



## Oxygen as a light element: A solution to single-stage core formation

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### ABSTRACT

The abundances of siderophile elements in the silicate Earth indicate that Earth's iron-rich core probably formed at high pressure and high temperature. A popular model of core formation considers that the concentrations of several moderately siderophile elements are consistent with a scenario of simple single-stage equilibration at the base of a magma ocean. However, recent work using temperature sensitive partitioning data for V and Nb have casted doubt on this interpretation since the required basal temperature would greatly exceed that of the mantle solidus. Here we show that single-stage core formation event could explain the mantle contents of siderophile elements best constrained by experiment (Ni, Co, V, Mn, Cr, and Nb) provided that the core contains a few weight percents of oxygen. Our calculations, based on partitioning and metallurgy data, reveal that V and Nb become significantly less siderophile with increasing the O content of core-forming materials, while the behaviour of Ni, Co, Cr and Mn is little affected. Since the other likely light element candidates C, Si and S do not drastically influence the siderophile behaviour, we conclude that a simple-equilibration scenario is a viable hypothesis only if O contributes partially to the core density deficit. This interpretation is consistent with the W budget of the silicate Earth and recently published W metal-silicate partitioning data. The presence of a few weight percents of oxygen in the core is also in agreement with recent high-pressure high-temperature solubility measurements in molten iron equilibrated with perovskite and ferropericlasite.

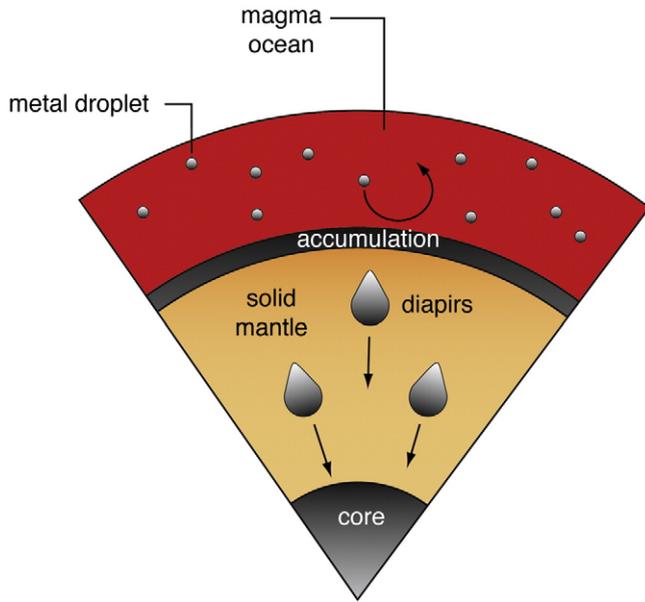
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### 1. Introduction

The mechanisms by which our planet differentiated into a central metallic core and a silicate envelope are still not well understood. Moreover, the identity of the light element(s) responsible for the density deficit of the core relative to pure Fe or Fe–Ni alloy is not known. One way of investigating core formation and core composition has been to study experimentally the partitioning of siderophile elements between silicate and metal phases as a function of the key controlling variables such as composition, pressure and temperature. Derived partitioning data have then been compared with the required 'natural' distribution estimated from terrestrial and meteoritic materials to shed light on the conditions of core formation. Since it is likely that extensive melting occurred early in Earth's history due to the high accretional and gravitational energies (e.g. Davies, 1985; Benz and Cameron, 1990; Tonks and Melosh, 1993; Abe, 1997), partitioning experiments have been carried out at high temperature on silicate and metal liquids. Early results have shown that low-pressure partitioning data are inconsistent with the depletion of many siderophile elements in the silicate Earth (e.g. Newsom, 1990; Capobianco et al., 1993). In contrast, data collected at high pressure indicate a fairly good agreement (e.g. Thibault and

Walter, 1995; Li and Agee, 1996; Righter et al., 1997). These results, in combination with results from planetary accretion modelling, have led to the development of a generally accepted theory, in which core formation occurred during a deep magma ocean event. In the traditional view of this theory, small molten droplets of core materials segregated through a silicate magma ocean and equilibrated with it until they reached its base. The metal then migrated rapidly to the centre of the planet without significant chemical exchange with the surrounding solid mantle via a mechanism of inverted diapirism or deformation-driven percolation (Stevenson, 1990; Karato and Murthy, 1997; Rushmer et al., 2000; Rubie et al., 2003) (Fig. 1). Among the models of core formation in a magma ocean, the single-stage model has brought more attention because of its relative simplicity. It is also popular because it can be tested explicitly, unlike heterogeneous models, which call for changes in oxygen fugacity and composition of the planet building blocks (e.g. Wänke, 1981; O'Neill, 1991). According to the single-stage equilibration model, conditions during core formation remained relatively unchanged. In other words, the pressure and temperature of last equilibration as well as composition (including oxygen fugacity) were kept relatively constant. It has also been proposed that the single equilibration conditions may more plausibly represent an average of a wider range of conditions during a more dynamic process (Li and Agee, 1996), which could have included late giant impacts. Based essentially on Ni and Co partitioning data, it has been proposed that the pressure of last equilibration should range

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**Fig. 1.** Cartoon illustrating the processes of core–mantle differentiation in a magma ocean event, as proposed by the homogeneous single-stage core formation model (Li and Agee, 1996; Righter et al., 1997; Chabot and Agee, 2003). In this model, the conditions of last equilibration at the base of the magma ocean, i.e. its depth, remained relatively unchanged with time. Fluid dynamics considerations (Stevenson, 1990; Karato and Murthy, 1997; Rushmer et al., 2000; Rubie et al., 2003) let us envisage the following scenario. Small metal droplets settle through the magma ocean, equilibrating with the surrounding silicate melt. The molten metal then accumulates at the base of the magma ocean, before forming periodically large diapirs, which descend rapidly to the growing core without significant equilibration with the solid mantle.

between 30–60 GPa (Li and Agee, 1996; Righter et al., 1997; Li and Agee, 2001; Walter and Tronnes, 2004; Chabot et al., 2005).

A blow to the single-stage model has come from the study of vanadium (V) and niobium (Nb), two moderately siderophile elements whose metal–silicate partition coefficients increase sensibly with an increase of temperature (Gessmann and Rubie, 2000; Chabot and Agee, 2003; Wade and Wood, 2005; Corgne et al., 2008; Wood et al., 2008). At the pressure conditions required to match Ni and Co mantle depletions, temperature conditions required to match Nb and V mantle depletions are several hundreds of degrees above the mantle solidus (Wade and Wood, 2005; Corgne et al., 2008; Wood et al., 2008). If equilibration took place in a partially molten mantle as suggested by metal–silicate partitioning studies, then the temperature at the base of the magma ocean should have been approximately on the mantle

solidus (transition solid–liquid mantle). If temperature and pressure conditions are fixed on the mantle solidus, bulk core–mantle partition coefficients for Nb and V are then too low to explain the mantle depletions in these two elements. To resolve this anomaly, it has been suggested that the building materials of the Earth were initially reduced materials and then became progressively oxidized with time (Wade and Wood, 2005; Corgne et al., 2008; Wood et al., 2008). Thus, rather than resulting from a single stage event at relatively fixed conditions of high pressure and high temperature, Earth's core may in fact have formed in a more complex event, imprinted by heterogeneous accretion and the progressive growth and oxidation of the planet and its magma ocean (Wade and Wood, 2005; Corgne et al., 2008; Wood et al., 2008). In this dynamic model, the effect of low initial oxygen fugacity overcomes the effect of low magma ocean temperatures in the small proto-Earth. This leads to overall Nb and V contents in the core larger than in the case of single-stage equilibration at solidus conditions. Another possibility, which is largely speculative in the absence of well-quantified physical constraints, is that giant impacts during the late stage of accretion may have induced complete mantle melting, leading on average to superliquidus conditions of equilibration. However, most fluid dynamics simulations suggest that even the largest impacts are unlikely to have melted the entire mantle (Davies, 1985; Tonks and Melosh, 1993; Solomatov, 2000).

Here, we present an alternative to these two hypotheses by showing that the hypothesis of single-stage equilibration is a viable one provided that a few weight percents of oxygen partitioned into the core. The reason for this is that the addition of oxygen in core materials mimics the influence of temperature on the siderophile behaviour of V and Nb. More specifically, a high O content in the iron alloy favours the incorporation of Nb and V, without affecting the other siderophile elements.

## 2. Method

Following the approach adopted by Wade and Wood (2005), Corgne et al. (2008) and Wood et al. (2008), the partition coefficient of an element  $i$  ( $D_i$ ) measured experimentally can be parameterized as follows:

$$\log D_i = a + \frac{b}{T} + c \frac{P}{T} + d(nbo/t) - \frac{v}{2} \log \left( \frac{X_{\text{FeO}}^{\text{silicate}}}{X_{\text{Fe}}^{\text{metal}}} \right) - \log \left( \frac{\gamma_i^{\text{metal}}}{(\gamma_{\text{Fe}}^{\text{metal}})^{v/2}} \right) \quad (1)$$

where  $P$  is the pressure in GPa,  $T$  is the temperature in K,  $nbo/t$  is the ratio of non-bridging oxygen atoms to tetrahedrally-coordinated cations,  $v$  is the valence of element  $i$ ,  $X$  the molar fraction and  $\gamma$  the

**Table 1**  
Compilation details and regression parameters used in Eq. (2).

Element $i^a$	Compilation	$n^b$	$P$ (GPa) <sup>c</sup>	$T$ (K) <sup>c</sup>	$a$	$b^d$	$c$	$d$
$\text{Ni}^{2+}$	Corgne et al. (2008)	81	0–42	1533–3000	0.5	3100	–78 (5) <sup>e</sup>	–0.073 (15)
	Wade and Wood (2005)	46	0–25	1560–3000	0.64	3097	–123 (9)	0
$\text{Nb}^{5+}$	Corgne et al. (2008)	21	2–25	2123–3000	4.09	–15500	–166 (31)	–0.75 (16)
	Wood et al. (2008)	20	1.5–25	1753–3000	2.84	–13240	–114 (43)	–0.47 (15)
$\text{Mn}^{2+}$	Corgne et al. (2008)	71	2–26	1723–3000	–0.02	–5600	38 (6)	0.036 (10)
	Wade and Wood (2005)	26	2–25	1973–3000	0.04	–5761	49 (16)	0
$\text{Cr}^{2+}$	Corgne et al. (2008)	65	2–25	1723–3000	0.09	–2845 (461)	–20 (10)	0.000 (13)
	Wood et al. (2008)	46	1.5–25	1753–3000	0.64	–4232 (538)	–22 (13)	0
$\text{Co}^{2+}$	Wade and Wood (2005)	35	0–25	1560–3000	0.01	2511	–45 (11)	0
$\text{V}^{3+}$	Wood et al. (2008)	46	1.5–25	1753–3000	0.86	–8548	–62 (19)	–0.101 (29)

<sup>a</sup> Valence states considered here are the dominant states expected at conditions of core formation.

<sup>b</sup> Number of experimental data in the compilation.

<sup>c</sup>  $P$ – $T$  ranges over which experimental data were collected.

<sup>d</sup> Free-energy data were used to estimate the temperature dependence ( $b$  parameters) of the Fe– $i$  exchange reaction. As shown by Wade and Wood (2005) and Corgne et al. (2008), the free-energy data parallel the trends of the partitioning results on the reciprocal temperature plots, suggesting that they provide a good approximation of the temperature dependence. Since there are no thermodynamic data available for solid and liquid CrO, the  $b$  coefficient for  $\text{Cr}^{2+}$  was treated as an unknown like the other coefficients and estimated by multiple-linear regression.

<sup>e</sup> Values in parentheses are one standard deviation in least digits cited.

activity coefficient. Coefficients  $a$ ,  $b$ ,  $c$  and  $d$  are regression coefficients obtained by Wade and Wood (2005), Corgne et al. (2008) and Wood et al. (2008) using published and their own partitioning data obtained over a wide range of pressure and temperature conditions (Table 1). Rearranging Eq. (1) to have  $P$  as a function of  $T$  gives:

$$P = \frac{T}{c} \cdot \left[ \log D_i - a - d(nbo/t) + \frac{v}{2} \log \left( \frac{X_{\text{FeO}}^{\text{silicate}}}{X_{\text{Fe}}^{\text{metal}}} \right) + \log \frac{(\gamma_i^{\text{metal}})}{(\gamma_{\text{Fe}}^{\text{metal}})^{v/2}} \right] - \frac{b}{c} \quad (2)$$

Using Eq. (2), it is possible to calculate the conditions of pressure and temperature, which satisfy the bulk core–mantle partition coefficients. The bulk  $D_i$  values listed in Table 2 were calculated from estimates of the bulk Earth and bulk silicate Earth compositions (Allègre et al., 1995; McDonough and Sun, 1995; Allègre et al., 2001; McDonough, 2003; Münker et al., 2003; Palme and O'Neill, 2003). For the silicate, we took an  $nbo/t$  value of 2.7 and a FeO content of 8 wt.% as in a fertile peridotite composition. The chosen FeO content implies that the oxygen fugacity ( $f_{\text{O}_2}$ ) remained relatively unchanged during core formation, in agreement with the idea that equilibration took place at a unique  $P$ – $T$ – $f_{\text{O}_2}$  condition (single-stage core formation). The modelled oxygen fugacity is about 2 log units below the IW buffer as given by the current mantle/core FeO/Fe ratio. The activity coefficients  $\gamma_{\text{Fe}}^{\text{metal}}$  and  $\gamma_i^{\text{metal}}$  were determined using the interaction parameter approach and the method described by Ma (2001). In this method, the activity coefficients of the solvent (here Fe) and the  $N-1$  solutes ( $i$ ) in a metallic solution containing  $N$  components can be expressed as follows:

$$\begin{aligned} \ln \gamma_{\text{Fe}} = & \sum_{i=1}^{N-1} \varepsilon_i^i (X_i + \ln(1-X_i)) \\ & - \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \varepsilon_j^k X_j X_k \left( 1 + \frac{\ln(1-X_j)}{X_j} + \frac{\ln(1-X_k)}{X_k} \right) \\ & + \sum_{i=1}^{N-1} \sum_{\substack{k=1 \\ (k \neq i)}}^{N-1} \varepsilon_i^k X_i X_k \left( 1 + \frac{\ln(1-X_k)}{X_k} - \frac{1}{1-X_i} \right) \\ & + \frac{1}{2} \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \varepsilon_j^k X_j^2 X_k^2 \left( \frac{1}{1-X_j} + \frac{1}{1-X_k} - 1 \right) \\ & - \sum_{i=1}^{N-1} \sum_{\substack{k=1 \\ (k \neq i)}}^{N-1} \varepsilon_i^k X_i^2 X_k^2 \left( \frac{1}{1-X_i} + \frac{1}{1-X_k} + \frac{X_i}{2(1-X_i)^2} - 1 \right) \end{aligned} \quad (3)$$

**Table 2**  
Likely ranges of core–silicate Earth partition coefficients.

Element $i$	$D_i$
Ni	24–28
Co	23–26
Mn	0–2
Cr	2–4
V	1.3–2.5
Nb	0.2–1.4

Ranges were calculated from estimates of bulk Earth and bulk silicate Earth compositions (Allègre et al., 1995; McDonough and Sun, 1995; Allègre et al., 2001; McDonough, 2003; Münker et al., 2003; Palme and O'Neill, 2003).

and

$$\begin{aligned} \ln \gamma_i = & \ln \gamma_{\text{Fe}}^0 + \ln \gamma_i^0 - \varepsilon_i^i \ln(1-X_i) \\ & - \sum_{j=1(j \neq i)}^{N-1} \varepsilon_i^j X_j \left( 1 + \frac{\ln(1-X_j)}{X_j} - \frac{1}{1-X_i} \right) \\ & + \sum_{j=1(j \neq i)}^{N-1} \varepsilon_i^j X_j^2 X_i \left( \frac{1}{1-X_i} + \frac{1}{1-X_j} + \frac{X_i}{2(1-X_i)^2} - 1 \right) \end{aligned} \quad (4)$$

where  $\gamma_i^0$  is the activity coefficient of solute  $i$  when it is infinitely dilute in pure liquid Fe and  $\varepsilon_i^j$  is the interaction parameter between element  $i$  and element  $j$  (Table 3, Japan Society for the Promotion of Science and the Nineteenth Committee on Steelmaking (JSPS-NCS), 1988). The interaction parameter approach was also used by Wade and Wood (2005), Corgne et al. (2008) and Wood et al. (2008) to ‘correct’ the metal–silicate partition coefficients ( $D_i$ ) for the effect of metal composition, given that the compilation of experimental data used by these authors span a fairly wide compositional range for the metal. The applied correction allows a precise parameterization of  $D_i$  as a function of pressure, temperature, silicate composition and oxygen fugacity (Table 1). In the present study, we use the interaction parameter approach to determine the activity coefficients  $\gamma_{\text{Fe}}^{\text{metal}}$  and  $\gamma_i^{\text{metal}}$  for various hypothetical core compositions (see Section 3). The following approximations are obtained when element  $i$  is present at trace levels ( $X_i \sim 0$ ) and taking account of minor amounts of a light element (LE):

$$\ln \gamma_{\text{Fe}} \approx \varepsilon_{\text{LE}}^{\text{LE}} [X_{\text{LE}} + \ln(1-X_{\text{LE}})] \quad (5)$$

$$\ln \gamma_i \approx \ln \gamma_{\text{Fe}}^0 + \ln \gamma_i^0 - \varepsilon_i^{\text{LE}} \ln(1-X_{\text{LE}}) \quad (6)$$

The  $\varepsilon_i^j$  approach takes into account the effects of temperature, but not those of pressure, due to the lack of high-pressure data. However, pressure should have a moderate influence on  $\varepsilon_i^j$ . Indeed, a good agreement is found using room pressure  $\varepsilon_i^j$  to fit the effect of light elements on high-pressure partitioning data for siderophile elements (Wade and Wood, 2005; Corgne et al., 2008; Wood et al., 2008).

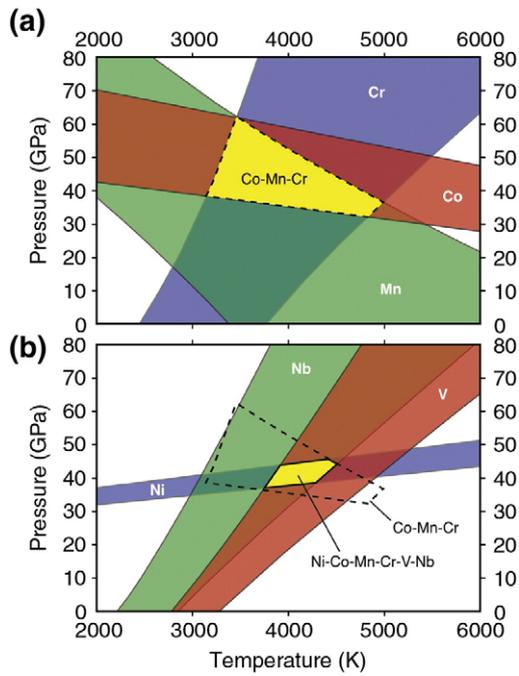
### 3. Results

Using Eq. (2), we calculated the conditions of pressure and temperature consistent with the bulk partition coefficients between the core and the silicate Earth (Table 2). The calculations were carried out for the moderately siderophile elements with the best constrained partitioning behaviours: Ni, Co, Mn, Cr, V and Nb. Five end-member core composition models are envisaged here. First, we consider the case where the core is made of 95 wt.% Fe and 5 wt.% Ni, i.e. it contains no light element. The limited variation of the Fe/Ni ratio in chondritic meteorites and in the silicate Earth constrain the Ni content of the core to about 5 wt.% (e.g. McDonough and Sun, 1995). The other four

**Table 3**  
Interaction parameters ( $\varepsilon_i^j$ ) and activity coefficients in the infinite dilute liquid iron solution ( $\gamma_i^0$ ) at 1873 K (JSPS-NCS, 1988).

Element $i$	$\ln \gamma_i^0$	$\varepsilon_i^{\text{C}}$	$\varepsilon_i^{\text{C sat.}}$	$\varepsilon_i^{\text{Si}}$	$\varepsilon_i^{\text{S}}$	$\varepsilon_i^{\text{O}}$
LE		12.8	12.8	12.4	–5.6	–10.5
Ni	–0.4	2.3	0.9	1.2	0.0	1.4
Co	–0.6	1.7	0.4	0*	0.6	1.9
Mn	0.4	–1.8	–0.7	–3.2	–5.7	–4.7
Cr	0*	–4.9	–1.0	0.0	–2.1	–11.7
V	–2.5	–6.0	–2.1	5.2	–3.8	–29.3
Nb	–1.6	–22.7	–2.6	–0.7	–5.5	–46.6

\*Interactions are assumed to be negligible given the magnitude of the interactions for elements with similar chemical behaviour. Interaction parameters at the temperature of interest are calculated from the tabulated values at 1873 K as suggested by JSPS-NCS (1988).

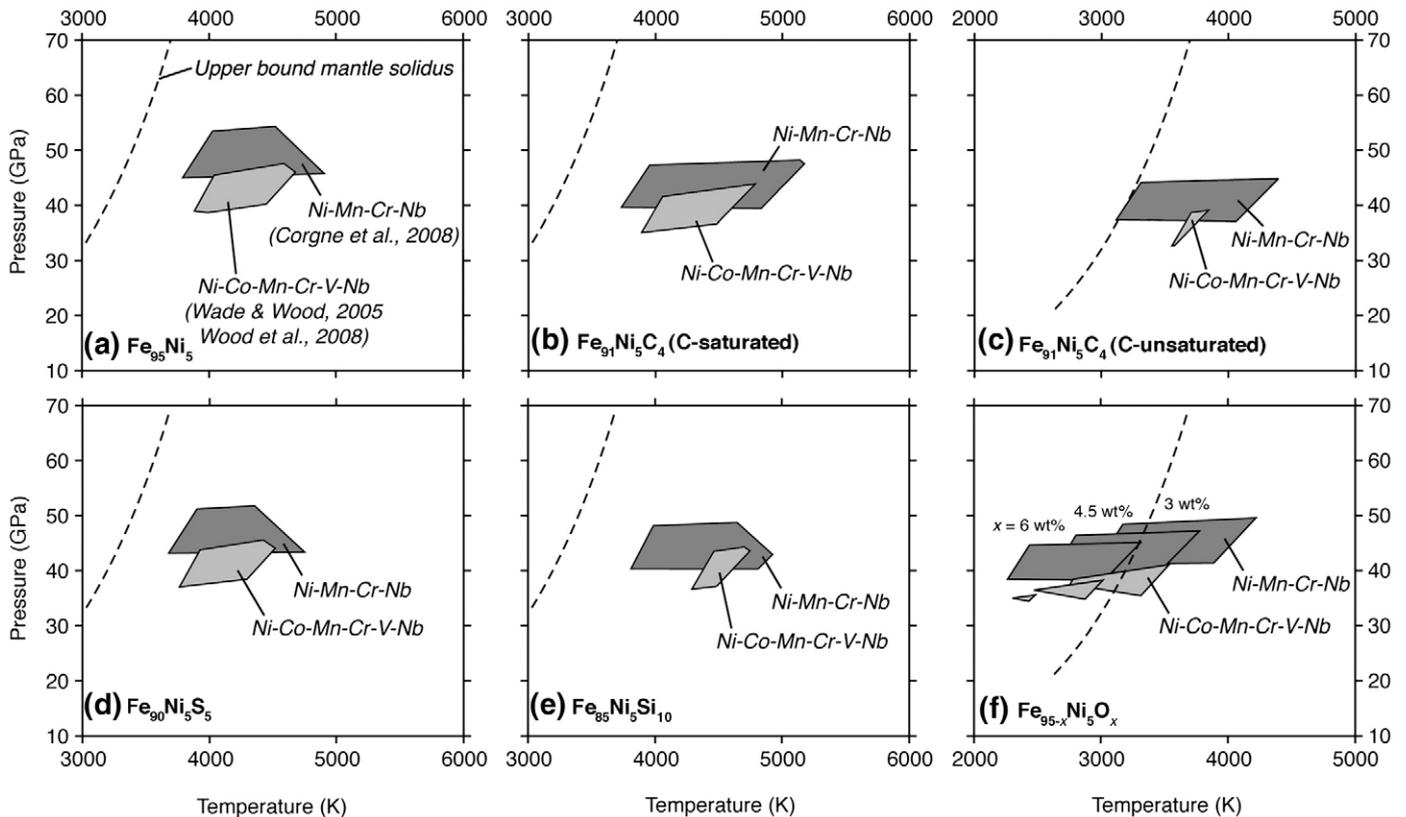


**Fig. 2.** Determination of the  $P$ - $T$  solution domain for the  $\text{Fe}_{95}\text{Ni}_5\text{S}_5$  core end-member composition using the partitioning parameterization for Ni-Co-Mn-Cr-V-Nb from Wade and Wood (2005) and Wood et al. (2008). The individual solution for each element is calculated using Eq. (2) and taking account of uncertainties on the  $a$ - $b$ - $c$ - $d$  regression parameters and  $D$  values. The solution domain is first constrained from the Co-Mn-Cr set in (a). It is further restricted in (b) when taking account of Ni, V and Nb.

end-member compositions correspond to a scenario where  $x$  wt.% light element is included into the core, with the remaining composition being  $95-x$  wt.% Fe and 5 wt.% Ni. The values of  $x$  are taken as a generous upper bound of the likely range of light element content estimated from cosmochemical, experimental and theoretical arguments:  $<5$  wt.% for S (e.g. Ganapathy and Anders, 1974; McDonough and Sun, 1995; Dreibus and Palme, 1996; Sherman, 1997),  $<10$  wt.% for Si (e.g. Allègre et al., 1995; Sherman, 1997; Gessmann et al., 2001; Malavergne et al., 2004),  $<4$  wt.% for C (e.g. Wood, 1993; McDonough, 2003; Dasgupta and Walker, 2008; Fiquet et al. 2009), and  $<10$  wt.% for O (e.g. Ringwood, 1977; Poirier, 1994; O'Neill et al., 1998; Alfè et al., 2002; Rubie et al., 2004; Asahara et al., 2007).

In some cases, the interaction parameters are valid for compositional ranges that are more restrictive than the ones considered in this study. These restrictions concern  $\varepsilon_{\text{V}}^{\text{S}}$  (11 wt.% S),  $\varepsilon_{\text{Mn}}^{\text{C}}$  (1.2 wt.% C),  $\varepsilon_{\text{Mn}}^{\text{Si}}$  (2.8 wt.% Si) and  $\varepsilon_{\text{Cr}}^{\text{Si}}$  (5 wt.% Si). Enokido et al. (1995) have shown however that  $\varepsilon_{\text{Mn}}^{\text{C}}$  tabulated by JSPS-NCS (1988) remains valid for C contents to at least 6.3 wt.%. For the parameterizations of Wade and Wood (2005), Corgne et al. (2008) and Wood et al. (2008) and the modelling of the present study, we considered that tabulated values provided good approximations in the absence of alternative values. Note that in the case of S, experiments with S contents above 10 mol% were excluded from the parameterizations of Wade and Wood (2005), Corgne et al. (2008) and Wood et al. (2008).

Fig. 2 presents an example (for the S-bearing core model composition) of how the final  $P$ - $T$  solution domain is obtained from the overlap between the individual solution domains for Ni, Co, Mn, Cr, V and Nb. Fig. 3 provides an illustration of the final  $P$ - $T$  solution domains for each end-member core composition models. In other

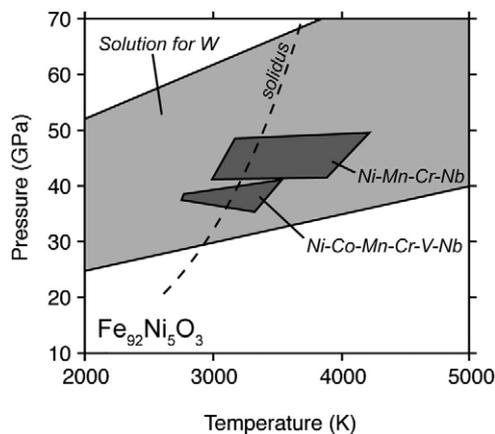


**Fig. 3.** Diagrams showing the conditions of pressure and temperature required to match the mantle abundances of Ni, Co, Mn, Cr, V and Nb as a function of the nature of the light element present in the core. End-member core compositions are given in weight percents. In (a) the core is made of 95 wt.% Fe and 5 wt.% Ni (i.e. no light element is present). In the other diagrams (b-f), light elements are included: 4 wt.% C in (b) and (c); 5 wt.% S in (d); 10 wt.% Si in (e); 3, 4.5 and 6 wt.% O in (f). Partition data used here are from Corgne et al. (2008) for the Ni-Mn-Cr-Nb compilation, and from Wade and Wood (2005) and Wood et al. (2008) for the Ni-Co-Mn-Cr-V-Nb compilation. Upper bound for the mantle solidus is from Zerr et al. (1998). As discussed in Section 3, the required  $P$ - $T$  conditions overlap the solidus curve only if oxygen is present in the core. Other potential candidates (S, Si and C) do not significantly shift the required conditions towards the mantle solidus.

words, these regions define the conditions of pressure and temperature required to explain concurrently the mantle depletions of the 6 best studied moderately siderophile elements. Two cases were envisaged for C depending on whether or not the core formed under conditions of C-saturation. As shown in Table 3, values of interaction parameters ( $\epsilon_i^C$ ) used for the modelling differ slightly between the two cases (except for Nb where it is more pronounced). As can be seen in Fig. 3, apart from the case where O is present in the core (Fig. 3f), the solution domains lie more than 500 K above the upper bound estimate for the mantle solidus (Zerr et al., 1998). As mentioned above, this is physically meaningless for a magma ocean model given that the mantle solidus defines the temperature at the base of the magma ocean. In the framework of the single-stage model for core formation, our results imply that neither Si, C and S can be the sole light element in the core. Note that in the case of a C-bearing core formed under C-unsaturation (i.e. if there is no residual carbon phase in the mantle), the  $P$ - $T$  solution for the Ni-Mn-Cr-Nb compilation of Corgne et al. (2008) comes close to the solidus curve as required (Fig. 3c). However, if one considers the  $P$ - $T$  domain obtained for the compilation including V (Wade and Wood, 2005; Wood et al., 2008), there is still a large mismatch. This is due to the fact that Nb is more sensitive than V to the presence of C under unsaturated conditions (Table 3). In contrast to Si, C and S, the addition of O to the core shifts the solution domain rapidly towards lower temperatures, hence towards the mantle solidus. A good match is obtained for average equilibrium conditions around 40 GPa and 3200 K with approximately a few weight percents of O in the core, between about 2 and 5 wt.% depending on the partitioning compilation used (Fig. 3f).

#### 4. Discussion

The behaviour of other siderophile elements could be used to test further the robustness of our model. A recent study by Cottrell et al. (2009), which was published after submission of the present manuscript, provides a first test. Cottrell et al. (2009) used published and new experimental data to parameterize the partitioning behaviour of W as a function of pressure, temperature, oxygen fugacity and composition. As done above for Ni, Co, V, Nb, Cr and Mn, we can use their parameterization to calculate the  $P$ - $T$  domain required to match the bulk core-mantle  $D_W$  ( $19 \pm 4$ ). As shown in Fig. 4, the solution domain calculated for the O-bearing core end-member largely

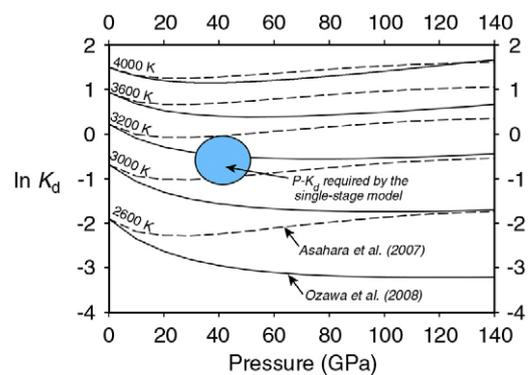


**Fig. 4.**  $P$ - $T$  solution domain for W and other siderophile elements for an end-member core composition containing 5 wt.% Ni and 3 wt.% O. The recent parameterization derived by Cottrell et al. (2009) was used for the calculation together with a core-silicate Earth partition coefficient of  $19 \pm 4$  estimated from concentrations in the bulk Earth and bulk silicate Earth (McDonough and Sun, 1995; Allègre et al., 2001; McDonough, 2003; Palme and O'Neill, 2003). Note that W partitioning is weakly dependent on temperature. Although not shown here, the W solution domain varies little over a range of oxygen contents between 0 and 10 wt.%, given the moderate value for  $\epsilon_W^O$  of 4.1 (JSPS-NCS, 1988).

overlaps the solution domains derived for the other siderophile elements. Therefore, this indicates that constraints from W partitioning are compatible with our interpretation that the viability of the simple-equilibration model requires the presence of some oxygen in the core.

There are at present no data for the partitioning of oxygen between molten metal and molten silicate that allows a direct estimation of the siderophile behaviour of oxygen during core formation in a deep magma ocean. However, recent studies have reported partition coefficients between deep mantle minerals and molten metal, which may be used as a proxy for molten silicate-molten metal partitioning as discussed in previous partitioning studies (e.g. Gessmann and Rubie, 1998; O'Neill et al., 1998). Interestingly, the estimate of the oxygen core content of a few weight percents is in good agreement with the derived oxygen solubility in molten iron coexisting with Mg-silicate perovskite at about 40 GPa and 3200 K. Takafuji et al. (2005) measured about 2 wt.% oxygen in molten iron coexisting with perovskite at 55 GPa and 3000 K, while Kawazoe and Ohtani (2006) reported contents between 2 and 3 wt.% at 27 GPa and  $\sim 3000$  K. A good agreement is also obtained with oxygen solubility data in molten iron coexisting with ferropericlasite. As shown in Fig. 5, oxygen contents between 2 and 5 wt.% required by the single-stage model are well fit by the solubility models established by Asahara et al. (2007) and Ozawa et al. (2008). These solubility models indicate that O solubility in molten iron is a strong function of temperature. At about 40 GPa, O contents of 2–5 wt.% correspond to a temperature range near 3200 K, in agreement with the average equilibrium temperature derived for the single-stage model. Therefore, based on the available O solubility data, it seems possible to incorporate the necessary amounts of oxygen during a scenario of single-stage core formation.

Another important constraint on the nature of the light element in the core comes from the seismic observation that the outer core is less dense than the inner core. This means that the outer core has a higher concentration of light element(s) than the inner core (e.g. Poirier, 1994). Using molecular dynamics simulations, Alfè et al. (2002) found that oxygen partitions more strongly in liquid iron during freezing due to its relatively small radius, whereas larger S and Si atoms partition equally between solid and liquid iron. The result of Alfè et al. (2002) is therefore consistent with the presence of oxygen in the core as required by the single-stage model. Alfè et al. (2002) further suggest that the outer core should contain  $\sim 8$  mol% O (i.e. 2–3 wt.% O).



**Fig. 5.** Partitioning of oxygen between molten iron and ferropericlasite. Solid lines and dashed lines represent the solubility models of Ozawa et al. (2008) and Asahara et al. (2007), respectively. The distribution coefficient  $K_d$  is a molar concentration ratio defined as  $K_d = X_{Fe}^{Metal} X_{O}^{Metal} / X_{FeO}^{Ferropericlasite}$ , with  $X_{FeO}^{Ferropericlasite} \sim 0.165$  in the mantle and  $X_{Fe}^{Metal} \sim 0.85$  in the core. The circular region indicates the  $P$ - $K_d$  conditions required by the single-stage model (i.e.  $P \sim 40$  GPa and  $\ln K_d$  between  $-0.1$  and  $-1.0$ ). Note the agreement in terms of  $P$ - $T$ - $K_d$  conditions between the solubility models of Ozawa et al. (2008) and Asahara et al. (2007) and the single-stage model requirements.

## 5. Conclusions and perspectives

Our main conclusion is that, in order for the scenario of simple equilibration at the base of a deep magma ocean to be viable, oxygen must be a contributor to the light element budget of the core. However, the amount of oxygen in the core required by the single-stage model (about 2–5 wt.%) is probably not sufficient to explain the entire density deficit of the core relative to pure Fe (e.g. Poirier, 1994). A combination of oxygen and one or more light elements should therefore be considered. Among the other potential candidates, silicon appears the most likely based on a wide range of arguments, including arguments from cosmochemistry, experimental petrology and mineral physics (e.g. Allègre et al., 1995; Sherman, 1997; Gessmann et al., 2001; Takafuji et al., 2005; Badro et al., 2007).

Future work should focus on improving the parameterizations used in this study and on developing new parameterization for other siderophile elements, such as the one recently proposed for W by Cottrell et al. (2009). In particular, partitioning data above 30 GPa and 3000 K would help test the accuracy of the extrapolations in temperature and pressure. Unfortunately, such melting experiments are technically challenging at present.

A final point should be raised regarding other possible scenarios of core formation. The single-stage model is attractive in its simplicity, but it may be too unrealistic to account for the complexity of events that occurred during Earth's accretion. A number of models have proposed a variety of potential complications: heterogeneous accretion (e.g. Wänke, 1981; O'Neill 1991, Wade and Wood 2005), incomplete re-equilibration between core and silicate Earth after a late Moon-forming giant impact (e.g. Halliday, 2004), inefficient core formation (e.g. Jones and Drake, 1986), addition of a late veneer (e.g. Kimura et al., 1974), and late addition of outer core materials to the mantle (e.g. Snow and Schmidt, 1998). Whatever the model put forward, our study underlines that oxygen – if it is considered as a light element in the core – has a significant control on the incorporation of siderophile elements in core-forming materials. Therefore, its influence should be carefully considered.

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