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## Heterogeneous accretion, composition and core–mantle differentiation of the Earth

David C. Rubie<sup>a,\*</sup>, Daniel J. Frost<sup>a</sup>, Ute Mann<sup>b</sup>, Yuki Asahara<sup>c</sup>, Francis Nimmo<sup>d</sup>, Kyusei Tsuno<sup>a,1</sup>, Philip Kegler<sup>e</sup>, Astrid Holzheid<sup>e</sup>, Herbert Palme<sup>f</sup><sup>a</sup> Bayerisches Geoinstitut, University of Bayreuth, D-95444 Bayreuth, Germany<sup>b</sup> Institut für Mineralogie und Petrographie, ETH Zürich, CH-8092 Zürich, Switzerland<sup>c</sup> Department of Earth and Space Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka-shi, Osaka 560-0043, Japan<sup>d</sup> Department of Earth and Planetary Sciences, University of California Santa Cruz, Santa Cruz, CA 95064, USA<sup>e</sup> Institut für Geowissenschaften, Universität Kiel, D-24098 Kiel, Germany<sup>f</sup> Forschungsinstitut und Naturmuseum Senckenberg, Senckenberganlage 25, D-60325 Frankfurt am Main, Germany

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## ABSTRACT

A model of core formation is presented that involves the Earth accreting heterogeneously through a series of impacts with smaller differentiated bodies. Each collision results in the impactor's metallic core reacting with a magma ocean before merging with the Earth's proto-core. The bulk compositions of accreting planetesimals are represented by average solar system abundances of non-volatile elements (i.e. CI-chondritic), with 22% enhancement of refractory elements and oxygen contents that are defined mainly by the Fe metal/FeO silicate ratio. Based on an anhydrous bulk chemistry, the compositions of coexisting core-forming metallic liquid and peridotitic silicate liquid are calculated by mass balance using experimentally-determined metal/silicate partition coefficients for the elements Fe, Si, O, Ni, Co, W, Nb, V, Ta and Cr. Oxygen fugacity is fixed by the partitioning of Fe between metal and silicate and depends on temperature, pressure and the oxygen content of the starting composition. Model parameters are determined by fitting the calculated mantle composition to the primitive mantle composition using least squares minimization. Models that involve homogeneous accretion or single-stage core formation do not provide acceptable fits. In the most successful models, involving 24 impacting bodies, the initial 60–70% (by mass) of the Earth accretes from highly-reduced material with the final 30–40% of accreted mass being more oxidised, which is consistent with results of dynamical accretion simulations. In order to obtain satisfactory fits for Ni, Co and W, it is required that the larger (and later) impactor cores fail to equilibrate completely before merging with the Earth's proto-core, as proposed previously on the basis of Hf–W isotopic studies. Estimated equilibration conditions may be consistent with magma oceans extending to the core–mantle boundary, thus making core formation extremely efficient. The model enables the compositional evolution of the Earth's mantle and core to be predicted throughout the course of accretion. The results are consistent with the late accretion of the Earth's water inventory, possibly with a late veneer after core formation was complete. Finally, the core is predicted to contain ~5 wt.% Ni, ~8 wt.% Si, ~2 wt.% S and ~0.5 wt.% O.

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## 1. Introduction

Early differentiation of the Earth involved the separation of Fe-rich metal from silicate material to form the core and mantle. High temperatures were necessary and differentiation likely occurred in response to large-scale melting, induced by high-energy impacts that resulted in one or more deep magma oceans (e.g. Rubie et al., 2007; Stevenson, 1990). Evidence for the pressure–temperature (*P–T*) conditions of metal–silicate segregation is provided by the concentrations of the siderophile (“metal-loving”) elements that remained in the

Earth's mantle, combined with experimental data on the partitioning of such elements between Fe metal and silicate liquid. Traditionally, *P–T* conditions at which experimental partitioning data are consistent with mantle and (assumed) core concentrations have been considered to indicate magma ocean depth (Rubie et al., 2007). However, in view of current models of Earth accretion (Agnor et al., 1999; Chambers and Wetherill, 1998; O'Brien et al., 2006), the quest to determine a unique set of *P–T–f*<sub>O<sub>2</sub></sub> conditions is unrealistic and magma ocean depths derived from such a “single-stage” model represent, at best, the averaged cumulative effects of a much more complex differentiation history (Frost et al., 2008; Wade and Wood, 2005; Wood et al., 2008). Because Earth's accretion history was dominated by tens of high-energy collisions with Moon- to Mars-sized bodies (O'Brien et al., 2006), core formation must be considered as a multistage process, involving one or a series of magma oceans, rather

\* Corresponding author. Tel.: +49 921 553711; fax: +49 921 553769.

E-mail address: [dave.rubie@uni-bayreuth.de](mailto:dave.rubie@uni-bayreuth.de) (D.C. Rubie).<sup>1</sup> Now at: Department of Earth Science, Rice University, 6100 Main Street, MS-126, Houston, TX 77005, USA.

than a single-stage process. A series of magma oceans is likely if the crystallisation time for the bulk of a deep magma ocean is short, i.e. on the order of  $10^3$  years (Solomatov, 2000).

Our aim here is to combine a simplified accretion model with a geochemical model for early differentiation of the Earth. We adopt a new approach that combines element partitioning with a rigorous mass balance that is based on the bulk composition of the accreting material. The model utilizes results of recent high-pressure metal–silicate partitioning experiments for the elements: Fe, Si, O, Ni, Co, W, Nb, V, Ta and Cr, which are chosen based on the availability of high-quality partitioning data obtained to at least 23–25 GPa (Cottrell et al., 2009, 2010; Frost et al., 2010; Kegler et al., 2008; Mann et al., 2009; Wade and Wood, 2005).

## 2. Bulk composition and mass balance

In order to determine the geochemical consequences of metal–silicate equilibration during core formation in the Earth, we calculate the compositions of chemically-equilibrated silicate and metallic liquids at high  $P$  and  $T$  after each impact. The calculations are based on mass balance for defined bulk compositions combined with element partitioning data.

### 2.1. Bulk composition and degree of oxidation of accreting embryos

Accreting bodies are assumed to have solar system (i.e. CI chondritic) element ratios for the elements: Si, Fe, Mg, Ni, Cr and Co, with enhanced abundances of the refractory elements Ca, Al, V, Nb, W and Ta relative to CI. The three elements Mg, Ca and Al are stable only as oxide components, whereas Fe, Si, Ni, Cr, Co, V, Nb, W and Ta may be present as oxide and metal components and thus partition between metal and silicate. As described below, the bulk compositions used in our calculations (a) are anhydrous and do not include volatile elements (apart from oxygen) and (b) are enriched in refractory elements relative to CI element abundances.

#### 2.1.1. Volatile elements

A critical question for core formation concerns the possible presence of volatile components during accretion because  $H_2O$  and C, in particular, could strongly affect oxygen fugacity and therefore the partitioning behavior of siderophile elements. We argue that the absence of volatile elements in our model is justified because (a) the initial volatile element inventory of Earth-forming embryos was low and (b) volatiles were added late in the accretion sequence. Meteorites such as Allende are depleted in volatile elements (including S) relative to CI chondrites. They contain essentially no water and also have very low carbon contents (Jarosewich, 1990). The abundance patterns of both moderately (Na, Mn, S, Zn etc.) and highly volatile elements (Pb, C, N etc.) in the bulk Earth are similar to those in CV-chondrites but with absolute concentrations that are even lower (Fig. 5 in McDonough, 2003). As there is no isotopic mass fractionation accompanying the depletions (e.g. Humayun and Clayton, 1995) volatile depletion is probably a consequence of incomplete condensation at high temperatures in the inner part of the solar nebula (Albarède, 2009; Humayun and Cassen, 2000; Palme et al., 1988).

From the work of Mann et al. (2009), there is strong evidence that the accretion of moderately volatile elements to the Earth occurred largely during the late stages of accretion but before core formation was complete. The Mn/Ga ratio is approximately chondritic in the present Earth's mantle, although both elements are significantly depleted relative to CI-chondrites. Core formation in the growing Earth must have occurred initially at low pressures and under reducing conditions to allow, for example, Cr to partition into metal (see Section 4.2). Such conditions would inevitably lead to a major loss of Ga into the core, because Ga is siderophile at low pressures. Because the metal/silicate partition coefficient of Mn is about two

orders of magnitude lower than that of Ga, Mn would not be depleted by metal segregation (see Fig. 1). At high pressures Ga becomes increasingly lithophile and Mn increasingly siderophile as shown in Figure 1 where the distribution coefficients  $K_D(\text{Ga})$  and  $K_D(\text{Mn})$  (see Eq. (1) below) are plotted against pressure. The only way of avoiding a large depletion of Ga relative to Mn is to deliver Ga only late in the accretion sequence when the metal/silicate partition coefficient of Ga is lower because then metal–silicate equilibration pressures are higher. This conclusion is fully supported (using identical arguments) by partitioning data for the volatile elements Zn and In (Mann et al., 2009; Rubie et al., 2010). In conclusion, all elements with volatilities similar to or higher than those of Ga and In must have been strongly depleted in the early accreting bodies due to incomplete condensation. Further evidence for the late addition of moderately-volatile elements (i.e. heterogeneous accretion) is provided by Pd–Ag isotope data (Schönbächler et al., 2010). O'Brien et al. (2006) also suggested, on dynamical grounds, that volatile-rich materials may have been accreted to the Earth at a late stage after radial mixing in the early solar system had progressed.

If highly volatile components, including water, were added in bodies that originally formed far out in the solar system (i.e. beyond the snow line), their accretion to the Earth would have occurred even later, most likely as a late veneer (i.e. after core formation was complete). Based on the  $H_2O$  content of CI chondrites (~20 wt.%, Jarosewich, 1990) and a late veneer mass =  $0.001\text{--}0.005 \times$  Earth's mass (Dauphas and Marty, 2002), water with a mass 1–5 times that of the current oceans could have been accreted to the Earth, which easily encompasses the Earth's total water budget (Hirschmann, 2006).

Based on the above points, we consider that a large proportion (e.g. >60–70% — see model results below) of the Earth accreted from anhydrous volatile-free material. Moderately volatile elements, including sulfur, were added to the Earth at a late stage, although before core formation was complete. The present inventory of terrestrial water was likely delivered by a small number of late-arriving volatile- and water-rich bodies that were accreted after core formation was complete. We therefore use anhydrous starting compositions that, with the exception of oxygen (and S), are free of volatile elements. The only moderately volatile element considered here is sulfur (see discussion later). Omitting other moderately volatile elements (e.g. Mn, Na, K, Zn) does not affect our results because their concentrations are low. The consequences of water being added at a

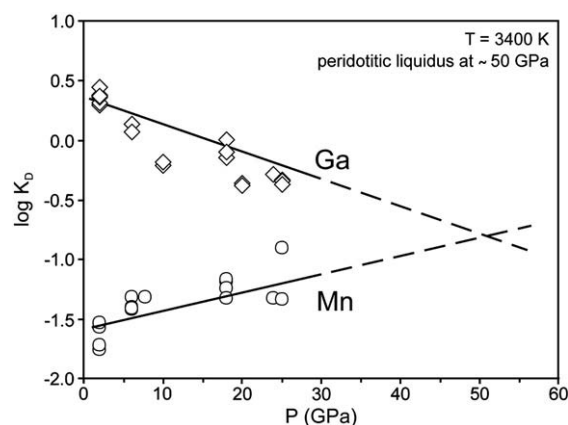


Fig. 1.  $\log K_D$  (see Eq. (1)) for the moderately volatile elements Ga and Mn plotted as a function of pressure at 3400 K. The symbols show data points from Mann et al. (2009) corrected to 3400 K using their derived temperature dependence and the lines show their  $\log K_D$  fits at the same temperature. In order to explain the approximately chondritic Mn/Ga ratio in the mantle, metal–silicate partition coefficients for these two elements must be approximately equal, which is the case at ~50 GPa and 3400 K when the temperature is defined by the peridotite liquidus (Mann et al., 2009). If these elements had been affected by core formation at low pressures, Ga would have been strongly depleted relative to Mn, which is not the case.

late stage but before the completion of core formation, as implied by Morbidelli et al. (2000), is discussed in Section 6.

### 2.1.2. Refractory elements

Of the elements considered in the model, six (Ca, Al, V, Nb, W, Ta) are refractory elements that condense into solids at temperatures above the condensation temperatures of the major phases, Mg-silicates and metal. To a first approximation, ratios among refractory elements are constant in all chondritic meteorites, i.e., primitive, undifferentiated meteorites. It was, however, noted early on that ratios of refractory to non-refractory elements in chondritic meteorites are not constant (e.g. Larimer, 1979), reflecting the addition of variable fractions of the refractory component. For example, the Al/Mg ratio shows a significant increase from enstatite chondrites (0.075), through ordinary (0.077) and CI (0.088) to CV chondrites (0.12). Palme and O'Neill (2003) derived an Al/Mg ratio of 0.1072 for the primitive upper mantle (PUM). Other PUM estimates are somewhat lower (e.g. McDonough and Sun, 1995), but they all have Al/Mg ratios significantly above the CI-ratio, which is identical, within error, to the Al/Mg ratio of the Sun of  $0.085 \pm 0.017$  (Lodders et al., 2009). Since we assume here that the PUM composition is representative of the bulk Earth's mantle and since neither Al nor Mg partition into the core it is obvious that bulk Earth has an enhanced Al/Mg ratio relative to the standard CI-composition. To account for the higher refractory element content in the Earth we have increased the abundances of Ca, Al, Nb, W and Ta by a factor of 1.22, using the CI and mantle abundances given in Palme and O'Neill (2003). Vanadium is the most volatile among the refractory elements and is approximately 50% less enriched in CV chondrites compared to the other refractory elements (Kallemeyn and Wasson, 1981). As an approximation, we assume therefore that V is enriched by a factor of 1.11 relative to Mg and CI-chondrites.

In summary, the enrichment in refractory elements of the Earth reflects the average composition of the accreting planetesimals. Individual accreting bodies may have quite variable compositions and some may even be depleted in refractory elements. Variations in refractory elements are common in chondritic meteorites and result from the incorporation of variable amounts of an early condensed refractory component during accretion (Palme and O'Neill, 2003).

### 2.1.3. Oxygen content

The bulk oxygen content of accreting material is of critical importance in defining oxygen fugacity. With the exception of Fe, most major elements considered here are assumed to occur initially as oxide components. The oxygen content and the  $\text{Fe}^{\text{metal}}/\text{FeO}^{\text{silicate}}$  ratio are defined by the fraction of total Fe present as metal ( $\phi_{\text{Fe}}^{\text{met}}$ ) (Rubie et al., 2004). To achieve highly-reduced starting compositions, a fraction of the total Si ( $\phi_{\text{Si}}^{\text{met}}$ ) is dissolved initially in the metal, thus reducing the bulk oxygen content. Note that ( $\phi_{\text{Fe}}^{\text{met}}$ ) and ( $\phi_{\text{Si}}^{\text{met}}$ ) are fitting parameters in the models described below and their values are not chosen arbitrarily.

The oxygen-free bulk starting composition is listed in Table S1 (supplementary data) as relative abundances and is identical for all embryos. Absolute element abundances depend on the oxygen content, i.e. on the values of ( $\phi_{\text{Fe}}^{\text{met}}$ ) and ( $\phi_{\text{Si}}^{\text{met}}$ ). Two examples of oxygen-bearing starting compositions are given in Table 1.

In the mass balance described below, we implicitly assume that oxygen is fully conserved and is not affected by volatile loss (e.g. as  $\text{CO}_2$  or  $\text{SO}_2$  species). The major gaseous species in equilibrium with ordinary chondrites at high temperatures are  $\text{CH}_4$  and  $\text{H}_2$  and the major S-bearing species is  $\text{H}_2\text{S}$  (Schaefer and Fegley, 2007). As this applies to a system considerably more volatile-rich and oxidised than the Earth, we can justifiably assume that oxygen is not lost by degassing.

**Table 1**  
Examples of reduced (1) and oxidised (2) starting compositions<sup>a</sup>.

		(1)	(2)
<i>Silicate</i>			
SiO <sub>2</sub>	wt.%	48.84	44.51
MgO	wt.%	41.79	31.05
FeO	wt.%	0.06	17.52
Al <sub>2</sub> O <sub>3</sub>	wt.%	5.13	3.81
CaO	wt.%	4.17	3.10
Ni	ppm	28	21
Co	ppm	1.3	1.0
Nb	ppb	79	59
Ta	ppb	4.5	3.4
V	ppm	16	12
W	ppb	29	21
Cr	ppm	694	516
<i>Metal</i>			
Fe	wt.%	85.59	91.04
Ni	wt.%	5.00	8.56
Co	wt.%	0.23	0.40
O	wt.%	0.00	0.00
Si	wt.%	9.17	0.00
Nb	ppb	1260	2158
Ta	ppb	72	124
V	ppm	252	432
W	ppb	461	789
Cr	wt.%	1.10	1.90
Metal <sup>b</sup>	wt.%	36.1	19.7

Trace elements are partitioned arbitrarily prior to the initial equilibration event.

<sup>a</sup> These compositions (prior to the initial equilibration) are based on the chondritic concentrations listed in Table S1 (supplementary data). The fraction of total Fe in metal ( $\phi_{\text{Fe}}^{\text{met}}$ ) is 0.999 in (1) and 0.62 in (2) and the corresponding fractions of total Si in metal ( $\phi_{\text{Si}}^{\text{met}}$ ) are 0.18 in (1) and 0.00 in (2).

<sup>b</sup> wt.% metal in the bulk metal–silicate system.

## 2.2. Element partitioning

The mass balance that is used to determine the compositions of coexisting metallic and silicate liquids is based on element partitioning data. The partitioning of element *M* between metal and silicate is described by the molar distribution coefficient:

$$K_D = \frac{X_M^{\text{metal}} [X_{\text{FeO}}^{\text{silicate}}]^{n/2}}{X_{\text{MO}}^{\text{silicate}} [X_{\text{Fe}}^{\text{metal}}]^{n/2}} \quad (1)$$

where *X* is molar concentration and *n* is the valence of *M*. In order to extrapolate partitioning data to higher *P–T* conditions the equation

$$\log_{10} K_D = a + b/T + cP/T \quad (2)$$

is used for most elements. The partitioning of low-valence elements, such as Ni and Co, is independent of silicate melt composition and for high-valence elements, such as W, we assume a fixed peridotitic composition (Section S1, supplementary data). Chosen partitioning models are based on data collected over a large *P–T* range (e.g. at least 2–23 GPa and 2000–2800 K). Parameterizations based on data obtained using graphite capsules were largely excluded (except for W) because C dissolved in metal drastically affects  $K_D$  (Cottrell et al., 2009; Mann et al., 2009). The parameter (*a*, *b* and *c*) values used and their uncertainties and sources are listed in Table S2 (supplementary data).

The partitioning of Si and O determines the FeO content of the mantle, oxygen fugacity and the composition of the core and is therefore particularly critical. For Si, we use the model of Mann et al. (2009) that is based on experimental data obtained up to 97 GPa and 3150 K (Section S1.3, supplementary data). The partitioning of oxygen between liquid silicate and liquid Fe is calculated using the model of Frost et al. (2010) which is consistent with experimental data obtained up to 70 GPa and 3500 K (Section S1.4, supplementary data).



**Table 2**

Final mantle and core compositions calculated from multistage core formation models. The most successful models are HET-2 and HET-3.

PM	Homogeneous accretion		Heterogeneous accretion			
	HOM-1	HOM-2	HET-1	HET-2	HET-3	
<i>Mantle composition</i>						
SiO <sub>2</sub>	45.40 (0.32)	49.12 (0.01)	45.44 (0.05)	45.75 (0.02)	45.85 (0.02)	45.86 (0.02)
MgO	36.77 (0.37)	34.84	39.03	37.55	37.47	37.46
FeO	8.10 (0.05)	8.07 (0.02)	6.37 (0.02)	8.11 (0.01)	8.10 (0.01)	8.10 (0.01)
Al <sub>2</sub> O <sub>3</sub>	4.49 (0.36)	4.28	4.79	4.61	4.60	4.60
CaO	3.65 (0.29)	3.48	3.90	3.75	3.74	3.74
Ni ppm	1860 (93)	1579 (270)	3581 (650)	1683 (190)	1774 (215)	1770 (185)
Co ppm	102 (5)	129 (25)	202 (45)	113 (16)	107 (16)	108 (15)
Nb ppb	588 (118)	647 (5)	591 (26)	518 (28)	513 (23)	512 (23)
Ta ppb	40 (4)	38 (1)	40.8 (0.4)	38 (1)	37 (2)	37 (2)
Nb/Ta *	14.0 (0.3)	17.1 (0.2)	14.5 (0.5)	13.6 (0.5)	14.0 (0.2)	14.0 (0.2)
V ppm	86 (4)	121 (14)	97 (31)	94 (24)	81 (21)	81 (22)
W ppm	16 (5)	30 (23)	59 (28)	22 (11)	22 (13)	22 (12)
Cr ppm	2520 (252)	4254 (468)	3090 (536)	3305 (418)	3010 (344)	3010 (346)
<i>Core composition and mass</i>						
Fe		89.8 (0.1)	81.1 (0.1)	83.2 (0.1)	83.7 (0.1)	83.7 (0.1)
Ni		5.8 (0.2)	4.6 (0.1)	5.3 (0.1)	5.3 (0.1)	5.3 (0.1)
Co		0.26 (0.1)	0.21 (0.01)	0.24 (0.01)	0.24 (0.01)	0.24 (0.01)
O		1.19 (0.01)	2.24 (0.01)	0.84 (0.00)	0.48 (0.01)	0.50 (0.01)
Si		1.01 (0.1)	9.91 (0.04)	8.5 (0.1)	8.3 (0.1)	8.3 (0.1)
S#		2.0	2.0	2.0	2.0	2.0
Nb ppb		32 (12)	297 (55)	431 (63)	441 (51)	443 (53)
Ta ppb		0.2 (0.1)	3.3 (1.1)	6 (2)	9 (3)	9.3 (3)
V ppm		29 (24)	101 (56)	107 (55)	137 (47)	136 (48)
W ppm		556 (61)	426 (56)	532 (26)	535 (28)	536 (26)
Cr ppm		4038 (1230)	6839 (1080)	6564 (935)	7255 (780)	7255 (782)
Core mass	32%	27.5%	33.1%	31.6%	30.7%	30.7%
<i>Model parameters</i>						
$f_p$	See Eq. (3)	0.32	0.53	0.48	0.67 (0.13)	0.65 (0.12)
$\phi_{\text{Fe}}^{\text{met}}(1)$	Fraction of Fe present as metal	0.839	0.999	0.999	0.999	0.999
$\phi_{\text{Si}}^{\text{met}}(1)$	Fraction of Si in metal	0.0	0.1	0.17	0.19 (0.01)	0.19 (0.01)
$\phi_{\text{Fe}}^{\text{met}}(2)$	Fraction of Fe present as metal	–	–	0.69	0.62 (0.04)	0.62 (0.04)
$I_n^{\text{het}}$	Impact no. for comp. change	–	–	21	21	21
$I_n^{\text{h}}$	See Eqs. (4), (5)	–	–	20	18	19
$\lambda$	See Eq. (4)	–	–	0.65	0.52 (0.09)	–
$\xi$	See Eq. (5)	–	–	–	–	0.13 (0.04)
$\Delta T$ (K)	See Eq. (9)	–	–	–	–396 (280)	–387 (260)
$\chi^2$	See Eq. (7)	433	2064	31.5	15.5	15.6

PM: Primitive mantle composition from [Palme and O'Neill \(2003\)](#). Element concentrations are listed as wt.% unless otherwise specified. Compositional uncertainties are based on log  $K_D$  error propagation and best-fit parameter uncertainties are based on fits in which log  $K_D$  (Si) is varied by  $\pm 1 \sigma$  (see text).

\* [Münker et al. \(2003\)](#); # 2 wt.% S content is assumed ([Dreibus and Palme, 1996](#); [McDonough, 2003](#)).

(1) and (2) refer to bulk compositions with different oxygen contents.

equilibration in the magma ocean is given as a fraction of the evolving core–mantle boundary pressure by

$$P_e = f_p \times P_{\text{CMB}}(I_n) \quad (3)$$

where  $f_p$  is a proportionality factor that is assumed (for simplicity) to be constant throughout accretion and is thus independent of the mass of colliding bodies.  $P_{\text{CMB}}(I_n)$ , the core–mantle boundary (CMB) pressure at the time of impact number  $I_n$ , is calculated using Equation 2.73 in [Turcotte and Schubert \(2002\)](#) assuming that (i) core density =  $2.5 \times$  mantle density and (ii) average mantle density scales linearly with planetary mass. The corresponding effective equilibration temperature ( $T_e$ ) is determined by assuming initially that it lies on the peridotite liquidus ([Herzberg and Zhang, 1996](#); [Wade and Wood, 2005](#); [Zerr et al., 1998](#)) at pressure  $P_e$ . As discussed below,  $P_e$  and  $T_e$  are empirical parameters that are unlikely to be direct indicators of magma ocean depth. Following partial or complete metal–silicate equilibration, the metal of an impactor core merges with the proto-core of the accreting Earth. We also assume that the Earth's proto-core, once formed, remains chemically isolated from the mantle/magma ocean because of the large density contrast. If the proto-core

did re-equilibrate extensively during each impact, average pressures recorded by siderophile elements would approach the CMB pressure (135 GPa), which is not the case.

We assume that impactors that accreted to form the Earth were already differentiated into silicate mantles and metallic cores (e.g. [Greenwood et al., 2005](#); [Taylor and Norman, 1990](#)). Based purely on gravitational energy, it is likely that larger (e.g. Mars-sized) bodies must have been differentiated, whereas for relatively small bodies, the assumption may not always be correct. However, differentiation of impactors only affects the results when their cores fail to completely re-equilibrate in the terrestrial magma ocean (termed here “disequilibrium”) – which is predicted below to occur only during the final few relatively large impacts.

The first stage of the model involves starting with bodies of mass  $0.01M_e$  (where  $M_e$  is the current mass of the Earth) and accreting these into sets of differentiated Earth-forming impactors with masses that range from  $0.01M_e$  to  $0.1M_e$ ; this is done for two bulk compositions (reduced, with high  $\phi_{\text{Fe}}^{\text{met}}$  and  $\phi_{\text{Si}}^{\text{met}}$  and oxidised, with lower  $\phi_{\text{Fe}}^{\text{met}}$  and  $\phi_{\text{Si}}^{\text{met}} = 0$ ) in order to model the effects of heterogeneous accretion ([Table 1](#); [Table S3](#) in supplementary data). The two compositions, the minimum number for modelling heterogeneous

accretion, represent averages of a range of compositions that presumably originate in inner and outer parts of the solar system, respectively (c.f. Wänke, 1981; O'Neill, 1991).

The second stage of the model involves accreting Earth by starting with a differentiated body of mass  $0.1M_e$  and assuming, for simplicity, that the mass of each subsequent impactor is  $\sim 10\%$  of the Earth's mass at the time of the impact, which is broadly consistent with the results of late-stage accretion simulations (Agnor et al., 1999; O'Brien et al., 2006). Twenty four impacts are then required to accrete the Earth's final mass ( $I_n$  ranges from 1 to 24). When modelling heterogeneous accretion, the bulk composition is changed from reduced to oxidised, or vice versa, at a given impact number  $I_n^{het}$ .

The model includes the possibility of only partial equilibration or "disequilibrium" – whereby differentiated impactor cores fail to re-equilibrate completely as they plunge through the terrestrial magma ocean before merging with the Earth's proto-core. It has been proposed that the timing of core formation determined using Hf-W isotopes can be reconciled with that of the U–Pb isotopes if some degree of disequilibrium occurred during accretion (Halliday, 2004; Nimmo and Agnor, 2006; Nimmo et al., 2010; Rudge et al., 2010). The degree of re-equilibration depends on the extent to which impacting iron masses emulsify as they sink in a magma ocean (Rubie et al., 2003). Re-equilibration may be complete for small impactors (especially when these are undifferentiated) but, according to a recent fluid dynamics study, not for large differentiated bodies (Dahl and Stevenson, 2010). Three disequilibrium models are considered. First, we consider that disequilibrium occurs only during the final few impacts and that the volume fraction  $\xi$  of an impactor core that re-equilibrates decreases exponentially with increasing impact number:

$$\begin{aligned} \xi &= 1.0 & 0 < I_n \leq I_n^* \\ \xi &= \exp[-\lambda(I_n - I_n^*)] & I_n > I_n^* \end{aligned} \quad (4)$$

Here  $\lambda$  is a constant,  $I_n$  is the impact number and  $I_n^*$  is the impact number immediately prior to the initial onset of disequilibrium. Second, we again consider that disequilibrium occurs only during the final few impacts but use a constant value of  $\xi$ :

$$\begin{aligned} \xi &= 1.0 & 0 < I_n \leq I_n^* \\ \xi &= \text{constant} (<1) & I_n > I_n^* \end{aligned} \quad (5)$$

Third, we use a constant value of  $\xi$  for all impacts:

$$\xi = \text{constant} (<1) \quad I_n > 0 \quad (6)$$

Initially we refined values of up to 7 parameters in the model ( $f_p$ ,  $\Phi_{Fe}^{met}(1)$ ,  $\Phi_{Fe}^{met}(2)$ ,  $\Phi_{Si}^{met}$  (for reduced compositions),  $I_n^{het}$ ,  $I_n^*$  and  $\lambda$  or  $\xi$  (depending on the disequilibrium model), where (1) and (2) indicate bulk compositions with different oxygen contents. In order to optimise these parameters, we minimized the sum of the squares of the weighted residuals:

$$\chi^2 = \sum ((C_C^i - C_M^i) / \sigma_M^i)^2 \quad (7)$$

where  $C_C^i$  is the calculated mantle concentration of component  $i$ ,  $C_M^i$  is the actual mantle concentration and  $\sigma_M^i$  is the uncertainty on  $C_M^i$  (Table 2). We used a combination of two approaches to perform this optimisation. First, we performed systematic grid searches of parameter space that involved calculating  $\chi^2$  for  $>3 \times 10^5$  different parameter combinations. These searches provided information about the approximate location of viable solutions. Second, based on the results of the grid searches, we used the simplex method (Nelder and Mead, 1965) to further minimize  $\chi^2$  and determine precisely the location of the minimum (Fig. S2, supplementary data). When doing this, integer values of  $I_n^{het}$  and  $I_n^*$  were not refined: instead, refinements of the other parameters were performed for

combinations of these two parameters in the ranges  $I_n^{het} = 16\text{--}22$  and  $I_n^* = 12\text{--}22$ . Minima are well defined but some parameters are correlated so that unique solutions do not exist (supplementary data, Sections S4, S5).

Uncertainties in the results are based on propagating uncertainties in the partitioning parameters (supplementary data). We assume that the best constraints on the model are the primitive mantle concentrations of  $SiO_2$  and  $FeO$ , so that uncertainties in the partitioning of  $SiO_2$  can strongly influence the results (see also below). Uncertainties in the fitting parameters (Table 2) were therefore determined by refitting with  $\log K_D(Si) \pm 1$  standard deviation for all equilibration steps. Most of the metal–silicate partitioning data used here were obtained up to pressures of  $\sim 25$  GPa. In order to propagate uncertainties when extrapolating to  $\sim 70$  GPa (see Table S3) we calculate results of the models using  $\log K_D \pm 1$  standard deviation (see error bars in Figs. 3 and 4). In the most successful models (HET-2 and HET-3), the extent of equilibration between metal and silicate at the highest pressures is very limited, which will minimize errors inherent in making large extrapolations. In addition, the very highest pressures are actually not essential for the success of the model and equally good results can be obtained by capping the maximum pressure at 50–60 GPa. Uncertainties on the calculated Fe and Si contents of the core are very small (Table 2) because these values are determined by mass balance based on a defined bulk Earth composition together with tightly-constrained mantle concentrations of  $FeO$  and  $SiO_2$ .

#### 4.1. Homogeneous accretion

In homogeneous accretion models, all accreting bodies have the same composition. Results of two such models, involving 2–3 fit parameters, are listed in Table 2. The observed primitive-mantle  $FeO$  concentration is reproduced in the best-fit homogeneous accretion model (HOM-1, Table 2) but results for  $SiO_2$ , V, Cr and Nb/Ta are poor because the bulk composition results in conditions that are too oxidising. The fit is poor ( $\chi^2 = 433$ ) and the predicted light element content of the Earth's core and its mass are both very low.

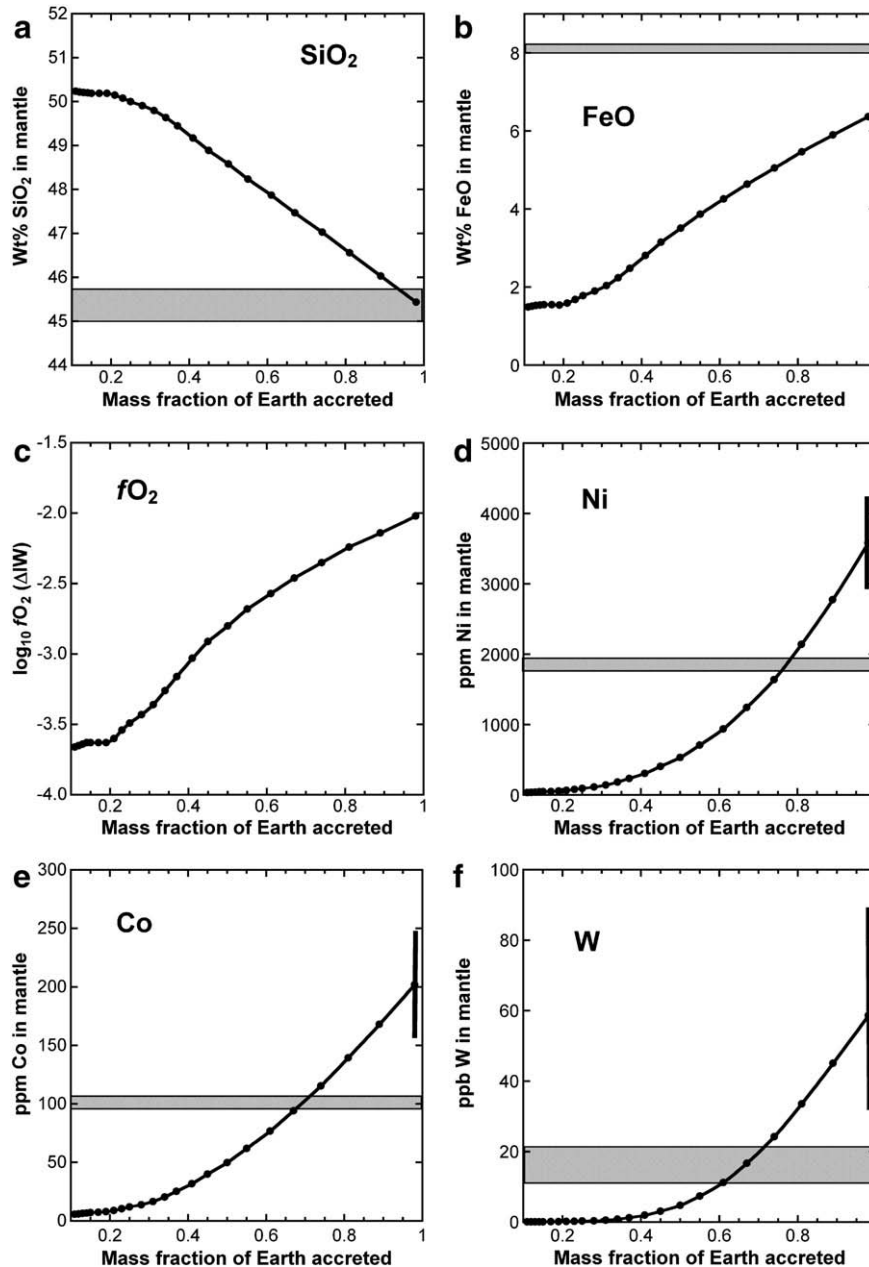
The observed primitive-mantle  $SiO_2$  concentration is reproduced perfectly in model HOM-2 (Table 2) by using a highly-reduced bulk composition. The mantle concentration of  $FeO$  is initially very low but increases during accretion to reach  $\sim 6.4$  wt.% (less than the primitive mantle value of 8%  $FeO$ ), while the mantle concentration of  $SiO_2$  progressively decreases (Fig. 3). These trends, which are associated with a continuous increase in  $f_{O_2}$  by  $\sim 1.6$  log units (Fig. 3c), are caused by the increased partitioning of Si into core-forming metallic liquid as  $T_e$  increases, which raises the mantle  $FeO$  concentration and thus the oxygen fugacity by the reaction:



(Javoy, 1995; Javoy et al., 2010). This homogeneous accretion model predicts mantle concentrations of the siderophile elements Ni, Co and W that are too high by factors of  $>2$  (Fig. 3, Table 2,  $\chi^2 = 2064$ ). Homogeneous accretion models that provide a reasonable fit to mantle composition (i.e.  $\chi^2 \ll 100$ ) have not been found.

#### 4.2. Heterogeneous accretion

The poor fit of model HOM-2 can be improved by invoking heterogeneous accretion by which late, relatively-oxidised impacting bodies increase the mantle  $FeO$  content. In addition, late-stage disequilibrium can result in the observed concentrations of Ni, Co and W, as described below. We therefore investigate models in which the bulk composition changes during accretion (at impact no.  $I_n^{het}$ ) and in which the cores of impactors only partially equilibrate with silicate liquid in the magma ocean. Extensive  $\chi^2$  minimization calculations



**Fig. 3.** Results of core formation involving homogeneous accretion and complete metal–silicate equilibration (model HOM-2, Table 2). Each symbol shows the result of an impact-induced core-formation episode. The evolution of mantle composition is plotted as a function of mass accreted; the error bars at 98% accretion are based on  $\pm 1$  standard deviation for the respective  $\log K_D$  values. The shaded bars show estimate mantle concentrations from [Palme and O'Neill \(2003\)](#). In this model, the Earth accretes entirely from high-reduced material in order to achieve the mantle SiO<sub>2</sub> concentration and impactor cores completely equilibrate (see Table 2 for model parameters). Although a realistic mantle concentration of SiO<sub>2</sub> is obtained (also Nb, V and Cr – see Table 2), the model fails badly for FeO, Ni, Co and W and the fit is very poor with  $\chi^2 > 2000$ .

show that viable solutions (e.g.  $\chi^2 < 50$ ) are confined to a restricted region of parameter space (see supplementary data, Section S5), as follows:

- 1) Material that accretes to form the initial 60–70% of the Earth's mass is highly reduced ( $\Phi_{Fe}^{met}(1) \geq 0.999$  and  $\Phi_{Si}^{met}(1) = 0.18$ –0.22). As noted above, an oxygen-poor bulk composition is required to produce a low  $f_{O_2}$  that makes Si, V and Cr siderophile such that the observed mantle concentrations of these elements are reproduced. When the initially-accreting material is more oxidised, viable solutions are not obtained.
- 2) The final 30–40% of the Earth accretes from material that is more oxidised ( $\Phi_{Fe}^{met}(2) = 0.60$ –0.76) but compared with CI chondrites, for example, is still quite reduced. As mentioned above, we assume that the Earth's water budget was delivered with a volumetrically-

small late veneer that is not considered here (see further discussion).

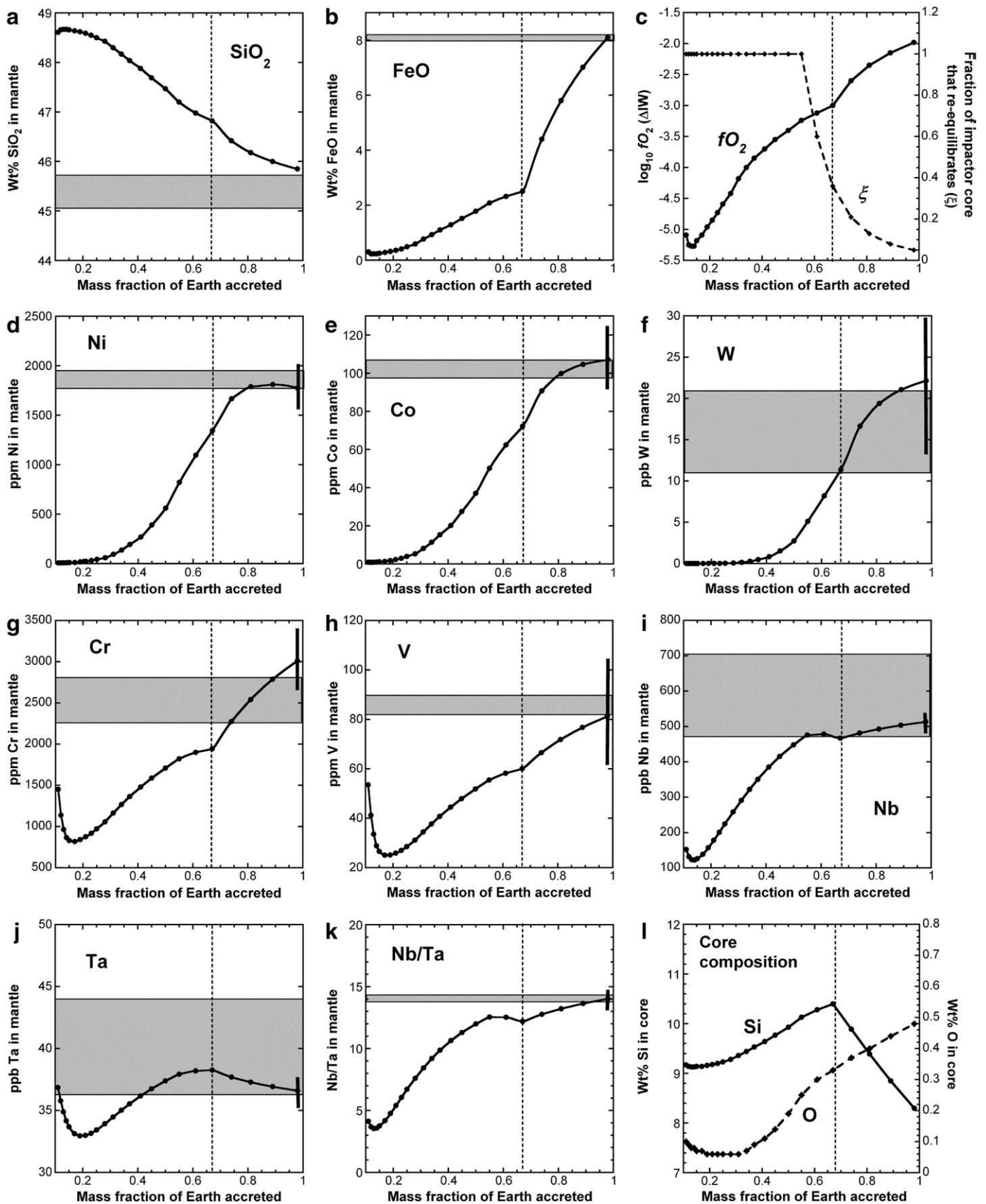
- 3) For acceptable fits, disequilibrium is required such that the cores of the final 4–8 impactors fail to equilibrate completely in the magma ocean. Identical fits are obtained when using Eqs. (4) or (5) (exponential and constant late-stage disequilibrium models, respectively). However, constant disequilibrium throughout accretion (Eq. (6)) produces very poor results and  $\xi$  refines to 1.0 in such models. This is because disequilibrium during early accretion produces low mantle concentrations of elements such as Nb and Ta because the mantle becomes dominated by material that equilibrated at low pressures and low oxygen fugacities.

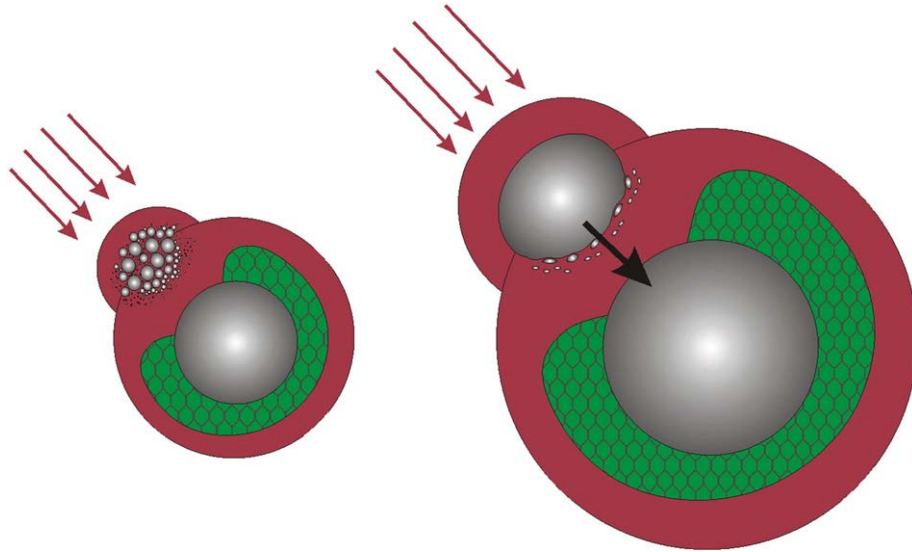
The best result based on optimising the seven parameters  $f_P$ ,  $\Phi_{Fe}^{met}(1)$ ,  $\Phi_{Si}^{met}(1)$ ,  $\Phi_{Fe}^{met}(2)$ ,  $I_n^{het}$ ,  $\lambda$  and  $I_n^*$  is obtained with model



HET-1 in Table 2 ( $\chi^2 = 31.5$ ). The high mantle concentrations of Ni, Co and W of the homogeneous accretion model HOM-2 (Fig. 3) are reduced significantly by disequilibrium. This is because when an impactor core

only partially equilibrates, the magma ocean becomes “diluted” with impactor mantle that previously equilibrated at low pressure and thus has low concentrations of Ni, Co and W. The addition of more-oxidised





**Fig. 5.** Cartoon summarizing the results of the model. The Earth accretes through impacts with planetary embryos that are ~10% of the mass of the proto-Earth at the time of impact. In the early stages, when the mass of the proto-Earth is less than ~60% of its final mass, metal and silicate equilibrate completely in the magma ocean, either because the impactor cores emulsify completely so that the small metal droplets formed equilibrate completely with the magma ocean (left) or because impactors are undifferentiated. In the later stages, when the proto-Earth is closer to its final mass, emulsification and chemical equilibration of the impactors' cores are incomplete so that much of it merges directly with the Earth's core (right). Core formation is very efficient because impact-induced magma oceans extend to the CMB. Grey: metallic cores; red: magma ocean; green: possible crystalline mantle.

material during the final stages of heterogeneous accretion is required to achieve the mantle FeO concentration of 8 wt.%. In model HET-1, the oxygen fugacity increases during Earth accretion by two log units, from IW-3.9 to IW-1.9 (relative to the iron-wüstite buffer, IW), partly as a consequence of reaction (8) but also because of the addition of oxidised material during the final 30–40% of accretion. Note that the “oxygen pump” mechanism, proposed by Wade and Wood (2005), that is related to the crystallisation of silicate perovskite, cannot be responsible for large increases in  $f_{O_2}$  during core formation (Frost et al., 2008).

### 5. $P$ - $T$ conditions of metal–silicate equilibration

The effective pressure ( $P_e$ ) of metal–silicate equilibration is unlikely to correspond to the pressure at the base of the magma ocean because equilibration rates between the bulk of a magma ocean and segregated metal are too slow (Rubie et al., 2003). If the magma ocean does not convect vigorously, metal droplets re-equilibrate progressively as they sink and equilibration is polybaric. In this case,  $P_e$  is on the order of  $\sim 0.6 \times P_{max}$  (Rubie et al., 2003), where  $P_{max}$  is the pressure at the base of the magma ocean, and  $P_e$  represents an “average” equilibration pressure (“Model 1” in Fig. 7 of Rubie et al., 2003). Two-dimensional simulations of the settling of metal droplets in a magma ocean support this polybaric equilibration model (Höink et al., 2006).

The energies of collisions with impactors that have a mass ~10% of the Earth's mass at the time of impact are sufficient to raise the average temperature of the Earth by 1000–3000 K (Rubie et al., 2007). Considering that the energy is concentrated in a hemispherical region on the side of the impact (Tonks and Melosh, 1993), such collisions are likely to result in extensive melting of the mantle down to the CMB (see Fig. 5). The value of  $P_e$  obtained in model HET-1 is  $\sim 0.5 \times P_{CMB}$

(Table 2) and may therefore be consistent with melting to the CMB provided that metal droplets equilibrate polybarically as they sink in a magma ocean. Such deep magma oceans would facilitate extremely efficient core formation and would eliminate the need to invoke liquid–metal diapirs that descend through a solid lower mantle (Stevenson, 1990).

If  $P_e$  represents an average of a range of polybaric equilibration pressures, there is no reason that the effective equilibration temperature ( $T_e$ ) should lie on the peridotite liquidus at pressure  $P_e$ , as assumed in models HOM-1, HOM-2, and HET-1 (Table 2). We therefore added an additional adjustable parameter,  $\Delta T$ , to the model:

$$T_e = T_L(P_e) + \Delta T \quad (9)$$

where  $T_L(P_e)$  is the nominal peridotite liquidus temperature at pressure  $P_e$ . The addition of this fitting parameter results in the reduction of  $\chi^2$  to ~15, with  $\Delta T$  in the range  $-300$  K to  $-530$  K, depending on the values of  $\phi_{Fe}^{het}$  and  $I_n^*$ . Three factors may contribute to this result: (1) as discussed for pressure,  $T_e$  may be an “average” of the (adiabatic?) temperature range over which equilibration occurs as metal droplets sink; (2) large uncertainties in peridotite melting temperatures at high pressure (Zerr et al., 1998); (3) uncertainties in the Si partitioning model that can increase  $\Delta T$  to  $-120$  K (Table 2).

The results of two best-fit models ( $\chi^2 = 15.5$ ), based on alternative disequilibrium models (Eqs. (4) and (5), respectively), that closely reproduce mantle concentrations of all elements considered here are listed in Table 2 (HET-2 and HET-3). The evolution of terrestrial mantle and core compositions,  $f_{O_2}$  and the extent of disequilibrium during accretion are shown in Figure 4 and the physical processes are shown schematically in Figure 5. Complete compositional results for

**Fig. 4.** Results of a best-fit ( $\chi^2 = 15.5$ ) core formation model based on heterogeneous accretion and disequilibrium (model HET-2, Table 2). The evolutions of mantle (a–k) and core (l) compositions,  $f_{O_2}$  and  $\xi$  (c) are shown as a function of mass accreted. In this model, the initial 67% of the Earth's mass accretes from high-reduced material ( $\phi_{Fe}^{met} = 0.999$ ,  $\phi_{Si}^{met} = 0.19$ ) and the final 33% from more oxidised material ( $\phi_{Fe}^{met} = 0.62$ ,  $\phi_{Si}^{met} = 0$ ); the vertical dashed lines mark the location of the compositional change. The starting compositions used in this model are the ones listed in Table 1. The disequilibrium model (Eq. (4)) is not unique and almost identical results are obtained when the extent of disequilibrium is kept constant at  $\xi = 0.13$  for the final 5 impacts (model HET-3, Table 2). Changes in element concentrations are caused mainly by the evolution of temperature, pressure,  $f_{O_2}$  and extent of disequilibrium. Note that the Earth's mantle achieves its current composition only at the end of accretion and that accretion of a planet with a mass different from that of the Earth would result in distinctly different mantle chemistry. Model parameter values derived by least squares regression are listed in Table 2 and details of the compositional evolution of impactors and the Earth, together with  $P$ - $T$  equilibration conditions, are given in Table S3 (supplementary data). See caption of Figure 3 for additional details.

the two sets of impactors and the accreting Earth in model HET-2 are given in Table S3 (supplementary data).

It has been proposed (Jacobsen et al., 2008) that metal and silicate equilibrated chemically at the extremely high temperatures (e.g. 10,000 K) that have been predicted in simulations of the Moon-forming giant impact (Canup, 2008). In addition, based on single-stage models of core formation, temperatures  $\geq 600$ –800 K above the peridotite liquidus have been proposed in order to make V siderophile in the Earth (Gessmann and Rubie, 2000; Wade and Wood, 2005). Based on mass balance, however, high temperatures actually make V and Cr more lithophile because reaction (8) is driven to the right which increases  $f_{O_2}$ . An even more serious problem is that at temperatures significantly above the peridotite liquidus (e.g.  $\Delta T = +1000$  K), the combined concentrations of Si and O in the core become excessively high (e.g.  $>25$  wt.%), the mantle concentration of SiO<sub>2</sub> drops below 40 wt.% and the mass of the core becomes too large (e.g.  $>0.38M_e$ ). Sustained extreme temperatures during core formation can therefore be excluded.

Alternative metal–silicate partitioning models provide comparable results. The Si partitioning model of Wade and Wood (2005) has a similar temperature dependence but opposite (weak) pressure dependence to that of the model of Mann et al. (2009) used here. Using the Wade and Wood (2005) Si model gives a good fit ( $\chi^2 = 22$ ) with fit parameters that lie close to the uncertainty ranges listed in Table 2 for HET-2; the main differences are that metal–silicate equilibration pressures are reduced ( $P_e = 0.5 \times P_{CMB}$ ) and  $\Delta T$  is increased to  $-130$  K. Comparable results are also obtained using the Ni and Co parameterizations of Wade and Wood (2005) except that the fit becomes distinctly worse ( $\chi^2 = 55$ ) because the calculated mantle concentration of Co (74 ppm) is too low.

## 6. The composition of the Earth and light elements in the core

With an anhydrous volatile-free CI composition and an enrichment of refractory elements by 22%, mantle concentrations of all elements considered here can be matched closely. In addition, the mass of the Earth's core is predicted to be  $\sim 0.31M_e$  (Table 2), which is close to the actual value of  $0.32M_e$ .

It is likely that the composition of accreting material changed with time as a consequence of initial radial heterogeneity of the solar nebula combined with the radial expansion of the Earth's feeding zone with time. Accretion models show that late accreting bodies, on average, come from larger heliocentric distances (Bond et al., 2010; O'Brien et al., 2006). The change from reduced to oxidised impactors, after 60–70% of the Earth accreted, is physically reasonable, because bodies that formed at greater distances from the Sun are more oxidised (as suggested by Mars). This is also in agreement with the present structure of the asteroidal belt that may reflect the gross structure of the primordial solar system, with material poor in volatile components being located near the Sun and material rich in water and other volatile constituents in the outer parts. Reflectance spectroscopy of asteroids shows bright silicate-rich, metal-containing objects in the inner belt and a prevalence of dark icy asteroids in the outer parts (Bell et al., 1989). Variations in the magnitude of the refractory component in the accreting bodies (as discussed in Section 2.1) may also show a systematic trend with increasing distance from the Sun, such as, for example, a systematic decrease with heliocentric distance in the early solar nebula as suggested by Bond et al. (2010).

As emphasized above, we have modelled accretion using water-free bulk compositions. In the unlikely case that early accreting material was hydrous (e.g. Stimpfl et al., 2006), hydrogen would either have partitioned into the Earth's core (Okuchi, 1997) or be lost by volatilization. This would lead to a significant increase in oxygen fugacity that is inconsistent with the present model – which requires initially very low oxygen fugacities ( $\Delta IW-5$  to  $\Delta IW-4$ ) in order that elements such as Si, V and Cr partition into the core. However, we

cannot exclude the possibility that H<sub>2</sub>O was added, together with moderately volatile elements, during the final 30–40% of accretion. This could provide an explanation for the more oxidised state of late accreted material.

Although primitive meteorites are representative of early-accreted material, there is no single type of chondritic meteorite that would represent a suitable parental material for the Earth, neither with regard to chemistry nor isotopic composition (Drake and Righter, 2002; Simon and DePaolo, 2010; Trinquier et al., 2007). The current model also gives poor results if non-volatile element ratios based on individual chondrites are used. With CV element ratios, for example, although the calculated best-fit mantle composition is excellent, the predicted mass of the core is only  $0.26M_e$ . With EH element ratios, the calculated mantle concentrations of SiO<sub>2</sub> and MgO and the mass of the core ( $0.43M_e$ ) are too high, and refractory element (Al, Ca, Nb and V) concentrations are too low. Any arguments for proposing an EH bulk composition have to be based on the composition of the lower mantle being distinctly different from that of the upper mantle (Javoy, 1995; Javoy et al., 2010).

Our model predicts that the Earth's core contains  $\sim 8$  wt.% Si and  $\sim 0.5$  wt.% O (Table 2), which, in terms of the Si content, is consistent with previous predictions (Alfè et al., 2002; Allegre et al., 1995; Fitoussi et al., 2009; Georg et al., 2007; McDonough, 2003; Wood et al., 2008; Ziegler et al., 2010). However, it has been proposed that the density difference between the inner and outer core is only consistent with the presence of a significant concentration of oxygen in the outer core, because *ab initio* calculations show it to be the only element that is suitably insoluble in the solid inner core (Alfè et al., 2002). The present results are inconsistent with this proposal for reasons that are currently not understood.

Our results are consistent with the Mg/Si ratio of the Earth's mantle being higher than the CI-chondrite ratio. Ringwood (1979) explained the high Mg/Si ratio by loss of Si and other comparatively volatile elements from the inner solar system in the early solar nebula but subsequently suggested that the Mg/Si of the Earth's mantle (and not the CI Mg/Si value) is the true solar ratio (Ringwood, 1991). According to the present study, the high Mg/Si ratio is the consequence of the extraction of Si into the Earth's core (e.g. Allegre et al., 1995; Wänke, 1981).

Finally, the Moon is believed to have formed largely from impactor material following the collision between the Earth and Theia (Canup and Asphaug, 2001). According to the results of model HET-2 (supplementary data, Table S3), the Earth's mantle and Theia's mantle immediately prior to the final giant impact contained  $\sim 7$  and  $16$ – $17$  wt.% FeO respectively. In order to produce  $13.6$  wt.% FeO in the Moon's mantle (Jones and Delano, 1989),  $\sim 70\%$  of the Moon would have to be derived from Theia. This value is very similar to the results derived from numerical simulations of the Moon-forming impact (Canup, 2008). In this case, the Nb/Ta ratio of the Moon's mantle would be  $16.4$ , which is close to the estimated value of  $17.0 \pm 0.8$  (Münker et al., 2003).

## 7. Concluding remarks

In summary, we show that the bulk composition of the Earth is well represented by solar system relative abundances of non-volatile elements but with enhanced concentrations of the refractory elements, Al, Ca, Ta, Nb and W and, to a lesser extent, V. In agreement with earlier models of heterogeneous accretion (O'Neill, 1991; Ringwood, 1984; Wänke, 1981) and a recent Pd–Ag isotope study (Schönbächler et al., 2010) we show that the Earth accreted initially from highly-reduced (oxygen-poor) material that was depleted in volatiles but that the final 30–40% of accreted mass was more oxidised. In contrast to the earlier heterogeneous accretion studies, metal–silicate equilibration at high pressures (e.g.  $>50$  GPa) was essential for core formation but extremely high equilibration temperatures that lie significantly above the silicate liquidus (Jacobsen et al., 2008)

can be excluded. Our results require that the metallic cores of the largest differentiated impactors only partially equilibrated with silicate liquid in magma oceans, which is in agreement with a recent fluid dynamics study (Dahl and Stevenson, 2010) and with Hf-W isotopic data (Halliday, 2004; Nimmo and Agnor, 2006; Nimmo et al., 2010; Rudge et al., 2010). Finally, we place new constraints on the composition of the core and conclude that Si is the most likely main light element.

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Computer codes used to generate the results of this study can be obtained from the corresponding author.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.epsl.2010.11.030.

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