Fe-Ni ideality during core formation on Earth

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ABSTRACT

Earth’s core is essentially composed of a light-element bearing iron-nickel alloy (Birch 1964). The nickel content in the core has negligible effects on physical properties such as density and compressibility (e.g., Lin et al., 2003; Kantor et al., 2007; Martorell et al., 2013; Badro et al. 2014). This deters any attempt to determine or even estimate the nickel content of the core using seismological models, as in the case of light elements. It was recently proposed that the presence of nickel should fractionate iron isotopes in small planetary cores (Elardo and Shahar 2017), but the effect for a large (hot) planet such as the Earth would not be measurable; this observation however opens up the possibility that Ni can have an effect on element partitioning between the metallic alloy and the silicate melt during core formation. In this case, the siderophile trace-element composition of the mantle would in turn allow to constrain the Fe/Ni ratio in the core.

Here, we investigated the effect of nickel concentration in the metallic alloy on the partitioning of other elements at conditions directly relevant to core formation, using the laser-heated diamond anvil cell. We found no measurable effect of nickel concentration on the partitioning of Ni, Cr and V; the Fe-Ni alloy is chemically ideal over a broad range of Ni concentrations (3.5 to 48.7 wt%). The ideality of the Fe-Ni solution across a wide range of nickel concentration shows that Fe and Ni are not only twins from the standpoint for material properties, but also from that of chemical properties in those high P-T conditions.

Keywords: Fe-Ni “ideality”, core formation, metal-silicate partitioning, high pressure
INTRODUCTION

Earth’s core is composed of Fe-Ni alloy with ~5-10% of light element(s) to account for the observed density deficit (Birch 1964). Assuming a chondritic bulk Earth and a known Fe/Ni ratio in the bulk silicate Earth (BSE), the Fe/Ni ratio can be estimated using mass balance to be ~16 in the core (Allègre et al. 1995; McDonough and Sun 1995). At outer-core conditions, the effect of nickel content is negligible with respect to density, compressibility and wave velocities (e.g., Lin et al., 2003; Kantor et al., 2007; Martorell et al., 2013; Badro et al. 2014). Therefore, it is common practice to ignore Ni when simulating or experimenting on core properties. A recent metal-silicate isotopic fractionation study (Elardo and Shahar 2017) found that nickel favors the fractionation of heavy iron isotopes in the core during planetary core formation. This raises the question whether nickel also affects the partitioning behavior of siderophile elements during core formation, which in turn would affect our current understanding of core formation.

Core formation on Earth occurs by metal-silicate differentiation in a magma ocean (e.g., Ringwood 1959; Li and Agee 1996; Wood et al. 2006). Accreting material melts in the magma ocean, and liquid metal separates and equilibrates with surrounding silicate melt as it gravitationally segregates towards the center of the planet to form the core. This equilibration process strips siderophile elements from the magma ocean (i.e., BSE) to the core, setting the trace-element composition of both reservoirs. Their relative depletion in the BSE is obtained by comparing the composition of the most primitive mantle-derived rocks with that of chondrites (proxy for bulk Earth composition). High pressure and high temperature experiments can then be used to match the observed depletions, and because metal-silicate partitioning is a function of pressure (P), temperature (T), composition (X) and oxygen fugacity ($f_{O_2}$), further constrain the thermochemical conditions of core formation (e.g., Li and Agee 1996; Wade and Wood 2005;
Siebert et al. 2013; Fischer et al. 2015). Core formation models show that the P–T conditions for metal-silicate equilibration range up to 75 GPa, with temperatures as high as 4350 K (Badro et al. 2014), establishing that the core formed in a deep magma ocean. The presence of various (major and trace) elements in liquid iron alloy have an influence on the partitioning of siderophile trace elements, and extensive experiments have been designed to investigate the effect of silicon, oxygen, carbon or sulfur (dissolved in metal) on element partitioning during core formation; however, the effect of nickel, another major element in the core, has never been experimentally tested, and it was always assumed that Ni-free or Ni-bearing systems behave similarly from the point of view of partitioning.

**EXPERIMENTS AND ANALYSIS**

In this study, we investigated the effect of nickel on the metal-silicate partitioning of three siderophile elements (Ni, Cr, V) by performing laser-heated diamond anvil cell (LHDAC) experiments up to 94 GPa and 4500 K. Starting materials were synthesized at IPGP using a gas-mixing aerodynamic levitation laser furnace (silicate) and a piston-cylinder press (metal). The samples were polished and cut using a picosecond laser-machining system (IPGP) then loaded in diamond anvil cells using rhenium gaskets and compressed to target pressures prior to heating with a double-sided laser heating system (IPGP) to temperatures above the metal and silicate liquidus, ensuring the samples were fully molten in each run. After quench and decompression, a focused ion beam (FIB) instrument (Zeiss Auriga 40, IPGP) was used to extract thin sections from the center of the laser-heated area (Fig. 1), which were analyzed on the same instrument using quantitative energy dispersive X-ray (EDX) spectroscopy. Detailed description of the experimental and analytical methods can be found in Supplemental Information. The composition of the starting material can be found in Table S1.
RESULTS

Four diamond anvil cell experiments were performed at various P-T conditions and summarized in Table S2, with metal phases displaying a range of Ni concentrations from 3.5 to 48.7 wt%.

The typical quench morphology consists of a spherical metallic blob (a few micrometers in diameter) embedded in a silicate melt surrounded by untransformed glass (Fig. 1). Quench texture in both silicate and metal was found in all experiments, similar to those seen in previous superliquidus (i.e., molten silicate–molten metal) partition experiments in the LHDAC (Siebert et al. 2012; Fischer et al. 2015; Badro et al. 2016; Blanchard et al. 2017). During quench, Si-O-rich phases and Fe-Ni-rich blobs (< 200 nm) exsolved in the metal and silicate, respectively. Large window (raster-scanned electron beam) was used whenever possible to average over quench textures. Areas containing larger metallic blobs (0.5-2 μm in diameter) trapped in the silicate were avoided during chemical analysis. The composition of quenched silicate and metal melts from each run are reported in Table S3.

The partitioning of Ni, Cr and V between metal and silicate is the results of an exchange reaction taking place between molten metal and silicate:

\[
\frac{MO_n}{2} + \frac{n}{2}Fe = \frac{n}{2}FeO + M\#(1)
\]

with a partition coefficient \(D_M = \frac{x_M}{x_{MO/n/2}}\), where \(n\) is the valence of the cation M in the silicate and \(x\) the molar fraction of M. Partition coefficient is a function of P, T, composition and oxygen fugacity. The exchange coefficient, \(K_D(M) = \frac{D_M}{D_{Fe}^{n/2}}\), is the ratio of the partition coefficient of element M to that of iron, and is therefore independent of iron concentrations in the metal and
silicate, i.e., the oxygen fugacity of the system. The equilibrium constant $K$ of reaction (1) can be defined in terms of the exchange coefficient and activity coefficients ($\gamma$) in the silicate and metallic phases, and is related to the fundamental thermodynamic functions according to:

$$\log K(M) = \log K_D(M) + \log \left( \frac{\gamma_{Fe}^{metal}}{\gamma_{Fe}^{silicate}} \right) + \log \left( \frac{\gamma_{FeO}^{silicate}}{\gamma_{FeO}^{metal}} \right) = a + \frac{b}{T} + c \cdot \frac{P}{T} \#(2)$$

where $a$ is the entropy, $b$ the enthalpy, and $c$ the volume change of reaction (1). The ratio of activity coefficients in silicate melt ($3^{rd}$ term in Eq. 2) is independent of melt composition in this relatively narrow range of composition (O’Neill and Eggins 2002; Wade and Wood 2005; O’Neill and Berry 2006) and it can safely be ignored; its thermal dependence ($-1/T$) is readily integrated in the $a$ and $b$ constants of Eq. 2. However, the ratio of activity coefficients in the metal can vary drastically with metal composition (Jana and Walker 1997a, 1997b; Tuff et al. 2011; Wood et al. 2014). We modelled them using the interaction parameter approach in a real solution, a formally correct thermodynamic model (see Supplemental Information) at all concentrations which has become a standard practice (e.g., Wade and Wood 2005; Corgne et al. 2009; Ricolleau et al. 2011; Siebert et al. 2013; Fischer et al. 2015) to calculate the activity coefficients of $\gamma_{Fe}$ and $\gamma_i$ as a function of activity coefficients at infinite dilution ($\gamma_i^0$) and interaction parameters ($\varepsilon_{ij}$) that express the influence of element $j$ on element $i$ in the liquid iron. Following previous studies (Corgne et al. 2008; Mann et al. 2009; Siebert et al. 2011) of the valence of siderophile elements in silicate melts, we fixed the valence ($n$ in Eq. 1) of Ni and Cr to divalent (2+) and V to trivalent (3+).

**DISCUSSION**

Partitioning data on Ni, Cr and V from previous studies (Hillgren et al. 1996; Jana and Walker 1997; Gessmann and Rubie 1998; Bouhifd and Jephcoat 2003, 2011; Chabot and Agee...
2003; Wade and Wood 2005; Kegler et al. 2008; Mann et al. 2009; Siebert et al. 2012, 2013, 2011; Fischer et al. 2015) were compiled and plotted in Fig. 2, along with our data. The statistics cover a wide range of P-T conditions: e.g., 99 data for Ni from 0 GPa and 1754 K to 100 GPa and 5700 K. All the data used for our thermodynamic model can be found in Table S4-S6. In order to avoid the spurious effects due to solute compositions (not to introduce an unnecessary variability to the consolidated dataset), we only used data with no carbon (only with very few exceptions in the case of Ni, which is insensitive to carbon, to better constrain the temperature effect) and (virtually) no sulfur (concentrations < 0.1 mol%) in the system. The equilibrium constant K was calculated using the interaction parameter model (Table 1), and then fitted to the thermodynamic model described in Eq. 2, using multivariate least-squares linear regression. Fitted thermodynamic parameters are listed in Table 1, and correspond to the dashed line plotted alongside the data in Fig. 2.

For nickel, the least-squares regression for 99 data points shows a remarkable fit to Eq. 2 with $R^2 = 0.923$, and log K is plotted in Fig. 2a as a function of reciprocal temperature (x-axis) and pressure (symbol color). As observed by several studies (e.g., Li and Agee 1996; Kegler et al. 2008; Bouhifd and Jephcoat 2011; Siebert et al. 2012; Fischer et al. 2015), Ni becomes less siderophile with increasing temperature ($b > 0$) and pressure ($c < 0$):

$$\log K(Ni) = -0.40(22) + \frac{4454(430)}{T} - 58(8)\frac{P}{T}$$

We find no significant compositional dependence across the wide range of Ni content in the metal investigate here, which can be seen more clearly in Fig. 2b, where the equilibrium constant (plotted in Fig. 2a) is adjusted to zero pressure, i.e., plotting a rewritten form of Eq. 3:
\[ \log K(Ni) + 58(8) \frac{P}{T} = -0.40(22) + \frac{4454(430)}{T} \] #(4)

With all pressure-dependence cancelled out, the color now corresponds to the Ni concentration in the metal, and the data for all Ni concentrations fall on a single linear trend; the broad range of Ni concentration (from 3.5 to 48.7 wt%) demonstrates that there is no dependence of partitioning on the nickel content in the metal. The absence of any deviation and excellent agreement between our data and previous results provide a strong argument for the “neutrality” (with regard to partitioning during core formation) of Ni in core-forming Fe–Ni alloy, with no observable effect on its own partitioning from trace amounts up to 49 % of Ni in the metal under these extreme P-T conditions.

Following the same procedure, Eq. 2 was fitted to chromium and vanadium partitioning data using a least-squares linear regression, yielding:

\[ \log K(Cr) = -0.20(7) - \frac{2625(184)}{T} \] #(5)

\[ \log K(V) = -1.83(12) - \frac{3433(313)}{T} \] #(6)

Partitioning of both chromium and vanadium shows a strong positive temperature dependence \((b=-2625(184) \text{ K and } -3433(313) \text{ K for Cr and V, respectively})\), indicating they become more siderophile with increasing temperature, and no measurable dependence on pressure \((c=0 \text{ K/GPa})\) as previously observed (e.g., Wood et al. 2008; Mann et al. 2009; Siebert et al. 2013) and these are plotted in Figs. 2c and 2d. Again, despite nickel contents varying between 3.5 wt% and 48.7 wt% in metal, the equilibrium constants obtained in our DAC experiments (Ni, Cr or V) are intrinsically identical to those previously determined (within uncertainties), confirming
experimentally that nickel has also no measurable effect on the partitioning of Cr and V between metal and silicate at the high P-T conditions of Earth’s core formation.

It is also important to consider the effect of other light elements (e.g., sulfur and carbon) because their strong influences on partitioning behavior. Carbon-unsaturated data were used in this study (i.e., (Fischer et al. 2015) containing 3 to 16 mol% carbon in the metal) and show excellent agreement with the C-free data in Figs. 2a and 2b. S-bearing data wasn’t available at high pressure and there is no indication whether S addition to the metal would change the conclusion as observed at room pressure in the Fe-S and Ni-S end-members (e.g., Chabot et al. 2007).

**IMPLICATIONS**

Extensive metal-silicate partitioning experiments have been conducted over various P-T-X conditions to constrain core formation. However, in order to obtain measurable concentrations in both phases, unrealistic high content of trace elements is often inevitable. Unlike sulfur, carbon or silicon, whose effects on partitioning are well studied and thus known to be of importance, the influence of Ni has always been assumed negligible in experiments designed to use pure Fe as starting material. For the first time, our DAC experiments performed at core-formation conditions confirm the chemical “neutrality” of nickel in an iron alloy under these extreme P-T conditions, over a wide range of nickel concentration.

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REFERENCES CITED


Figure captions:
FIGURE 1. Backscattered electron image of a FIB section recovered from a super-liquidus metal-silicate equilibration at 73 GPa and 4300 K in the laser-heated diamond anvil cell.

FIGURE 2. Equilibrium constants (log K) for Ni, Cr and V as a function of reciprocal temperature (1000/T). The dashed lines correspond to least-squares linear regressions to the data, and error bars (only for the data from this study, shown where larger than symbols) were propagated from the analytical uncertainties in Table S3. (a) Ni. Experimental data are taken from (Hillgren et al. 1996; Jana and Walker 1997; Gessmann and Rubie 1998; Bouhifd and Jephcoat 2003, 2011; Kegler et al. 2008; Siebert et al. 2011, 2012, 2013; Fischer et al. 2015) and this study (squares). Pressure is reported in symbol color. (b) Equilibrium constant for Ni adjusted to 0 pressure (i.e., log K – c P/T) as a function of reciprocal temperature, for the same data as in (a). Symbol color corresponds to Ni concentration (molar fraction) in liquid metal. (c–d) Cr and V equilibrium constant (log K) versus reciprocal temperature. Experimental data are taken from (Hillgren et al. 1996; Jana and Walker 1997; Gessmann and Rubie 1998; Bouhifd and Jephcoat 2003, 2011; Chabot and Agee 2003; Wade and Wood 2005; Kegler et al. 2008; Mann et al. 2009; Siebert et al. 2012, 2013, 2011; Fischer et al. 2015) and this study (squares).

TABLE 1. Thermodynamic parameters of the metal-silicate partitioning of Ni, Cr and V.

<table>
<thead>
<tr>
<th>Element (i)</th>
<th>a</th>
<th>b (K)</th>
<th>c (K/GPa)</th>
<th>εᵢ搦</th>
<th>εᵢ딸</th>
<th>lnγᵢ₀</th>
<th>N</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>-0.40(22)</td>
<td>4454(430)</td>
<td>-58(8)</td>
<td>-6.2</td>
<td>1.16</td>
<td>0</td>
<td>-0.42</td>
<td>99</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.20(7)</td>
<td>-2625(184)</td>
<td>0</td>
<td>-8.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>45</td>
</tr>
<tr>
<td>V</td>
<td>-1.83(12)</td>
<td>-3433(313)</td>
<td>0</td>
<td>-24.4</td>
<td>4.4</td>
<td>6.57</td>
<td>-2.53</td>
<td>46</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td>-5</td>
<td>-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: Parameters of Eq. 2 for Ni, Cr and V partitioning: a, b and c represent the entropy, enthalpy and volume change of the reaction, values in parenthesis are standard errors (1σ) obtained from the least-squares regressions. εᵢ is the interaction parameter of element j on element i and lnγᵢ₀ the activity coefficient of solute i at infinite dilution in liquid iron; interaction
parameters in boldface are calculated from this study, other values are taken from *Steelmaking Data Sourcebook* (1988). Interaction parameters and activity coefficients are reported at 1873 K (details are given in Supplementary Information). N is the number of data used in each thermodynamic modeling, and $R^2$ the coefficient of determination of the fitted model.