The accretion and differentiation of Earth under oxidizing conditions

R. Bastian Georg[1,a] & Anat Shahar[2]

[1] Trent University, Water Quality Centre, Trent University, 1600 West Bank Dr., Peterborough, K9J

7B8, Ontario, Canada

[2] Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. NW,

Washington DC 20015

[a] corresponding author:

Tel: +1-705-748-1011 ext. 7318

e-mail: rgeorg@trentu.ca

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Abstract

We present a new approach to model planetary accretion and continuous core formation, and discuss the implications if Earth accreted under conditions initially more oxidized than the modern day mantle. The modified model uses the same partitioning data that were previously used to model accretion under reducing conditions, however, changing the partitioning between accreting metal and silicate mantle means that reducing conditions fail to meet expected core/mantle values. Instead, the model requires conditions more oxidized than the modern day mantle in order to converge and to yield expected elemental core/mantle distribution values for moderately siderophile elements. The initial oxygen fugacity required to provide the crucial level of oxidation is approximately $\Delta IW \sim -1.2$ to -1.7 and thus is in the range of carbonaceous and ordinary chondrites. Core formation under oxidizing conditions bears some interesting consequences for the terrestrial Si budget. Although the presented partitioning model can produce a Si content in the core of 5.2wt%, oxidizing accretion may limit this to a maximum of $\sim$3.6 to 2.7 wt%, depending on the initial fO_2 in BSE, which places bulk earth Mg/Si ratio between 0.96-1.0. In addition, under oxidizing conditions, Si starts partitioning rather late during accretion, e.g. when model earth reached >60% of total mass. As a consequence, the high P/T regime reduces the accompanied isotope fractionation considerably, to 0.07 ‰ for 5.2 wt% Si in the core. The isotope fractionation is considerably less, when a maximum of 3.6wt% in the core is applied. Under oxidizing conditions it becomes difficult to ascertain that the Si isotope composition of BSE is due to core-formation only. Bulk Earth's Si isotope composition is then not chondritic and may have been inherited from Earth's precursor material.

Keywords: Terrestrial Accretion, Core Formation, Si isotopes, Terrestrial Building Blocks

Introduction

The formation of the Earth's core was one of the most significant differentiation processes during planetary formation and evolution. Accreting metal and silicate components segregating under chemical equilibrium created a net flux of siderophile elements into the core, thereby modifying the chemical composition of the silicate component. Knowing the exact chemical composition of the Earth's core is therefore fundamental to the understanding of Earth's origin and the composition of it's very building blocks (e.g. McDonough 2003 and references therein). Unfortunately, direct sampling is not possible due to the inaccessible location of Earth's core and therefore, the accurate composition of the core will remain elusive. Compositional constraints will have to rely on indirect approaches, such as theoretical models of core and mantle composition (e.g. Allègre et al. 1995; McDonough and Sun 1995; McDonough 2003), laboratory high P/T experiments (e.g. Thibault and Walter 1995; Li and Agee 1996; Righter and Drake 1997; Li and Fei 2004; Walter and Trønnes 2004; Chabot et al. 2005; Wade and Wood 2005; Corgne et al. 2008; Jephcoat et al. 2008; Wood et al. 2009; Bouhifd and Jephcoat 2011; Siebert et al. 2011) and geo/cosmochemical studies (Palme and O'Neill 2003). For such comparisons it is paramount to have a sound understanding of the conditions that prevailed during the formation of the core and accompanied metal-silicate equilibration. The partitioning of elements between the metallic core and the silicate mantle depends on a number of parameters, such as temperature (T), pressure (P), oxygen fugacity (fO_2) and composition of the metal and silicate phases in question, all of which evolved during accretion as a result of planet growth and chemical evolution (e.g. Wade and Wood 2005; Corgne et al. 2008; Wood et al. 2009; Siebert et al. 2013).

To infer P, T and fO_2 conditions of core formation, a common approach is to use experimental results of elemental partitioning (commonly siderophile and chalcophile elements) in accretion models. This is done in an attempt to simulate metal-silicate partitioning during core formation under different conditions, and to match the results of such accretion models with compositional models for core and

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mantle compositions. One key aspect of such core formation models is the parameterization of the

elemental partitioning between metal and silicate. To that end, experimental data are used to obtain

regression parameters, typically called *a, b, c,* and *d* (Righter and Drake 1997; Righter et al. 1997;

Wade and Wood 2005; Corgne et al. 2008; Wood et al. 2009; Siebert et al. 2013). Despite large

variations in these regression parameters among published datasets (c.f. compilation in Siebert et al.

2011), most models of continuous core formation predict initial planetary accretion from reduced

materials, and more oxidized conditions during later stages of accretion (Wade and Wood 2005;

Corgne et al. 2008; Wood et al. 2009; Ricolleau et al. 2011; Siebert et al. 2011; Tuff et al. 2011; Siebert

et al. 2013). In a more recent study, Siebert et al. (2013) provided new experimental data and

concluded that Earth accretion might also have started under conditions more oxidizing than modern

day mantle and that such scenarios would satisfy the core/mantle distribution of crucial elements such

as Cr and V, both of which were previously used as strong indicators for accretion under reducing

conditions (Chabot and Agee 2003; Wade and Wood 2005; Wood et al. 2006; Rubie et al. 2011). The

new experimental data in Siebert et al. (2013) were obtained in diamond anvil experiments at pressures

and temperatures that more directly resemble conditions of core formation, while most previous data-

sets were obtained from experiments that were carried out at lower pressure and temperatures and then

extrapolated to the conditions of core-formation in a planet of the size of Earth. Siebert et al. argue that

extrapolation of data-sets may fail to adequately describe the partitioning of Cr and V at higher

pressures and temperatures and that previous models of core formation therefore imply accretion and

core formation under reducing rather than oxidizing conditions (Siebert et al. 2013). Not only are the

fO_2 conditions during core formation crucial to determining the elemental exchange between Earth's

mantle and the core, the oxidation state of accreting material will also determine the potential building

blocks of planet Earth. In support of the work by Siebert et al. (2013), Badro et al. have recently

compared the calculated density and bulk sound velocity in liquid alloys and compared these results to

seismological models in finding that oxygen is the main light element in the core (Badro et al. 2014).
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This would imply that the fO_2 in the magma ocean during core formation was higher than it is in the present-day mantle and that the partitioning of O (as FeO) into the core was the driving force behind the lowering of the mantles oxidation state to modern day FeO contents (Siebert et al. 2013; Badro et al. 2014). Siebert et al (2013) and Badro et al (2014) provide new evidence indicating that Earth's accretion might have taken place under oxidizing conditions, however, the question remains whether or not the discrepancy between "older" and some of the latest accretion models is solely a reflection of data extrapolation from lower to higher P/T regimes? In this study we do not provide new experimental data, but test whether a core formation model can be consistent with accretion under oxidizing conditions using regression data that were previously used to model accretion and core formation under reducing conditions. Using regression parameters published by Corgne et al. (2008), Siebert et al. (2011), Wade and Wood (2005) and Wood et al. (2009), we show that slight changes to accretion models can yield drastic effects and require very different conditions of core formation, especially in terms of oxygen fugacity.

The Modified Accretion Model

Accretion models either probe equilibrium or disequilibrium scenarios (O'Neill 1991; Li and Agee 1996; Righter et al. 1997; Halliday 2004; Wade and Wood 2005; Corgne et al. 2008; Rudge et al. 2010; Rubie et al. 2011). The equilibrium scenario requires all accreting material to be adsorbed into the target's mantle. This means quantitative emulsification of the impactor's core with the target's silicate mantle, which is realized when the impactor's core disperses into droplets sufficiently small in diameter to allow for chemical equilibrium (Stevenson 1990; Rubie et al. 2003). In a disequilibrium scenario, a fraction of the accreting metal does not equilibrate with the Earth's mantle owing to the size of the impactor, but is instead added straight to the core (Rubie et al. 2011). Depending on the size of the impactor's core relative to the target's mantle, hydrodynamic models predict metallic cores smaller in diameter than the depth of the target's magma ocean may disintegrate sufficiently upon impact to

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allow for efficient emulsification of the metal with the target's silicate mantle (Ichikawa et al. 2010; Deguen et al. 2011; Samuel and Tosi 2012; Morishima et al. 2013). The disequilibrium scenario holds less metal available for elemental partitioning and can limit elemental transfer from mantle into the core. In either scenario, emulsified liquid metal equilibrates with the silicate phase to reach a chemical equilibrium that is determined by partition conditions. If Earth accreted from already differentiated planetary embryos with an existing elemental equilibrium between a core and silicate mantle (Figure 1) (Rudge et al. 2010; Rubie et al. 2011), one has to assume the bulk of highly and moderately siderophile elements to be concentrated in the core of the planetary embryo:

$$c_{ce} = \frac{D_c c_{be}}{FD_c + (1-F)} \tag{1}$$

If partition conditions of the planetary embryo produce partition coefficients (D_c) of 10^2-10^3, the bulk concentration (c_{be}) of the element under consideration is highly enriched in the metal phase (c_{ce}). The corresponding concentration of that element in the embryo's mantle (c_{me}) is accordingly smaller:

$$c_{me} = \frac{c_{be}}{FD_c + (1-F)} \tag{2}$$

Assuming now, several of these planetary embryos, each with elementary budgets c_{ce} and c_{me}, accrete to form a planet. The initial partition coefficients in this newly accreting planet are in approximation similar to those in the embryos and that created the budgets c_{ce} and c_{me}. In the newly forming planet, quantitative or partial emulsification of metal within the silicate mantle produces two separate immiscible phases (Karato and Murthy 1997), each phase with the according elementary

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budgets; the metal will hold the gross proportion of the siderophile elements (c_{ce}) and the silicate the gross of the lithophile elements (c_{me}). If the two-phase emulsion was subject to the same or even higher partitioning coefficient D_c, the metal would strongly hold on to its siderophile element budgets (e.g. Co and Ni), but may take up some lithophile elements that show siderophile character under reducing conditions (e.g. Si, Cr, V). The silicate phase would not acquire elements Co and Ni in significant proportions, and as a result, the planet's mantle would remain devoid of these elements, unless oxidizing partitioning conditions would promote the exchange of Co and Ni from the accreting metal into the silicate phase. If we assume that all necessary pre-requisites for efficient emulsification of the impactor's core within the target's mantle are given (Kraus et al. 2015), an exchange of elements between the target's silicate mantle and the impactor's metal depends on partitioning conditions. During Earth's accretion, at least some of the elements that were concentrated in the embryos' metal phase had to partition into the Earth's mantle in order to produce known abundances of elements such as Ni and Co in BSE, therefore, some of Earth's accretion must have happened under oxidizing conditions.

Although an accretion model may define the degree of disequilibrium, if it lacks partitioning control over the elemental transfer of siderophile elements from the impactor's metal into the target's silicate mantle, chemical equilibrium is not fully described. For instance, to simulate accretion and elemental partitioning Rudge et al. (2010) used the following equation:

$$\frac{dc_m}{dt} = \left[c_{me} + \frac{kF}{1-F} c_{ce} - \left(1 + \frac{kD_c F}{1-F} \right) c_m \right] \frac{1}{M} \frac{dM}{dt} \qquad (3)$$

This equation shows the evolution of the elemental concentration c_m (in wt%) in BSE. Here k is the disequilibrium coefficient that defines the proportion of accreting metal that is allowed to equilibrate with silicate mantle, *i.e.* full equilibration when $k = 1$. Earth accretes from material that has a fixed

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proportion (F) of metal and (1-F) silicate mantle, with $F = 0.323$. The partitioning of element c from

silicate into metal is controlled by partition coefficient D_c, which may be a function of ambient pressure,

temperature and oxygen fugacity in the mantle. Multiplying out the terms in the square brackets

essentially yields the "elemental fluxes" into and out of the mantle; c_{me} is the weight concentration

added by accreting silicate material, kFc_{ce} /1-F is the proportional input of metal phase and associated

elemental budgets c_{ce} into the silicate mantle. Note, the addition of c_{ce} to c_m lacks control by partition

coefficients. Any elemental budget that is concentrated in the metal phase of the impactor is

quantitatively transferred into the target already. We argue above that this carte-blanche transfer may

not be an accurate assumption. If the partitioning coefficient is, under the given accretion conditions,

on the order of several 10^2 or 10^3, the element in question is considered siderophile and most likely

would not partition into the silicate at all, but would remain in the metal phase. As a consequence, this

additional flux of siderophile elements into the silicate mantle (when $k \neq 0$) is not taking place. The

output from the silicate mantle into the core is the metal-silicate partitioning, which is controlled by

$kD_c\,c_m$, the elemental concentration in the mantle multiplied by the partition coefficient D. The

coefficient D_c controls the elemental partitioning of elements from the silicate into the metal phase as a

function of ambient conditions, however, not the partitioning of elements from metal into silicate.

    In the following we explicitly add the partition coefficients to control to the elemental exchange

from incoming metal c_{ce} into silicate mantle c_m in the form of $c_{ce} \times 1/D_c$, and have factor k defining the

amount of metal that is available for equilibration (all metal available when $k = 1$). For simplicity we

assume that all accreting metal fully emulsifies with the silicate mantle (Kraus et al. 2015), which

means liquid metal and liquid silicate being immiscible and are present in discrete phases, henceforth

the factor k equals 1. As we will show in the following section, controlling the elemental flux of

siderophile elements from accreting metal into the silicate by partitioning conditions has important

consequences for the accretion model. We stress that unlike in previous models (e.g. Rudge et al. 2010),

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in our model a factor $k = 1$ does not necessarily mean elemental addition from the accreting metal, as this will depend on the ambient partitioning conditions for each element.

Planetary accretion, evolution of P and T

The accretion model simulates the linear accretion of Earth to 100% by adding mass in discrete steps. For each step, a new set of P, T and fO_2 are calculated, partitioning and isotope fractionation are evaluated and applied to elemental as well as isotopic species. Metal-silicate partitioning is allowed to take place over the entire process of accretion. The accretion function M is given as:

$$M(x) = \varsigma \cdot \mathbf{x} \qquad (4)$$

Where M(x) is the mass of earth accreted at step x and ς is the final mass of Earth ($\varsigma = 1.0$), and $\mathbf{x}$ is a vector, e.g. $\mathbf{x} = [0, 0.001, 0.002, 0.003 \ldots 1.0]$. The pressure at the base of the magma ocean is assumed to increase as the square of the planet's radius (Rudge et al. 2010):

$$P(x) = P_0(M(x))^{2/3} \qquad (5)$$

Where M(x) is the fraction accreted at step x and P_0 is the peak pressure of accretion (in GPa), e.g. when P_0 set to be 54 GPa, the final equilibrium for silicate-metal partitioning is located at ~40% depth of the core-mantle boundary (Corgne et al. 2008; Rudge et al. 2010). Please note that the average pressure during metal-silicate partitioning is then ~29 GPa and that partitioning effectively ceases when the pressure reaches >40GPa. The temperature T of metal-silicate equilibration is fixed to the peridotite liquidus (Wade and Wood 2005; Rudge et al. 2010):

$$T(x) = P(x) \cdot 28.57 + 1973 \qquad (6)$$

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Elemental partitioning $D_{Si,Ni,Cr,V,Co}$

Partitioning of Si, Ni, Cr, V and Co into metal is a function of the ambient P, T and fO_2 in the silicate mantle at time of metal-silicate partitioning. The partitioning is parameterized as (Ziegler et al. 2010):

$$\log\left(\frac{x_m^{metal}}{x_m^{silicate}}\right) = a + \frac{b}{T} + \frac{cP}{T} + d\frac{nbo}{t} - \frac{v}{4}\Delta IW + 2\log\left(\frac{\gamma_{FeO}^{silicate}}{\gamma_{Fe}^{metal}}\right) - \log\left(\frac{\gamma_m^{metal}}{\left(\gamma_{Fe}^{metal}\right)^{v/2}}\right) \quad (7)$$

where m is the respective element (Si, Ni, Cr, V or Co). The regression parameters a,b,c,d and valence v were taken from Corgne et al (2008) for Si, and from Siebert et al. (2011) for Ni, Co, V and Cr[1], nbo/t = 2.7 is the ratio of non-bridging oxygen to tetrahedrally-coordianted cations in the silicate melt, $-\Delta IW$ is the oxygen fugacity ($fO2$) expressed as log units from the iron-wüstite buffer, x_i is the mole fraction of species i in the specified phase and γ_i is the activity coefficient of species i in the specified phase. Equation 7 gives the molar partitioning coefficient, which we found, in agreement with Rudge et al. (2010), to be sufficiently similar to respective weight partition coefficient. The temperature dependency of the activity coefficients is given by:

$$\ln\gamma_i^{\circ}(T) = \frac{T^{\circ}}{T}\ln\gamma_i^{\circ}(T^{\circ}) \quad\quad\quad (8)$$

where γ_i° and T° represent the respective reference states (Wade and Wood 2005; Corgne et al. 2008; Wood et al. 2009; Siebert et al. 2011). The oxidation state of the mantle is introduced as the molar fraction of FeO in the silicate mantle over the amount of Fe in the core and converted into log units from the IW buffer (ΔIW) (Siebert et al. 2013):

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[1] Using regression parameter data from other sources, e.g. Wade & Wood (2005) for Co, Ni, and Wood et al. (2009) for Cr and V, gives comparable results. For Si, regression parameters from Wade & Wood (2005) result in unrealistically high Si contents in the core, alternatively data from Tuff et al. (2011) may be used for Si.

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$$\Delta IW = 2\log\left(\frac{x_{silicate}^{FeO}}{x_{metal}^{Fe}}\right) \tag{9}$$

where x is the mole fraction of FeO and Fe in the silicate and metal phase, respectively. The oxidation stage of Earth's silicate mantle may have changed during accretion (Wade and Wood 2005; Corgne et al. 2008; Wood et al. 2009; Ricolleau et al. 2011; Siebert et al. 2011), and is often modeled by step-wise changes (Wade and Wood, 2005; Wood et al. 2009; Corgne et al. 2008), but can also be represented as linear functions or combinations of step- und linear functions (Rudge et al. 2010). We use a more general approach to implement the change in fO_2 in the form of:

$$FeO_{BSE}(x) = \left[\varphi + (1-\varphi)\cdot\left(\frac{x}{\varsigma}\right)^{\frac{p}{q}}\right]\cdot\kappa \tag{10}$$

This function describes the continuous change in FeO_{BSE} over the course of accretion, with x = accretion step, κ representing the final FeO_{BSE} (e.g. 0.081), p and q are shape parameters, φ representing the FeO_{BSE} at the beginning of accretion as fraction of κ, and ς being again the final stage of accretion for metal-silicate partitioning (Figure 2).

Isotope fractionation

Besides elemental partitioning, we also add isotope fraction of Si to simulate the accompanied isotope fractionation during Si partitioning. Although, elemental partitioning of Si and isotope fractionation are somewhat decoupled during core formation (Savage et al. 2014), the isotopes nonetheless may represent an important measure for the amount of Si being transferred between silicate mantle and core; excessive amounts of Si in the core result in isotope fractionations that are typically larger than

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observed (Georg et al. 2007; Fitoussi et al. 2009; Chakrabarti and Jacobsen 2010; Armytage et al.

2011). The isotope fractionation is defined in terms of isotope fractionation factor α_{Si}. Recent studies

have shown that Si isotope fractionation between a metal and silicate phase is depending on T, but less

so on P, at least to the conditions that have been experimentally attained thus far (Shahar et al. 2011).

The fractionation term (α_{Si}) is implemented in the model as a function of T (Shahar et al. 2009; 2011):

$$\varepsilon^{30/28} Si = \ln 1000\alpha \text{, where } \varepsilon^{30/28} Si = 7.45 \times (1 \times 10^6 / T^2) \tag{11}$$

The fractionation factor (ε is the isotope fractionation factor in ‰) scales inversely with temperature

and will be largest during the early stages of accretion and then decreases with increasing T.

Mass accretion and elemental budgets

The model accretes the proto-Earth by adding mass in 1000 discrete steps according to equation

4. The accreting mass is composed of mass fraction $F = 0.323$ metal and $1-F$ silicate (Rudge et al.

2010). The mass of BSE through time is:

$$\frac{dM_{BSE}}{dx} = \frac{dM}{dx} \cdot M_{\oplus}(1-F) + \frac{dM}{dx} \cdot M_{\oplus}(kF) - \frac{dM}{dx} \cdot M_{\oplus}(kF) = \frac{dM}{dx} \cdot M_{\oplus}\left[(1-F) + kF - kF\right] \tag{12}$$

where, $M_{\oplus}$ is the total mass of fully accreted Earth and dM/dx is the first derivative of function M(x),

the term ($1-F$) describes the addition of silicate material form the impacting object, $+kF$ is the addition

of metal (this is the metal proportion available for elemental partitioning) and $-kF$ is the core formation

with the metal that has undergone elemental partitioning. When $k = 1$, all accreting metal is initially

added to the mantle, subject to elemental partitioning exchange, and then descending to form the core.

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When $k < 1$, some proportion (1-k) of metal is added straight to the core, thereby not adding mass to the mantle or exchanging elements with the mantle. The mass of the core is then given as:

$$\frac{dM_{core}}{dx} = \frac{dM}{dx} \cdot M_{\oplus}(kF) + \frac{dM}{dx} \cdot M_{\oplus}\left((1-k)F\right) = \frac{dM}{dx} \cdot M_{\oplus}\left[kF + (1-k)F\right] \qquad (13)$$

where, kF represents the fraction of metal added to the core after equilibration with the mantle and $(1-k)F$ is the metal fraction added straight to the core without the potential for chemical equilibration.

The next step is to compute the elemental budgets and partitioning between metal and silicates. Based on the assumption that planetary embryos have already experienced chemical differentiation, we treat the evolution of the elemental budgets slightly different, depending on whether or not the element in question is likely be enriched in the planetary embryo's metal or silicate phase. The lithophile elements are assumed to be quantitatively concentrated in the silicate phase of the impactor. The budgets for these elements (here Si, Cr, and V) are given as:

$$\frac{dC_{BSE}^{e}}{dx} = \frac{dM}{dx} \cdot M_{\oplus}(1-F) \cdot \frac{c_{BE}^{e}}{(1-F)} - \frac{dM}{dx} \cdot M_{\oplus}kF \cdot c_{BSE}^{e}D_{met}^{e} = \frac{dM}{dx} \cdot M_{\oplus}\left[c_{BE}^{e} - kF \cdot c_{BSE}^{e}D_{met}^{e}\right] \quad (14)$$

Here C_{BSE}^{e} is the absolute amount of element e in BSE at given accretion step x, c_{BSE}^{e} (lower case c) is the weight-% concentration of element e in BSE, $c_{BSE}^{e} = C_{BSE}^{e}/M_{BSE}$, c_{BE}^{e} is the concentration of element e in bulk earth, k and F are defined above and D_{met}^{e} is the partitioning coefficient for element e at each accretion step x. With increasing P, T, these lithophile elements become more siderophile and might partition into the metal. Their concentration in the core is given by integrating the flux of element e out of BSE caused by metal-silicate partitioning:

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$$\frac{dC_{core}^{e}}{dx} = \frac{dM}{dx} \cdot M_{\oplus}\left[kF \cdot c_{BSE}^{e}D_{met}^{e}\right] \tag{15}$$

As explained in section 2.1, the model uses an additional partitioning control to model the exchange of siderophile elements with initial D values of $>10^{2}$-10^{3} and their release into the mantle (Figure 1). The elemental budget of elements with $D \gg 1$ is defined as:

$$\frac{dC_{core}^{e}}{dx} = \frac{dM}{dx} \cdot M_{\oplus}c_{BE}^{e} - \frac{dM}{dx} \cdot M_{\oplus}(1-F)k \cdot \frac{c_{core}^{e}}{D_{met}^{e}} = \frac{dM}{dx} \cdot M_{\oplus}\left[c_{BE}^{e} - \frac{k(1-F)c_{core}^{e}}{D_{met}^{e}}\right] \tag{16}$$

where, C_{core}^{e} is the absolute amount of element e in the metal/core at given accretion step x, c_{core}^{e} (lower case c) is the weight concentration of element e in the core, $c_{core}^{e} = C_{core}^{e}/M_{core}$, c_{BE}^{e} is the concentration of element e in bulk earth, k, F and D_{met}^{e} are defined above. The concentration of element e in the core is given by the amount added during accretion minus the amount that partitions into the silicate mantle, here controlled by partition coefficients D_{met}^{e}. In the case that D_{met}^{e} is far greater than 1, the resulting flux from metal into silicate becomes negligible, although all or a fraction k of metal is allowed to equilibrate with the mantle. The concentration of element e in BSE is simply given by the partitioning flux through,

$$\frac{dC_{BSE}^{e}}{dx} = \frac{dM}{dx} \cdot M_{\oplus}\left[\frac{k(1-F)c_{core}^{e}}{D_{met}^{e}}\right]. \tag{17}$$

With the metal-silicate partition coefficient being 2 or 3 orders of magnitude above 1, the term in the brackets becomes rather small and so does the contribution of siderophile or moderately siderophile

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elements from accreting metal to BSE.

Isotope Fractionation of Si during metal-silicate partitioning

We are only interested in the isotopic offset created by Si partitioning into the core and the model calculates this offset relative to the accreting material, e.g. starting point of BSE, and therefore the exact isotope composition of the accreting material becomes irrelevant. The accretion adds Si with the starting composition to the mantle and the equation for the isotopic evolution of the mantle is:

$$\frac{dR_{BSE}^{Si}}{dx} = \frac{1}{M_{BSE}}\left(\frac{dM}{dx} \cdot M_{\oplus}\left[c_{BE}^{e} \cdot R_{ini} - kF \cdot c_{BSE}^{e} D_{met}^{e} \cdot \alpha_{Si}^{30/28} \right] \right) \tag{18}$$

The isotope fractionation factor is given as $a_{Si}^{30/28} = e^{-\varepsilon^{30/28}/1000}$. The isotopic offset (in ‰) of Si in BSE from the starting value is simply:

$$\Delta^{30}Si_{BSE} = \left(\left(\frac{R_{BSE}^{Si}}{R_{ini}} \right) - 1 \right) \cdot 1000 \tag{19}$$

Comparing model results to expected values

Rather than to a single value, each modeled parameter is compared to a range of likely values and the ability of the model to converge is given by how well the model matches the range of expected core/mantle and isotope ratios (Allègre et al. 1995; McDonough 2003; Palme and O'Neill 2003; Georg et al. 2007; Armytage et al. 2011; Savage et al. 2014). A convenient way to express the concordance is to use z-scores:

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$$z_{D_e} = \frac{D_e^{\mathrm{mod}} - \overline{D}_e^{\mathrm{exp}}}{\sigma_e^{\mathrm{exp}}} \tag{20}$$

Where, e is the respective element (or isotope ratio), D_e^{mod} is the modeled result at the end of accretion,

$\overline{D}_e^{\mathrm{exp}}$ is the mean of the expected range of values and σ_e^{mod} is the deviation or range around the

expected mean value. The z-score expresses the match of the modeled value to the expected mean

value in terms of the value's range. A z-score of $-1 \leq z_{D_e} \leq 1$ means the modeled value lies within the

expected range, a negative z-score means the modeled D-value lies below the expected mean, and vice

versa. The overall model performance is evaluated as the pooled z-score from all individual scores:

$$z_{\mathrm{mod}} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left(z_{D_e} \right)_i^2} \tag{21}$$

Where N is the number of modeled observations (N=6) and $\left(z_{D_e} \right)_i$ the individual z-score of observation

i.

Discussion

Elemental partitioning and isotopic fractionation

If our accretion model lacked the additional control of how the partitioning of already

differentiated objects will behave in the mantle, it does work under reducing conditions. The initial

reduced state is required in order to partition lithophile elements, such as Si, V and Cr in sufficient

proportions into the metal and eventually core. Less reducing conditions are then required towards the

end of accretion to keep moderately siderophile elements such as Co and Ni in the silicate phase in

order to meet expected mantle abundances of these elements. Initially reducing scenarios work,

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because all Ni and Co from the accreting metal gets simply added into BSE, even though the conditions

are reducing and do in fact not promote the partitioning of Ni and Co from metal into silicate (c.f.

section 2.0 and equation 1-3), The model only has to ensure retention of some of the siderophile

elementary budgets during later stages of accretion in order to meet expected core/mantle values.

However, we argue that reducing conditions would prevent the addition of siderophile elements into

the silicate mantle from accreting metal, as high D-values would diminish the term in the brackets in

equation 17, and BSE failed to build up significant budgets of Ni and Co. An example model run is

shown in Figure 3, where the peak pressure is set to 40GPa and starting fO_2 is given by an initial

FeO_{BSE} of ~2%. Lithophile elements, such as Si, V and Cr gain siderophile character as P and T

increase, and the elemental as well as Si isotope ratios yield final results in accord with expected ranges.

Moderately siderophile elements, Ni and Co for example, are orders of magnitude above expected

values. This is simply a reflection of the partitioning behavior during metal-silicate equilibration with

the accreting metal and the fact that conditions have never been in the appropriate oxidation regime to

allow for Ni and Co to enter the silicate mantle in sufficient proportions. Under reducing conditions,

these elements are quantitatively retained in the metal/core. With the additional partition control, the

model has to provide suitable conditions to promote the release of elements, such as Ni and Co, into the

silicate mantle in the first place. If the partition conditions were in fact more oxidizing than commonly

proposed (Wade and Wood 2005; Corgne et al. 2008; Wood et al. 2009; Ricolleau et al. 2011; Rubie et

al. 2011; Siebert et al. 2011), lower partition coefficients for Ni and Co would promote the exchange

between accreting metal and the silicate mantle can build up expected Co and Ni budgets. Starting

accretion under conditions more oxidized than modern mantle, with an initial FeO_{BSE} of ~20wt%,

provides the required environment to promote significant partitioning of elements such as Co and Ni

from the accreting metal into BSE (c.f. Siebert et al 2013), and a linear decrease of fO_2 brings Co and

Ni closer to the expected ranges. Lithophile elements and Si isotopes may, however, not match

expected values, as these elements require less oxidized conditions in order to yield expected
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concentrations and isotope ratios within BSE and the core. One way to aid the partitioning is to increase the peak pressure and thus temperature of accretion, facilitating elemental partitioning for a given set of fO_2 conditions and thus producing core/mantle partition ratios closer to expected ranges.

We tested multiple scenarios with different starting values for fO_2 and also peak pressures to check for potential solutions for scenarios starting under reducing conditions (Figure 4). The contour plot in Figure 4 represents 10,000 model runs testing a combination of different starting FeO_{BSE} values and peak pressure of accretion settings. For a linear decrease in fO_2, the model finds multiple solutions for wide ranges of peak pressures (between ~53 and 65 GPa) and initial FeO in BSE (between ~13 and 26 wt%). The estimates for pressures and starting FeO contents are in agreement with the work recently published by Siebert et al. (2013). However, different from Siebert's work, our model produces these results using the regression parameter that were previously used to model accretion under reduced conditions (Wade and Wood 2005; Corgne et al. 2008; Wood et al. 2009; Siebert et al. 2011). No solutions were found for initially reducing scenarios, in which initial FeO BSE was lower than modern mantle.

All of the above model runs assume a linear decrease in fO_2 during accretion. However, similar plots exist for different fO_2 gradients. By modifying the shape of the fO_2 gradient, it is possible to simulate either an initial steep decline in fO_2, or scenarios in which fO_2 is kept rather constant for the first stages of accretion (Figure 5). The sensitivity analyses in Figure 5 represent 2,500 model runs, for all of which the FeO_{BSE} gradient shape parameter was set to $p = 8$. The starting FeO_{BSE} remains constant for some part of accretion (up to 60%) and is then decreasing to meet modern day FeO_{BSE} towards the end of accretion. By holding the initial FeO_{BSE} constant over some of the accretion process, the model is able to converge despite a lower initial FeO_{BSE}. Conditions are sufficiently oxidizing to yield expected core/mantle partition coeffcients for Ni and Co, and the lower initial FeO_{BSE} also improves the partitioning of less siderophile elements Si, Cr, and V. There are again multiple solutions for a wide range of initial FeO contents, (10 to 15 wt%) and peak pressure settings (54 – 65 GPa).

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The shape of the fO_2 gradient can be further modified to test the relation between initial FeO$_{BSE}$ and the shape of the fO_2 gradient. The contour plot in Figure 6 represents a sensitivity analysis based on 2500 model runs. Here the peak pressure is set to 61 GPa, averaging the pressure ranges of the model runs shown in figures 7 and 8, and we test the model convergence as a function of starting FeO$_{BSE}$ and the shape of the fO_2 gradient defined by the shape parameter p. Depending on the shape parameter p, the model converges for a wide range of initial FeO contents (10.5 – 20 wt%). Note that all solutions for $p > 2$ require initial ΔIW values that are consistent with ordinary and carbonaceous chondrites (Ringwood 1966; Righter and Drake 1996; Li and Agee 2001; Asahara et al. 2004; Siebert et al. 2013). There were no solutions found for a gradient that shows an initial steep decline in FeO, e.g. when parameter $q > 1$ and $p = 1$. The data in figure 6 were obtained for a peak pressure of 61 GPa, but additional solution spaces exist for other configurations using different peak pressures. Our model shows a range of solutions for major- and trace-metal partitioning for a planet that accreted from material having an oxygen fugacity higher than modern day mantle.

We also have tested the convergence of the model using regression parameters from other studies, such as Wade & Wood (2005) for Co, Ni and Si and Wood et al. (2009) for Cr and V. If we allow for each parameter to be adjusted within the stated uncertainties, the model will converge for the trace-metals to produce results comparable to the results presented above. The only distinction is that Wades & Wood's regression parameters for Si produce a core with an unrealistic amount of Si (>15 wt%), probably owing to the higher peak-pressure in our study. We also used more recent regression parameters from Siebert et al. (2013) and found good fits for Cr and V, however, their parameter's for Ni and Co did not produce model results within the range of expected core/mantle values for Ni and Co. When comparing the elemental partitioning of these elements between the different sets of regression parameters, it appears that the diamond-anvil data produce lower partitioning for Ni and Co at lower pressures, and higher partitioning at higher pressures. Both sets of regression parameter, obtained from low-P/T multi-anvil experiments (Siebert et al. 2011) and high-P/T diamond-anvil experiments (Siebert

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et al. 2013), produce identical partitioning results at about 20 GPa pressure. The reason for the differential behavior during the modeling is unclear, it could be the extrapolation of high-P/T experimental data to lower P/T regimes. Despite using different regression parameters, the results of our study nonetheless agree well with the Siebert et al. (2013) study and predict similar levels of initial oxygen fugacity as well as P/T conditions during core formation.

Bulk Earth's Si budgets

Accreting Earth under oxidizing conditions bears some interesting implications for the Si budget of bulk earth. Although the computation of partitioning allows for up to 5.2 wt% Si in the core (isotopic offset of 0.07-0.08‰), the model might overestimate the Si content by several wt%, as the amount of Si may be limited by O partitioning into the core (Badro et al. 2015). The oxidized accretion model has initial FeO contents in BSE higher than modern day mantle, but has to lose some of that FeO in order to reach modern mantle values. Partitioning of FeO into the core, however, may limit Si partitioning into the core (Rubie et al. 2011; 2015):

$$SiO_2(silicate) + 2Fe(metal) \rightarrow Si(metal) + 2FeO(silicate) \quad (22)$$
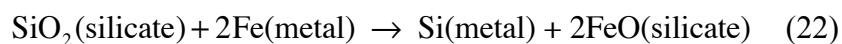
For every mole of SiO_2 being reduced to Si, two moles of O become available and increase the oxidation level in the mantle. However, at higher P/T, O partitions into the metal as well (Ricolleau et al. 2011; Badro et al. 2014) alongside Si. The core has to take up O that becomes available according to reaction (22), and in addition the O from the partitioning of FeO, which lowers the oxygen fugacity in the mantle. Mass balance considerations then show that the amount of Si is limited to values below the model results. For instance, if the model has an initial FeO in BSE of 12wt%, the core has to take up an equivalent of ~8.2 wt% FeO (approx. O ~1.8 wt%). At the end of accretion, the core contains Fe (~85.9wt%), Ni (~5.2wt%), O (from FeO partitioning ~1.8wt%) and Si (~5.2wt%). Converting into

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molar fractions and adding up the molar fractions of O from FeO partitioning and the reduction from SiO$_2$ to Si, the core would contain total O of ~7.6 wt%, to give a total (Fe + Ni + Si + O) of ~104%. Note that Co, Cr and V are not sufficiently abundant to have much of an impact on the mass-balance calculations. In order to keep a core with ~86wt% Fe, ~5wt% Ni and ~9wt% lighter elements, it seems reasonable to adjust the amount of Si in the core and therefore the amount of O that is released by reduction of SiO$_2$. Balancing the budget of the core's major constituents limits the Si content in this scenario to ~3.4 wt%, or ~2wt% lower than predicted by the model based on partitioning parameterization. Using the feasible limits for initial FeO from figure 10 (e.g. 11 – 15wt% FeO) yields a maximum amount of Si in the core of ~3.6 wt% to ~2.7wt%.

Regardless of the maximum amount of Si in the core, accretion under oxidized conditions also means the isotope fractionation due to Si partitioning is smaller. Silicon partitioning into the core starts rather late during accretion, and in most cases proto-Earth has to reach >60% of its current mass before the core contains 1wt% of Si. At this point, the temperature of partitioning is high and the isotope fractionation term becomes rather small. If the partitioning of O and the resulting mass-balances restrictions place further limits on the amount of Si in the core, e.g. 3.6 wt%, core formation would not produce any significant Si isotope fractionation in BSE. In general, it then becomes difficult to ascertain that the silicon isotopic difference between BSE and chondrites is solely due to core formation. Recent work has shown that angrite meteorites have Si isotope compositions enriched in heavy Si similar to BSE (Pringle et al. 2014; Dauphas et al. 2015). Although it is very likely that the angrite parent body had a metallic core (Kleine et al. 2012), Si isotope fractionation due to core formation seems an unlikely process to have produced the Si isotope compositional range seen in angrites (Dauphas et al. 2015). Pringle et al. (2014) suggested evaporative loss of Si could have produced the BSE like Si isotope composition, while Dauphas et al. (2015) argue that the Si isotope composition of solar system components may indeed reflect the formation of forsterite rich condensates in equilibrium with nebular SiO$_2$. In the latter case the Si isotope signature of BSE would not reflect

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core formation, but nebular processes that were mostly inherited from the building blocks of bulk Earth (Dauphas et al. 2015). The small isotopic offset in our model supports the notion that core formation alone might not be able to explain the isotopic enrichment of heavy Si isotopes in BSE.

Even though the Si isotope composition may not be that unique after all, the Mg/Si ratio of BSE certainly is. The presence of Si in the core could rectify the super-chondritic Mg/Si ratio of BSE to yield a bulk earth with a Mg/Si composition matching that of carbonaceous chondrites (Allègre et al. 1995; McDonough 2003; Palme and O'Neill 2003). Using the theoretical maximum of Si in the core (3.6wt%) and the best estimate for Si content in BSE of 21.22 wt% (McDonough 2003), the bulk earth Si content comes to 15.5 wt%. Depending on the value used for the Mg content of bulk earth we obtain Mg/Si weight ratios for bulk earth of ~0.992 (15.4 wt% Mg) (Hart and Zindler 1986; McDonough 2003) or ~0.965 (15.0 wt% Mg) (Palme and O'Neill 2003), at the high end of the range observed in carbonaceous chondrites (Palme and O'Neill 2003). Correcting bulk Earth's Mg/Si ratio and Si isotope composition for Si partitioning into the core produces different silicate reservoirs (bulk earth, carbonaceous chondrites and angrite achondrites) with very similar Mg/Si ratios, but different Si isotope compositions, with carbonaceous chondrites and angrites falling on either side of bulk Earth (Armytage et al. 2011; Pringle et al. 2014; Savage et al. 2014).

Conclusions

In this paper we argue that when taking into account the partitioning of elements from the cores of already differentiated objects accreting to Earth might change the outcome of accretion models. Our model requires oxidizing initial conditions, with as much as 11-15wt% FeO in BSE, to match expected ranges for core/mantle partitioning, despite using partitioning data that were previously used in support of reducing accretion. If accretion takes place under initially reducing conditions, the model fails to meet expected core/mantle values for moderately siderophile elements Ni and Co. This is because of

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siderophile elements are concentrated within the accreting metal and will remain in that phase as long as conditions are oxidizing. The range of peak pressures for metal silicate partitioning is 60±6 GPa and oxygen fugacity must decrease to meet modern FeO mantle contents as accretion continues. There is thus a wide space for solutions in terms of initial FeO, as well as the range of pressures, both of which agree well with recent work by Siebert et al. (2013).

Implications

Metal-silicate partitioning and core formation under oxidizing conditions has some interesting implications for the terrestrial Si budget, as the amount of Si potentially present in the core is limited by O partitioning into metal. The partition model overestimates the Si content in the core by almost 2-3 wt%, depending on the initial FeO in BSE. The higher the initial FeO BSE, the more FeO and thus O has to partition into the core, which places some limits on the amount of Si in the core. By mass-balance considerations, the maximum Si content in the core is about 3.6wt%, when the initial FeO BSE was ~11wt%, and decreases to a Si maximum of about 2.5wt% for initial FeO BSE of ~15wt%. These rather low Si contents are comparable with other accretion models that predict core formation under oxidizing conditions (Siebert et al. 2013; Badro et al. 2014). The implications are far reaching; core formation and accompanied Si partitioning are unlikely to produce a significant isotopic offset and therefore render bulk earth's Si isotope composition non-chondritic, although the effect of pressure on the isotopic fractionation factor for Si has yet to be investigated. From comparison to recent angrite data, it seems that nebular (or other planetary) processes rather than core formation are more likely to be the reason for Si isotope variations among major solar system reservoirs (Dauphas et al. 2015). Correcting bulk earth's Si content for Si in the core, yields Mg/Si weight ratios of 0.965 and 0.992, respectively – both estimates are at the higher end of the range observed for carbonaceous chondrites.

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Figure Captions:

Figure 1: Schematic box-model representation of the accretion model used in this study. Planet Earth is accreting from already differentiated planetary embryos with a fixed metal proportion $F = 0.323$. Silicate material is added to Earth's mantle, accreting metal can follow two pathways; for $k = 1$ all accreting metal is first added to the silicate mantle and subjected to silicate-metal partitioning as well as accretion metal-silicate partitioning, e.g. accreting metal is contributing elemental load to the silicate mental, here controlled by partition coefficients. Even though $k = 1$ and all accreting metal is allowed to equilibrate with the silicate mantle, the metal might - depending on prevailing partitioning conditions - not contribute to the elemental budget of the silicate mantle.
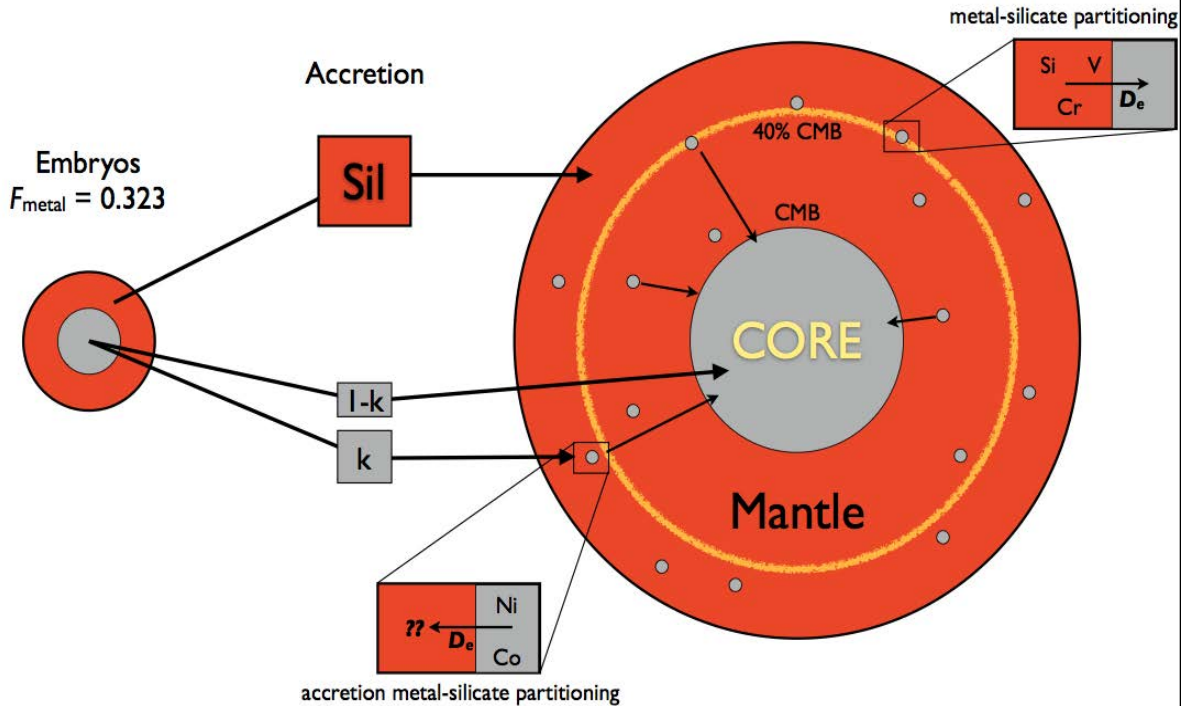
Figure 2: The diagram shows the function used in the model to simulate the change in FeO_{BSE} during accretion of Earth M(x). The final FeO_{BSE} (κ) is 0.0810 (or 0.063 wt% Fe in BSE), the initial FeO_{BSE} is given by ($\varphi = 1.4 \Rightarrow \varphi\kappa = 1.4 \times 0.081 = 0.1132$) and the division of x by ς (=1.0) ensures that final FeO_{BSE} is reached when M(x) = 1.0 (100%). Parameter p and q to define the mode of FeO_{BSE} change; depending on a chosen set of p and q the model can hold the initial FeO_{BSE} for a certain period of accretion decreasing (e.g. $p/q = 6/1$), or have an early drop in FeO_{BSE} and slow decrease thereafter (e.g. $p/q = 1/6$). Linear increase for $p/q = 1$.

Figure 3: Modeling accretion under initial reduced conditions (FeO_{BSE} of ~2wt%) and a peak pressure of accretion of 40 GPa. Chromium, Si and V partitioning as well as Si isotope offset match expected ranges. Moderately siderophile elements, Ni and Co, are not sufficiently abundant in BSE to yield expected core/mantle abundance ratios. Regression parameter used: Si: Corgne et al. (2008), Co, Ni, Cr, V: Siebert et al. (2011).
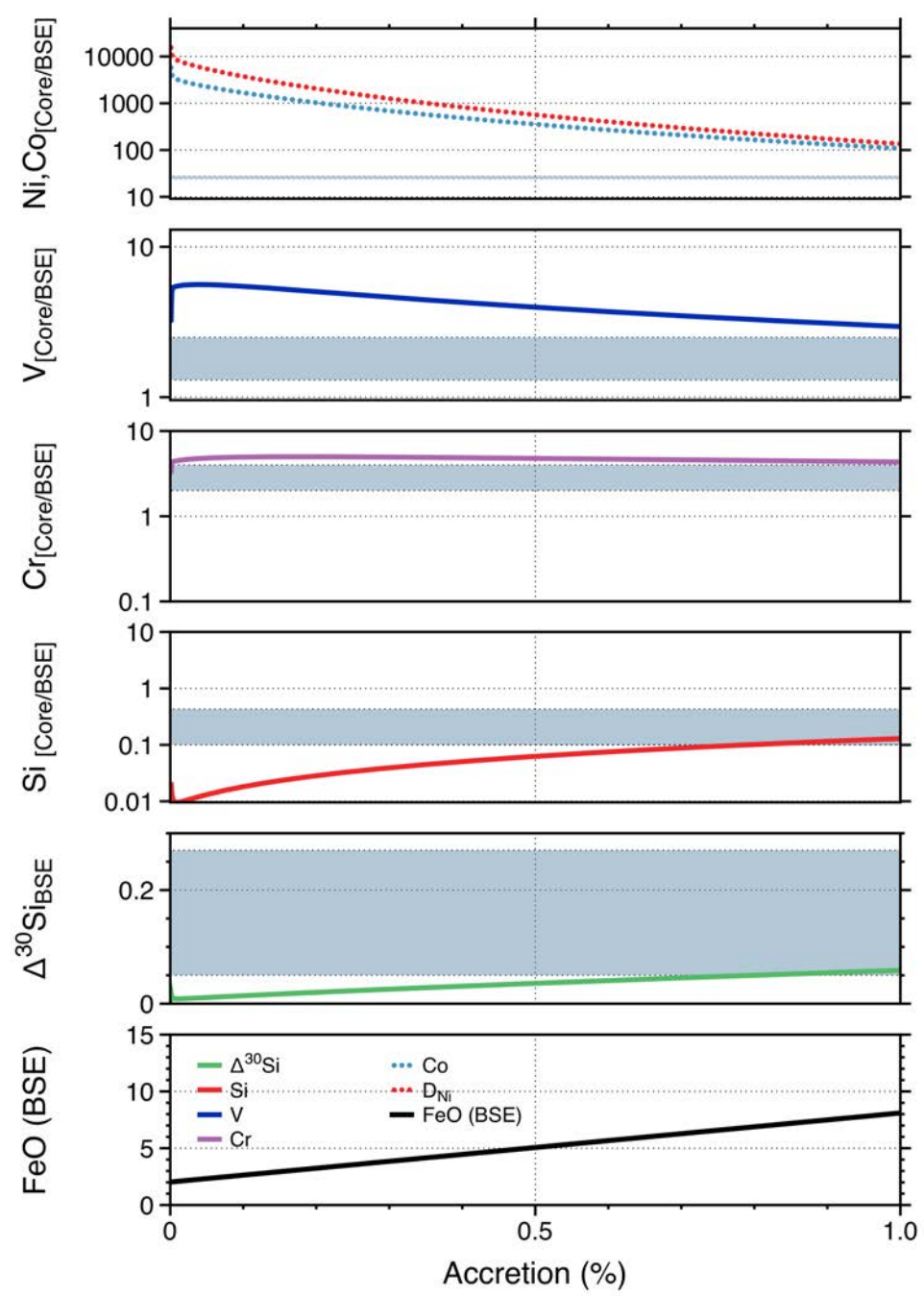
Figure 4: A contour plot of 10,000 model runs showing the relationship between peak pressure of accretion P_0 and the starting FeO content in BSE. Oxygen fugacity decreases in linear fashion.

Figure 5: A contour plot of 2,500 model runs showing the relationship between peak pressure of accretion P_0 and the starting FeO content in BSE. Because of shape parameter $p = 8$, initial oxidation state remains stable for a larger fraction of accretion.

Figure 6: A contour plot of 2500 model runs showing the relationship between initial fO_2 in BSE and the fO_2 gradient shape parameter p, peak pressure $P_0 = 61$ GPa.
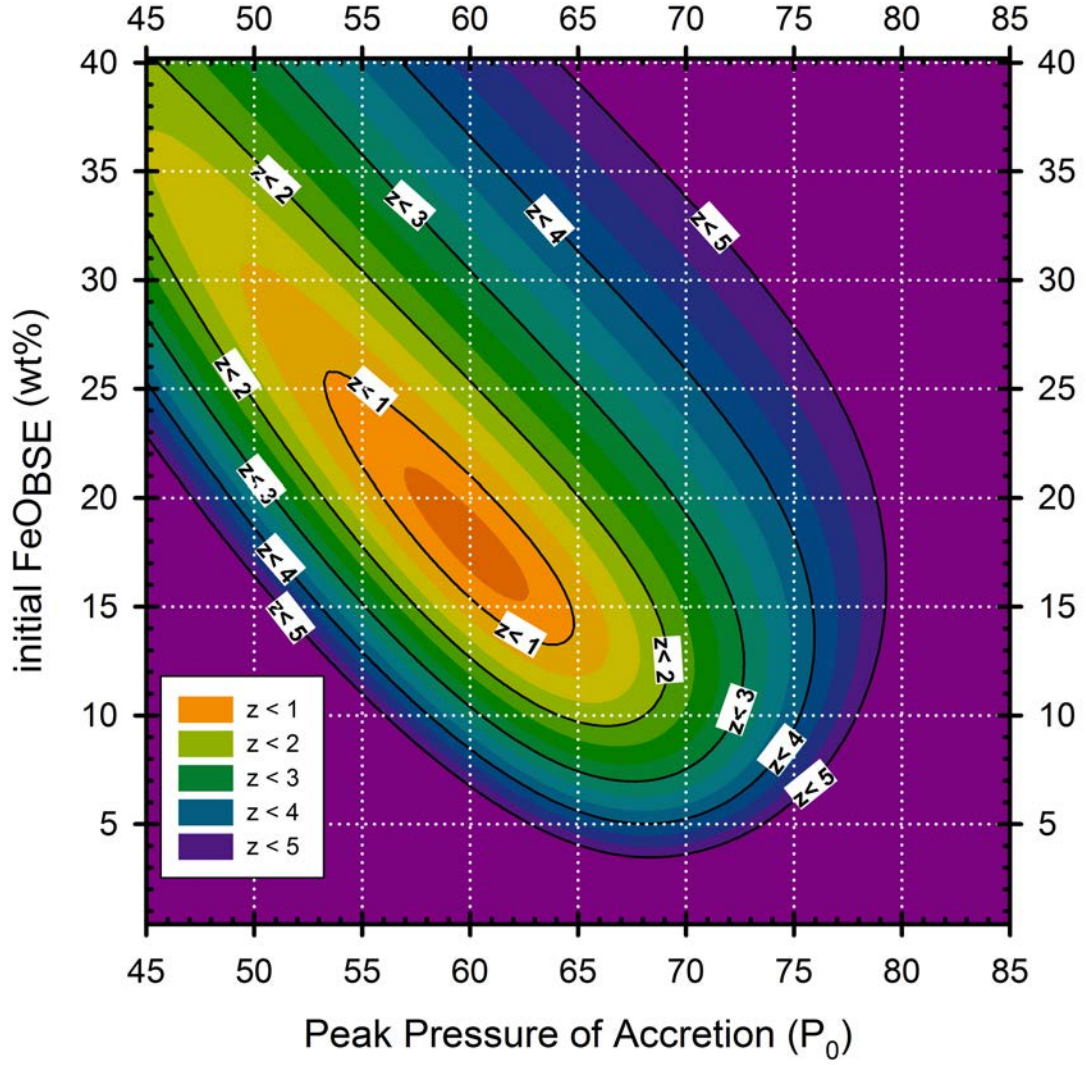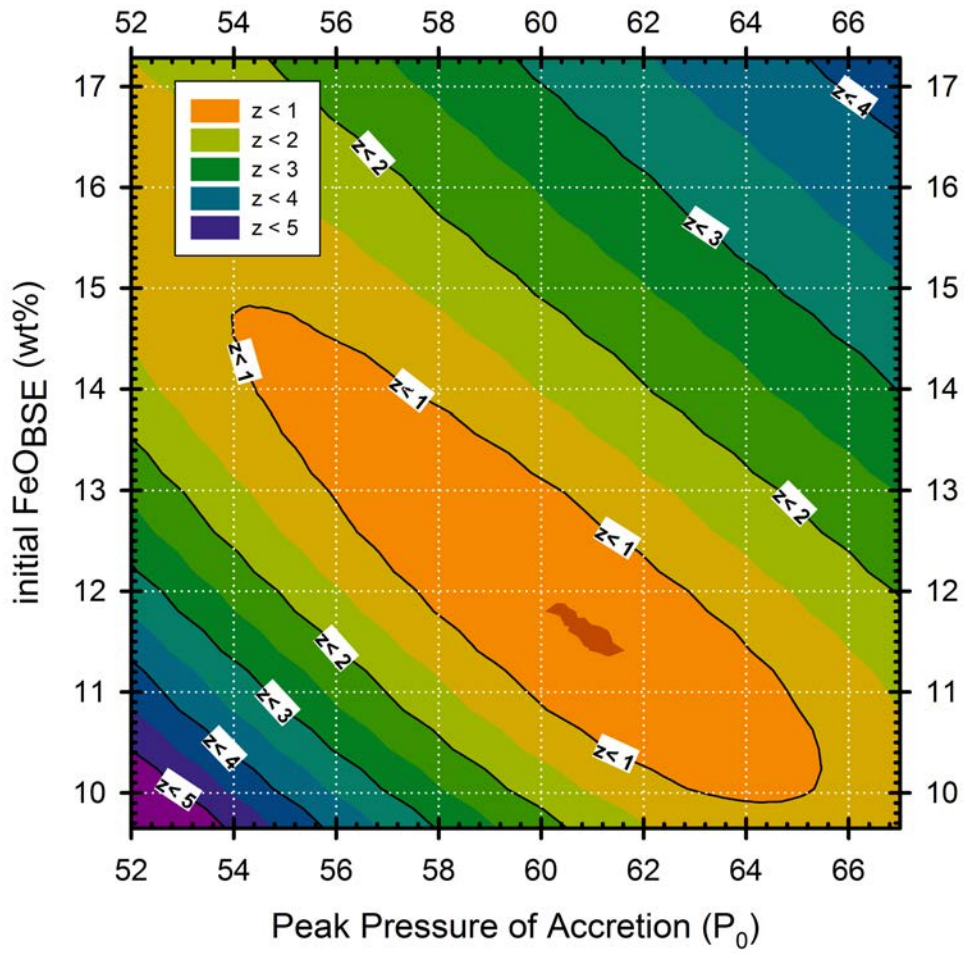
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Embryos
$F_{metal} = 0.323$

Accretion

Sil

metal-silicate partitioning

| Si | V | D_e |
| Cr | | |

40% CMB

CMB

CORE

Mantle

l-k

k

Ni
?? D_e Co

accretion metal-silicate partitioning

FeO$_{BSE}$ as function of accretion

p/q = 6/1

p/q = 2/1

p/q = 4/1

p/q = 10/1

p/q = 1/2

p/q = 1/1

p/q = 1/6

FeO$_{BSE}$ at M = 100%

FeO$_{BSE}$ (wt%)

M(x)

Starting FeO$_{BSE}$ vs. Peak Pressure
(linear fO$_2$ gradient)

Starting FeO$_{BSE}$ vs. Peak Pressure
(fO$_2$ gradient, p = 8)

Starting FeO$_{BSE}$ vs. Shape of fO$_2$ Gradient
P$_0$ = 61 GPa