used in turn to refine the Earth composition.

It can be seen in Figs. 5 and 3 that the Ni content of the proto-core is not well constrained. This is related to a relatively general lack of constraints for this element in the lower mantle, and to the variable Ni concentration in E-chondrites (e.g., 1.3–1.8 wt%, Zhang et al., 1995). Since the proto-core composition is obtained by mass balance, the precision of the determination of its Ni content reflects directly the propagation of those uncertainties. However, the P,T conditions of the proto-core, obtained using O and Si, imply that the Ni partition coefficient was larger than 0.7 (Chabot et al., 2005). This additional constraint can be used to reject all bulk Earth compositions yielding a smaller coefficient, hence to refine the Ni concentration of the proto-core and of the proto-mantle.

A second kind of argument, linked to the Lithophile Elements, can be used to further refine the composition of the silicate Earth. In the present model the higher Si and Fe contents in the deep mantle (and the associated lower Mg content), closer to the EBB, are due to the lower PT conditions during the formation of the proto-core, which corresponded to a lesser Si and O uptake by the metal extract. Because Mg, Ca and Al do not enter the metal, their relative contents are not affected by this change in P,T conditions. Hence, the Al/Mg and Ca/Mg ratios of the Primitive Lower mantle should be the same as the ratios in the Primitive Upper mantle, which allows a better determination of the Ca and Al contents of the lower mantle, which were not well resolved in Javoy et al. (2010) due to the small sensitivity of PREM inversion to Ca and Al contents (Matas et al., 2007).

We give in Table 4 the refined estimates resulting from the filtering described above, for the compositions of the three main Earth's envelopes in the E-chondrite formalism: the Primitive Upper mantle, extending down to 1350 km, the Primitive Lower

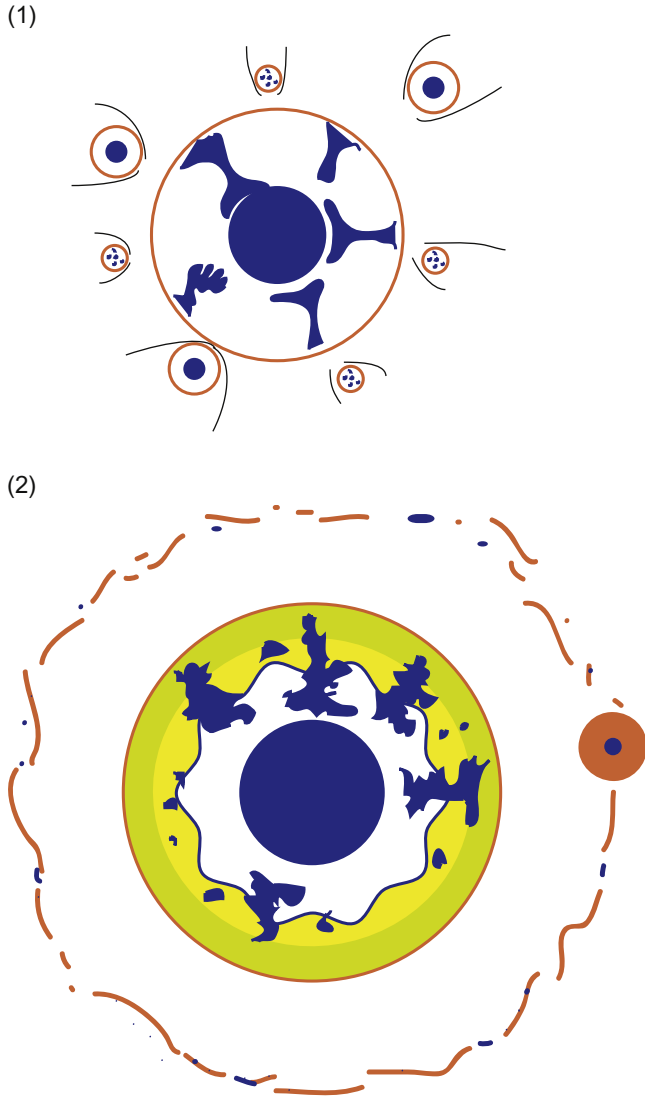


Fig. 6. Schematic summary of the two-stage scenario for core formation. (1) the first stage corresponds to the formation of the proto-core by low P,T metal extraction from the E-chondritic accreted material, which produced the Primitive Lower mantle (PLoM). In dark blue the metallic core of the planetesimals and/or the metallic phase of the undifferentiated impactors is represented. (2) the second stage corresponds to the formation of the pyrolitic Primitive Upper mantle (in green if molten, in yellow if crystallized) by high P,T metal extraction associated with the giant impact. The composition of the core results from the merging of this metal extract (in dark blue) with the proto-core. In this scenario, the composition of the proto-mantle (in white) remains largely unaffected by the second stage of core formation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4
Composition (wt%) of Primitive Upper mantle (PUM), Primitive Lower mantle (PLoM), Earth's core, and bulk Earth composition. The PUM represents about 44% of the Bulk Silicate Earth.

Element	PUM	PLoM	Core	Earth
Mg	23.3 ± 0.13	20.4 ± 0.14	–	14.6 ± 0.07
Al	1.79 ± 0.09	1.57 ± 0.09	–	1.13 ± 0.05
Si	21.8 ± 0.15	24.2 ± 0.14	6.89 ± 0.27	18.0 ± 0.11
Ca	1.83 ± 0.08	1.61 ± 0.08	–	1.15 ± 0.05
Fe	6.59 ± 0.18	7.02 ± 0.24	85.5 ± 0.71	32.3 ± 0.25
Ni	0.20 ± 0.01	0.11 ± 0.03	5.43 ± 0.67	1.86 ± 0.22
O	44.5 ± 0.07	45.1 ± 0.09	2.19 ± 0.30	31.0 ± 0.11

mantle (which is here also the proto-mantle), and the Core. The compositions fall within the range of E-Earth compositions of Javoy et al. (2010), but the average Mg content of the PLoM is slightly higher and the Al and Ca contents slightly lower. This is due to the constant Mg/Al and Mg/Ca ratios in PUM and PLoM. The Ni amount in PLoM is also more tightly constrained by the filtering on K_d^{Ni} in the proto-core. These are minor improvements, which do not change the conclusions of Javoy et al. (2010) concerning for example a lower heat production in the E-Earth's mantle relative to CI-based Earth composition (Dye, 2010).

4.2. A refined link between Earth and E-chondrite material

4.2.1. Chemistry

In the present framework of homogeneous accretion, it is likely that the Earth can be linked to a precise E-chondrite type or E-chondrite mixture. Because the composition of the Earth corresponds to the composition of a sulfur-free E-chondrite, it is practical to use ratios of element concentrations to track the relationship between the Earth and the E-chondrites. We compare in Fig. 7 the location of E-Earth relative to known EH and EL chondrites in a Mg/Ca vs Fe/Al diagram. The E-Earth plots in a “focal” zone close to the center of the most primitive E-chondrites (E3 type). This suggests a genetic link between EH3 and/or EL3 chondrites and the Earth. To confirm that point, we use Mg/Si ratios, which are known to evolve significantly between EH and EL chondrites (Wasson and Kallemeyn, 1988).

There has been no systematic determination of the Mg/Si ratios in EH3 and EL3 chondrites (mostly because data are dominantly from Instrumental Neutron Activation Analysis), but it is possible to calculate them when the modal abundance and composition of minerals containing Mg and/or Si (quartz, olivine, enstatite, plagioclase, niningerite) are given. Using the petrologic study of E3 chondrites from Antarctica by Weisberg et al. (1995), and the mineral compositions of Keil (1968), Zhang et al. (1995) and Weisberg et al. (2011), we estimate the range of variations of the Mg/Si ratios in EL3 and EH3 chondrites, and compare it with the Mg/Si ratio in the E-Earth. The result shown in Fig. 8

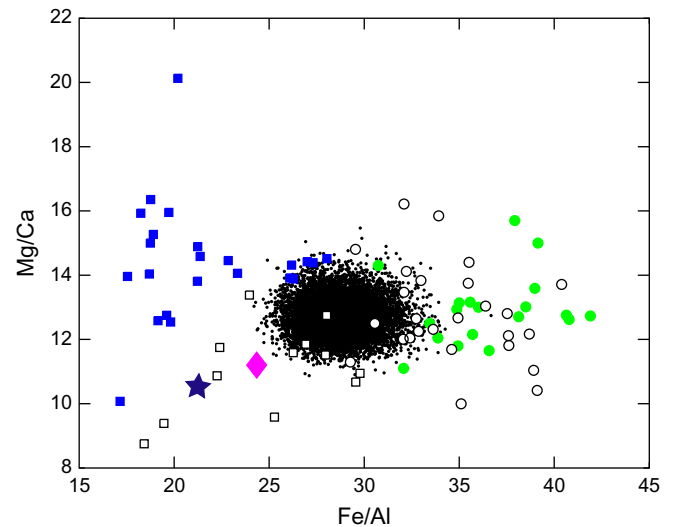


Fig. 7. Location of E-Earth compositions (black dots) relative to EH and EL chondrites (EH3, white circles; EH4-5, green circles; EL3, white squares; EL4-5-6, blue squares). The pink diamond corresponds to an average H chondrite, and the star corresponds to the CI chondrite (Wasson and Kallemeyn, 1988). EH and EL data are from Baedeker and Wasson (1975), Weeks and Sears (1985), Kallemeyn and Wasson (1986), Zhang et al. (1995), Kong et al. (1997) and Rubin et al. (2009). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

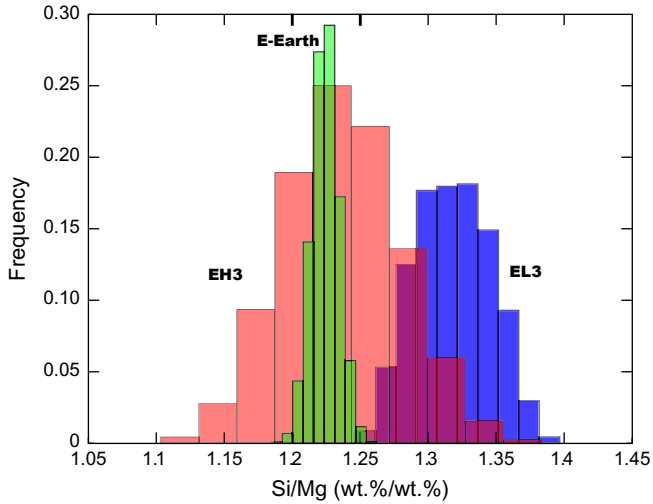


Fig. 8. Comparison between Si/Mg ratios in EH3 (red bars) and EL3 (blue bars) chondrites and in the Bulk E-Earth (green bars). Si/Mg in E3 chondrites has been calculated using the modal abundances given by Weisberg et al. (1995). The parenthood between E-Earth and EH3, as suggested in Fig. 7, is confirmed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

illustrates the continuity between EH3 and EL3 chondrites found also for their Fe/Mg ratio (Rubin et al., 2009), and a closer relationship between EH3 chondrites and E-Earth.

4.2.2. Isotopes

The close isotopic relationship between Earth and E3 chondrites does not imply that E3 was as such as the Building Blocks of the Earth. For example, E-chondrites contain much more sulfur than the Earth (4.5–6 wt% for E3 type, Weisberg and Kimura, 2012). Isotopic proximity does not mean full identity either. For example, the silicon of E-chondrites is isotopically lighter, by about -0.3‰ , than the Earth's mantle (e.g., Armitage et al., 2011; Fitoussi and Bourdon, 2012; Savage and Moynier, 2013).

Isotopic equilibration is the simplest way to account for a multi-elemental isotopic coincidence such as that observed between the Earth's Mantle and E-chondrites. That coincidence is limited by the variation of isotope fractionation with temperature, and is all the more perfect that fractionation is small at a given temperature. For example, whereas the difference between EC and Earth tends to zero for Strontium (Moynier et al., 2010) and Calcium (Huang and Jacobsen, 2012), it is significant for Si because the two gaseous species SiS and SiO show a large fractionation with silicates, from 4‰ to 5‰ at 1000 K (Javoy et al., 2011). Hence, both the difference in Si isotopic composition between E-chondrites and the Earth and their different S content probably correspond to a different temperature of equilibrium in the same Nebula (and to a related difference in their degree of silicon condensation). The isotopic equilibrium relationships in the Nebula for a given element (bulk equilibrium or Rayleigh distillation) are respectively:

$$\delta_N = \delta_{EC} + [1 - f(T_{EC})] \Delta(T_{EC}) = \delta_{EBB} + [1 - f(T_{EBB})] \Delta(T_{EBB}), \quad (12)$$

$$\begin{aligned} \delta_N &= \delta_{EC} - [1 - f(T_{EC})] \frac{\ln[1 - f(T_{EC})]}{f(T_{EC})} \Delta(T_{EC}) \\ &= \delta_{EBB} - [1 - f(T_{EBB})] \frac{\ln[1 - f(T_{EBB})]}{f(T_{EBB})} \Delta(T_{EBB}). \end{aligned} \quad (13)$$

where δ are isotopic compositions, $f(T)$ are condensed fractions, $\Delta(T)$ are the equilibrium fractionation between gas and silicates, and the indices N , EC and EBB refer to Nebula, EC and Earth's Building Blocks, respectively. In the hypothesis of nearly total

condensation of Si in Enstatite chondrites ($f_{EC} \approx 1$) (Hutson and Ruzicka, 2000), the isotopic composition of EC is identical to the nebular composition, and the isotopic difference ($\delta_{EC} - \delta_{EBB}$) is a function of f_{EBB} and T_{EBB} only. Taking into account the effect of metal extraction at 3300 K during the magma ocean episode, with an associated dissolution of $\approx 12 \text{ wt\%}$ of Si in metal, and the available metal–silicate isotopic fractionation (Ziegler et al., 2010) the ^{30}Si composition of PUM relative to EBB should be $\approx 0.15\text{‰}$ heavier. Taking ($\delta_{EC} - \delta_{PUM}$) $\approx 0.31\text{‰}$ (e.g., Armitage et al., 2011) thus yields ($\delta_{EC} - \delta_{EBB}$) $\approx 0.16\text{‰}$. We illustrate in Fig. 9 the likely relationship between the Si fraction condensed in EBB and the equilibration temperature in the Nebula to account for this “residual” difference with $\Delta(T) = -5.27 \cdot 10^6 / T^2$ from Javoy et al. (2011). For example, silicon is condensed to $\approx 96.5\%$ in the Earth Building Blocks at 1150 K. That temperature is $\approx 200 \text{ K}$ higher than the temperature derived by Hutson and Ruzicka (2000) from the silicate–gas equilibrium in E-chondrites, and well above the temperature they obtain for sulfur condensation. This suggest that E-chondrites may correspond to the sulfuration of remnants of Earth's building material at a lower temperature, during outward migration towards the asteroid belt (Walsh et al., 2011).

A similar calculation could be performed from the Chromium isotopic difference between the Earth's mantle and E-chondrites when more data are obtained (presently only one analysis for EC, Moynier et al., 2011) and when the condensation of Chromium in the Nebula is quantitatively modeled.

4.3. Comparison with models of heterogeneous accretion

Schönbächler et al. (2010) propose a model of heterogeneous accretion, based on the palladium–silver isotopic compositions of CI chondrites, in which the volatile content of the impactors increases in the course of accretion. A first stage corresponds to the accretion of $\approx 86\%$ of volatile-depleted material, followed by the accretion of $\approx 13\%$ of a material with the volatile content of a CV3, and 1% of late veneer with a higher Pb/Ag ratio. The first stage of this model is consistent with our present model's framework in which Earth Building Blocks are considered as sulfur-free (more generally volatile-free) E-chondrites. We do not exclude that later stages of accretion involved more volatile-rich material, as long as this material keeps a constant composition in terms of refractory and transitional elements. Its volatile content could be simply closer to the composition of “regular” E3 chondrites, which are indeed very rich in volatile. The accretion of

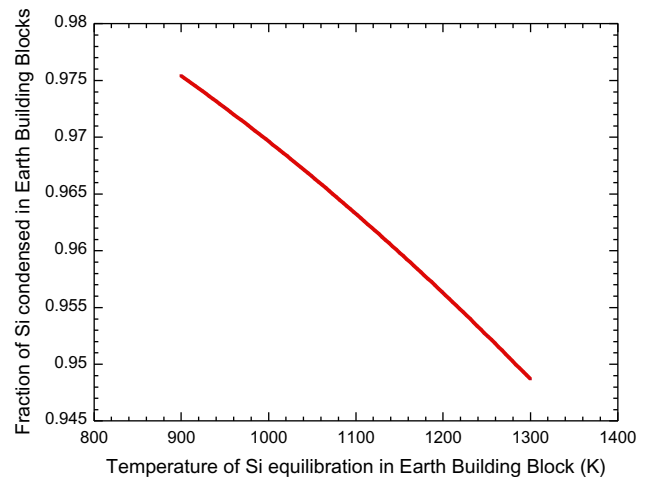


Fig. 9. Prediction of the degree of condensation of Si (f_{Si}) in Earth Building Blocks (EBB), as a function of the condensation temperature in the Nebula, corresponding to a $\delta^{30}\text{Si}$ anomaly of -0.16‰ between Enstatite chondrites (EC) and EBB.

raw E3-type material would not change the predictions of our model for the Earth's envelopes major elements and the P,T conditions for the two stages of Core forming metal extraction, but would be a consistent way to bring some sulfur into the Earth. S is more depleted in the Earth's mantle relative to Zn than in CI and E-chondrites (Dreibus and Palme, 1996), which can be taken as an argument of the incorporation of S into the core. However, as noted by Dreibus and Palme (1996) from S/Zn considerations, it is possible that the “missing” sulfur was never accreted in the Earth. In such a case, the amount of S in the core could be much smaller than the upper bound of 1.7 wt% estimate of Dreibus and Palme (1996). The addition of a maximum 2 wt% of S into the core would increase the total amount of light elements to about 11 wt% in the model, which remains below the upper limit compatible with seismic constraints. Because S does not enter Eqs. (5)–(7) used to calculate the Si and O content of the core and the FeO and SiO₂ content of the mantle, its amount in the lower mantle or in the core is not presently constrained. Anyway, the S content of the core does not change the conclusions of our model. Better constraints will come from quantitative estimates of the contribution of the volatile-rich material, which would require a reassessment of the model of Schönbachler et al. (2010) using the isotopic compositions of E-chondrites rather than those of CI-chondrites (which are ruled out as Earth building material from isotopic arguments, e.g., Warren, 2011).

A model of heterogeneous accretion has been proposed by Rubie et al. (2011) using several metal–silicate partition coefficients for siderophile and moderately siderophile elements. These authors conclude that the best fit to an Earth's homogeneous mantle composition is obtained with models of multi-stage core-formation involving about 60–70% of reduced material at the beginning of the accretion, and 30–40% of more oxidized material at the end of the process. These results are however mainly based on high *P* and *T* extrapolations of experimental data obtained at pressures smaller than 23 GPa and temperatures smaller than 2800 K. The uncertainties linked to that process can affect the robustness of the conclusion, and may account for the rather different conclusion reached by Righter (2011) based on a similar set of elements. Furthermore, this model of heterogeneous accretion considers a *homogeneous* mantle composition, and is based on CI-chondritic abundances of non-volatile elements. That clearly prevents this approach to provide a consistent test of the E-Earth model. Hence, even if Rubie et al. (2011) show that homogeneous accretion of a CI-parented material cannot account for the composition of a supposedly homogeneous mantle, that conclusion does not invalidate our conclusion that homogeneous accretion of EC-like material can lead to a heterogeneous mantle composition.

We have shown in this paper that a two-stage homogeneous accretion of sulfur-free E-chondrites provides a consistent scenario of Earth differentiation accounting for both the composition of the core and the heterogeneous composition of the mantle, without requiring a massive silicate differentiation following the episode of magma ocean. This result is consistent with the conclusions of Liebske et al. (2005) that the maximum extent of a fractionated crystal pile generated during the cooling of the magma ocean – and with a distinct chemical composition from the upper mantle – could not represent more than 13 wt% of the mantle. Cosmochemical analyses and mass balance calculations by Carlson and Boyet (2008) based on ¹⁴²Nd compositions of Earth and CI chondrites conclude that the hidden reservoir may attain the size of the D layer (≈ 4% of the Mantle). As E-chondrites are closer to the Earth's Upper Mantle in terms of ¹⁴²Nd compositions (Gannoun et al., 2011) they will yield an even smaller reservoir, possibly as small as the patchy ultra-low velocity zones (ULVZ) detected at the core mantle boundary. The generation of such a reservoir (and its preservation, Touboul et al., 2012) has important implications for

the dynamics of the present and Early Earth, but is probably not related to the massive differentiation of the Earth into a core and a chemically heterogeneous mantle.

5. Conclusion

The E-Earth model, based on the isotopic similarities between the Earth and E-chondrites, provides a consistent framework to test scenarios for the accretion and differentiation of the Earth. Using a combination of mass balances and experimentally determined repartition coefficients for Si, O and Ni between silicates and metal, we show that the homogeneous accretion of building material akin to sulfur-free EH3 chondrites accounts for the present day composition of the mantle and core. The chemical heterogeneity between the upper and lower mantles essentially reflects the evolution of P,T conditions during the segregation of the Earth's core. The first stage of metal extraction occurred at relatively low temperature and pressure (≈ 20 GPa, 2550 K) in the proto-Earth or/and its planetary precursors, and resulted in a proto-core less Si and O-rich than the present day core. The giant impact episode induced latter melting of about 44% of the mantle, concurrent with an efficient HP–HT dissolution of Si and O in the metal, extracted down to the Earth's core, and leading to its present composition. The pyroclitic upper mantle today contains less Si and less FeO than the lower mantle due to the variation in the efficiency of Si and FeO extraction from the two mantles during the two stages of core formation. The differentiation of the Earth might have been more complicated and more continuous than the simple two-stage scenario presented here. This simple model is however a first step towards more complete studies of Earth formation, which shall use additional minor elements (Righter, 2011) and incorporate a more detailed modeling of temperature and pressure evolution in the Earth during the course of accretion.

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