Core formation and core composition from coupled geochemical and geophysical constraints

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The formation of Earth’s core left behind geophysical and geochemical signatures in both the core and mantle that remain to this day. Seismology requires that the core be lighter than pure iron and therefore must contain light elements, and the geochemistry of mantle-derived rocks reveals extensive siderophile element depletion and fractionation. Both features are inherited from metal–silicate differentiation in primitive Earth and depend upon the nature of physiochemical conditions that prevailed during core formation. To date, core formation models have only attempted to address the evolution of core and mantle compositional signatures separately, rather than seeking a joint solution. Here we combine experimental petrology, geochemistry, mineral physics and seismology to constrain a range of core formation conditions that satisfy both constraints. We find that core formation occurred in a hot (liquidus) yet moderately deep magma ocean not exceeding 1,800 km depth, under redox conditions more oxidized than present-day Earth. This new scenario, at odds with the current belief that core formation occurred under reducing conditions, proposes that Earth’s magma ocean started oxidized and has become reduced through time, by oxygen incorporation into the core. This core formation model produces a core that contains 2.7–5.5% oxygen along with 2–3.6% silicon, with densities and velocities in accord with radial seismic models, and leaves behind a silicate mantle that matches the observed mantle abundances of nickel, cobalt, chromium, and vanadium.

The primary observations that constrain core formation models are (i) siderophile abundance patterns in the silicate mantle, (ii) the geophysically inferred requirement that the core contains elements lighter than iron (12), and (iii) the concentration of FeO (e.g., redox) in the primitive upper mantle. Assuming that core formation proceeds under conditions where metal–silicate equilibrium is maintained, it should be possible (13, 14) to invert for the pressure (P), temperature (T), composition (X), and oxygen fugacity (fO\textsubscript{2}) conditions of core formation that satisfy all of these constraints.

Depletion of siderophile elements in the present-day mantle (relative to chondrites) is the direct result of metal–silicate equilibration and core formation (5, 7–9, 11) during which these elements were scavenged from the silicate and sequestered in the core. Numerous experiments (5, 7–11, 14–18) have been performed to determine the metal–silicate partitioning of siderophile elements, parameterizing these results as a function of thermodynamic variables. Here we consider four siderophile elements: nickel, cobalt, chromium, and vanadium. These are the only elements whose metal–silicate partitioning has been studied under the broadest range of P–T conditions, thanks to recent experimental advances with the laser-heated diamond anvil cell (16, 17, 19); therefore, we expect the most-accurate predictions with no recourse to extrapolation. These partition coefficients have then been extensively used to model diverse core formation scenarios, characterized by various P–T–X–fO\textsubscript{2} paths, to determine conditions that produce a model silicate mantle that has the same siderophile element patterns as Earth’s mantle for all four elements. As illustrated below, many P–T–X–fO\textsubscript{2} paths yield satisfactory agreement, but no unique solution has been identified.

Additional constraints arise from consideration of the composition of the core, which can be constrained through geophysical inference. If metal–silicate equilibrium was maintained along a particular P–T–X–fO\textsubscript{2} path, then the composition of the core is thermodynamically linked to that of the silicate magma ocean, and numerous metal–silicate partitioning experiments have shown that two of silicate mantle’s major elements, silicon and oxygen, can partition into the metallic liquid. As is the case for trace elements, the amount of Si and O dissolved in the core must have accreted material that is more oxidized than the present-day mantle, similar to that of planetesimals such as 4-Vesta, and got reduced to its present state during core formation.

Significance

We combine, for the first time to our knowledge, two approaches to study Earth’s core composition: a geochemical approach based on trace element depletion in the mantle and a geophysical approach based on a seismically lighter and faster (than pure iron–nickel) core. The joint approach allows making strong statements; first of all, as opposed to the current belief, Earth must have accreted material that is more oxidized than the present-day mantle, similar to that of planetesimals such as 4-Vesta, and got reduced to its present state during core formation. Secondly, core light-element concentrations in those conditions are 2.7% to 5% oxygen alongside 2% to 3.6% silicon; the oxygen concentrations in the core are higher than previously thought, and, conversely, silicon concentrations are lower than previous estimates.

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is directly linked to the conditions of equilibrium prevailing during differentiation in the magma ocean. Core composition (in terms of light elements) produced from a particular core formation model must satisfy the geophysically observed seismic velocities and density of the core, and more specifically of the outer core; because the inner core represents only 5% of the core’s mass, its crystallization barely changes the composition of the outer core in terms of light elements, and this minor adjustment is much smaller than the uncertainties on the compositional models.

**Methods**

To produce a geochemically and geophysically consistent model of the terrestrial core formation, we use the following procedure (details described below and in SI Appendix). First, core and mantle compositions resulting from the various core formation models are calculated using a broad range of model parameters. A geochemical filter is applied eliminating models that fail to satisfy the present-day mantle concentrations of Ni, Co, Cr, V, and FeO (20). The geophysical constraints are then applied to the remaining models to eliminate those with core Si and O concentrations that do not yield seismic parameters consistent with the AK135 (21) radial seismological model. The resulting models define a set of allowable P–T–X–FO2 paths that, for the first time to our knowledge, agree with both the existing mantle siderophile abundance patterns and geophysically inferred core compositions.

The standard model of core formation stipulates that the core formed in ~30 Ma (22, 23) and therefore took 1,000 stages. Each accretion–mantle equilibration was added to the proto-Earth, the metal separated from the silicate and equilibrated in the magma ocean, and was then transported to the core without further equilibration with the solid silicate mantle (5, 24). This evolutionary process, known as multistage core formation, was used here and discretized here in 1,000 steps. At each stage (or accretion step), the pressure at the base of the magma ocean is calculated as a function of total accreted mass, and the magma ocean depth, which is a free parameter, is determined at the base of the magma ocean as well as that of the coexisting magma ocean, using Monte Carlo simulations (see SI Appendix) to fully propagate all uncertainties (SI Appendix, Table S1). Finally, the metal is extracted to the core. The process is repeated (1,000 times) until Earth is fully accreted, and the core is fully formed. At the end of accretion, the mantle and core reach their final composition for the six aforementioned elements. This can be conveniently expressed as either concentrations (in the case of Si and O) in the metal, or as metal-silicate partition ratio (i.e., an effective core–mantle partition coefficient) in the case of Ni, Co, Cr, V, and FeO. The final composition is the metal, or as a metal

results and discussion

The main parameters of the model (magma ocean depth, geotherm, and redox path) were tested over the broadest possible range. The final depth of the magma ocean was varied from 0 km to 2,900 km: in other words, from an evanescent thin magma ocean to a fully molten mantle, respectively. Four magma ocean geotherms spanning the whole plausible temperature range were used: peridotite solidus (25), two (cool and hot) peridotite liquidus (25, 26), and an intermediate average liquidus. Last, 14 magma ocean redox paths, equilating to the variation in the magma ocean FeO content during accretion, were tested (Fig. 1) with initial conditions spanning 4 log units of FO2 and ranging from very reduced conditions (below those existing in enstatite chondrites) to very oxidizing conditions (those observed in CI carbonaceous chondrites). The final redox condition for each model is required to yield the present-day value for the mantle (5.9 mol% FeO). All details are in SI Appendix.

The metal–silicate partition coefficients (SI Appendix, Figs. S1 and S2) vary as a function of final magma ocean pressure for the whole range of model parameters (geotherm and redox). In addition, siderophile element activity coefficients in the metallic phase are also dependent upon the concentrations of Si and O in the metallic melt (16, 18, 27, 28). Geochemically consistent models are those for which the mantle abundances for Ni, Co, Cr, and V are simultaneously satisfied, within uncertainties. As most recent findings (16, 17, 29) show, this analysis does not yield a unique solution to the problem, especially when properly propagating all uncertainties (29) on the thermodynamic parameters. Here we find solutions for all geotherms and all redox paths, meaning that there is always a range of magma ocean depths where core formation leaves behind a geochemically consistent mantle, regardless of temperature and redox. The allowable depth range is fairly narrow, however, and spans the 42–75 GPa range for reducing conditions to 50–63 GPa for oxidizing conditions (Table 1 and SI Appendix, Table S2), limiting the magma ocean to midmantle depths.

The low-FO2 models (Fig. 1: blue curves, paths 1–4) have solutions over a large range of temperature and pressure conditions, whereas the higher FO2 models (Fig. 1: greens to reds, paths 6–14) have solutions in a smaller range of magma ocean pressures and are restricted to warmer geotherms. This is because core formation models at low FO2 can occur over a much larger P and T range than at higher FO2; this is seen in Table 1, where the most-reducing models have solutions for all geotherms and for a pressure range spanning more than 30 GPa (42–75 GPa) and a temperature range spanning 1,500 K. This is a consequence of the partitioning behavior of Ni, Co, Cr, and V, which have a natural tendency to be very lithophile. Low FO2 makes them more siderophile (SI Appendix, Eq. 2) across the board, irrespective of P–T conditions, and therefore their concentration in the mantle after core formation can be satisfied for a large P–T range of metal–silicate equilibration. High FO2, on the other hand, makes them even more lithophile, and it is rather the incorporation of Si and O in the metal that increases their siderophile character, tipping the balance in the right way. To be effective and have a strong quantitative effect, this process requires a significant amount of Si and especially O to be present in the metal, which in turn requires high equilibration temperatures. Therefore, as seen in Table 1, the oxidizing models are restricted to the single hottest geotherm, naturally yielding a narrower P–T range where core formation could have taken place. In turn, this narrow P–T range is characterized by a narrow Si–O range for core composition, as can be seen in Fig. 2.

Core Si and O concentrations of these geochemically consistent models are plotted in Fig. 2, and grouped by redox condition (the numbers and colors matching the redox paths in Fig. 1 and Table 1). As expected, highly reducing conditions in the magma ocean produce cores that have high silicon and low oxygen contents, whereas oxidized magma oceans show the opposite behavior. Also, the larger P–T solution range for the low-FO2 models translates into a broad range in Si and O concentrations in the core, and, conversely, high-FO2 models with a smaller P–T solution range generate a more compact Si–O band.

To eliminate geophysically unacceptable models, we use recent results from ab initio molecular dynamics simulations to calculate the density and bulk sound velocity of liquid alloys in the (Fe,Ni)–O–Si–S–C system at core–mantle boundary (CMB) and inner-core boundary (ICB) pressure and temperature conditions (30). The details of the calculations can be found in SI Appendix. We fixed the core’s Fe/Ni ratio to 16, and let S and C concentration fluctuate to somewhere in their plausible concentration range: 0–2% for S, and 0% to no upper limit on C. We then searched for all of the oxygen and silicon concentrations that matched the density and bulk sound velocity in the core, determined with the AK135 radial velocity model (at the CMB and ICB simultaneously). The O–Si solution space is plotted in Fig. 2, and is an area bounded by the dashed black line: O and Si compositions that lie outside of this area cannot fit the seismic constraints, meaning that a core with such a composition would not be consistent the AK135 radial seismic model. The gray shaded area inside the solution space corresponds to the subset of solutions for a C/S-free core (i.e., where C and S
A more granular depiction of the solution space and O-Si boundaries can be found in SI Appendix, for various S and C contents. However, the polygon defined by the gray dashed line encompasses all possible oxygen and silicon concentrations that fit the seismic data, for any plausible carbon and sulfur concentration; it therefore defines the broadest possible oxygen and silicon concentration range that can produce a seismologically consistent core. It is clear from Fig. 2 that the cores produced under highly reducing conditions have O-Si concentrations outside of that range (Si too high, or O too low) and are therefore not geophysically consistent. The same applies for cores produced in the most oxidizing conditions, which have O concentrations higher than geo-physically allowable. Only geochemically consistent cores with initial magma ocean FeO content ranging between 10 mol% (path 7) and 25 mol% (path 12) have Si-O contents that match seismicity. These models define a very narrow pressure range, 57-62 GPa, corresponding to a final magma ocean depth of 1,400-1,500 km, roughly the midmantle. This has strong implications for core composition: Combining the O and Si contents for all redox paths from 7 to 12 that are compatible with the seismic data yields a rather tightly constrained core composition of 2.7–5.5% oxygen and 2–3.6% silicon.

Our range of silicon concentrations is in agreement with inner core compositional models. Inner core light-element concentration derives from that of the outer core and is dependent on liquid–solid phase equilibrium (31, 32) in the metal. In a silicon- and oxygen-bearing outer core, only silicon is compatible in the solid phase and can enter the inner core, whereas oxygen is substantially incompatible and can only exist as trace amounts in the inner core (33). Hence, silicon represents the only light-element candidate for the inner core (34), and recent models have constrained the maximum amount to be 1–2% silicon (35). Assuming a solid/melt partition coefficient for Si in iron (33) around 1.2 ± 0.5, this implies that the outer core must contain between 0.7% and 3.5% silicon, hence entirely consistent with our range of 2–3.6%.

On the other hand, the high oxygen concentration in the outer core elegantly solves for one of the core’s most perplexing observations: that of the very strong density jump (4.8–7.4%) at the ICB (36, 37), between the liquid outer core and solid inner core. The density change due to melting is on the order of 1.7% (38), and the observation naturally calls for strong chemical buoyancy and a stark chemical contrast between the inner core and outer core; this can only be achieved by the presence of a very
Table 1. Model outputs of multistage core formation model for which Ni, Co, V, and Cr concentrations in the mantle match the present-day geochemical observables

<table>
<thead>
<tr>
<th>Model Path</th>
<th>Initial Redox (mol%)</th>
<th>Initial FeO</th>
<th>Magma Ocean Range (at base, at end of accretion), GPa</th>
<th>Magma Ocean Temperature Range (at base, at end of accretion), K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Solidus</td>
<td>Cool Liquid</td>
</tr>
<tr>
<td>1</td>
<td>NW-4.5</td>
<td>0.6</td>
<td>49–75</td>
<td>54–74</td>
</tr>
<tr>
<td>2</td>
<td>NW-4.5</td>
<td>0.6</td>
<td>66–75</td>
<td>73–79</td>
</tr>
<tr>
<td>4</td>
<td>NW-2.7</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>NW-2.3</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>NW-2.1</td>
<td>5.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>NW-1.9</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>NW-1.7</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>NW-1.4</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>NW-1.3</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>NW-1.3</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>NW-1.2</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>NW-1.0</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>NW-0.8</td>
<td>34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>NW-0.6</td>
<td>43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The four sections represent, from top to bottom, (i) final magma ocean pressure range, (ii) final magma ocean temperature range, (iii) final oxygen core concentration, and (iv) final silicon core concentrations; these are given for each redox path (Fig. 1) and each geotherm (solidus in blue, cool liquidus in yellow, average liquidus in orange, hot liquidus in red). When no solution for the relevant redox/geotherm pair is found, no numbers were reported (empty cells). It noteworthy that low fO₂ models have solutions for all geotherms from cold to hot. Thus, the combined pressure and temperature range where solutions can be found is large, and so are the Si and O concentration ranges in the core. A natural result is the breadth of the solutions for those models in Fig. 2. Conversely, high fO₂ models have solutions only with the hottest geotherm, yielding narrow pressure and temperature ranges, and therefore narrow Si and O concentration ranges in the core. A more detailed table can be found in SI Appendix, Table S2, containing additional information such as average pressure and temperature, depth, and total light-element content for each model.
incompatible light element in the outer core. Oxygen is the only candidate among the four (C, O, Si, S) to exhibit that behavior (33), and concentrations between 2% and 5% at the ICB produce a 2.5–5.3% density contrast with respect to the oxygen-free composition (all other things being equal) assumed for the inner core. Adding the density change due to melting, the density contrast between our oxygen-rich outer core (4.2–7%) and an oxygen-free inner core is consistent with seismology.

Accretion under higher $\text{O}_2$ requires higher FeO concentrations than that of the present-day mantle. The core is an obvious sink for that excess FeO, because its incorporation increases the oxygen content of the core. Using simple mass balance constraints, we can calculate the amount of oxygen added to the core by assuming that all of the excess FeO in the mantle (in excess of the 5.9 mol% in the present-day mantle) was added to the core during the differentiation process. At constant redox (Fig. 1: path 5), there is no excess FeO to add to the core. A redox path starting with 8 mol% FeO, path 6, produces a total of 0.7% O in the core, less than that of the present-day mantle. A redox path starting with 8 mol% O in the core, less than that of the present-day mantle (Fig. 2: curve 6). On the other hand, path 10 yields a total of 4.5% O in the core, more than that required by equilibrium metal–silicate partitioning (Fig. 2: curve 10). Path 9 yields good agreement between the calculated equilibrium oxygen content of the core and mass balance, yielding 2.3% O in the core. Of course, this argument neither rules out the possibility of FeO enrichment in the lower mantle (39) nor the simultaneous dissolution of Si and O in the core from the SiO2 component of the mantle (40). Rather, it demonstrates that accretion, initiated under conditions more oxidizing than the present-day mantle, provides a necessary mechanism for an oxygen-rich core, and that the core can be the natural sink for the excess FeO supplied during accretion.

We have shown that geochemistry can constrain a range of conditions of core formation based on compatibility of Ni, Co, V, and Cr concentrations in present-day bulk silicate Earth, and that only a subset of these geochemically consistent models satisfies the present-day seismic density and bulk sound velocity of the core, constraining the Si–O concentration in the core. These geophysically consistent models are limited to those for which accretion proceeds from a redox state more oxidized than the present-day mantle. Accretion of objects with a high bulk FeO content, such as asteroids like 4-Vesta, is at odds with the standing paradigm that the core formed in reducing conditions, and constrains the light-element composition of the core to 2.7–5% oxygen and 2–3.6% silicon.

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Supporting Information

1. Core Formation Modeling

Core formation was modeled as a multi-stage process occurring during accretion, in a terrestrial magma ocean, adapted from Wood and Wade. The Earth, which is covered by a magma ocean, grows by accretion, during which the molten metal of the accretionary material separates form the molten silicate. The metal sinks to the base of the magma ocean, acquires a particular composition by equilibrating with the surrounding magma ocean, and is then transported to the core through the solid mantle with no (or little) further equilibration. At the end of accretion, the core and mantle have acquired a certain composition, which is the integral of this process.

The multi-stage model was discretized in 1000 steps, each bringing an additional 0.1% total Earth mass influx to the proto-Earth. At each step, the Earth grows larger, the magma ocean grows deeper, and its pressure and temperature increase, and its composition changes because of the mass influx. All these parameters are used to calculate metal-silicate partition coefficients, in turn used to calculate element concentrations in the metal and silicate. These are then used to calculate the integral path and the final composition of the core and mantle. The elements we focused on in this study are 4 siderophile trace elements: Ni, Co, Cr, and V, and the two major elements that tend to partition into metallic iron at high temperatures: O and Si.

As described below, we explored all possible magma ocean depths (from 0 to 100% of the mantle), all possible geotherms relevant to the base of that magma ocean (temperatures between the mantle solidus and liquidus), and magma ocean compositions spanning 4 orders of magnitudes in oxygen fugacity and covering the entire range of the cosmochemically observed compositional range for planetary building blocks (ordinary, carbonaceous, and enstatite chondrites).

a. Metal-Silicate Partitioning

Metal-silicate partitioning was modeled based on a compilation of data in the literature, Siebert et al. and references therein.

The partition coefficients are defined as:

\[ D_i = \frac{X_{metal}^i}{X_{silicate}^i} \]  
(Eqn. 1)

where \( i \) is Ni, Co, Cr, V, Si, or O; and \( X \) the molar concentrations in the metal or silicate. They are parameterized as follows:

\[ \log(D_i) = a + \frac{b}{T} + \frac{c}{T} - \frac{n}{2} \log \left( \frac{X_{silicate}^i}{X_{FeO}^i} \right) - \log \gamma_i + \frac{n}{2} \log \gamma_{Fe} \]  
(Eqn. 2)
where \( a, b, \) and \( c \) are regression constants corresponding to entropy, enthalpy, and volume terms; \( X_{FeO} \) and \( X_{Fe} \) are the FeO concentration in the silicate and Fe concentration in the metal, respectively; \( n \) is the valence of element \( i \) \((i=\text{Ni}, \text{Co}, \text{Cr}, \text{V}, \text{Si}, \text{O})\); \( \gamma_i \) and \( \gamma_{Fe} \) are the activity coefficient (in the metal) of element \( i \) \((i=\text{Ni}, \text{Co}, \text{Cr}, \text{V}, \text{Si}, \text{O})\) and iron, respectively. Those were calculated using the interaction parameter approach (1), and self-consistently evolve along with the composition of the metal. This approach allows the use of interaction parameters \( \varepsilon \) to calculate the activity of multicomponent metallic solutions. In a metallic solution containing \( N \) components, the activity coefficients of Fe and the \( N-1 \) solutes \((i)\) is given by:

\[
\ln \gamma_{Fe} = \sum_{i=1}^{N-1} \varepsilon_i^i (X_i + \ln(1 - X_i))
\]

\[
- \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \varepsilon^j X_j X_k \left( 1 + \frac{\ln(1 - X_j)}{X_j} + \frac{\ln(1 - X_k)}{X_k} \right)
\]

\[
+ \sum_{i=1}^{N-1} \sum_{k=1}^{N-1} \varepsilon^i X_i X_k \left( 1 + \frac{\ln(1 - X_k)}{X_k} - \frac{1}{1 - X_i} \right)
\]

\[
+ \frac{1}{2} \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \varepsilon^j X_j^2 X_k \left( \frac{1}{1 - X_j} + \frac{1}{1 - X_k} - 1 \right)
\]

\[
- \sum_{i=1}^{N-1} \sum_{k=1}^{N-1} \varepsilon^i X_i^2 X_k \left( \frac{1}{1 - X_i} + \frac{1}{1 - X_k} + \frac{X_i}{2(1 - X_i)^2} - 1 \right)
\]

\( (\text{Eqn. 3}) \)

and

\[
\ln \gamma_i = \ln \gamma_{Fe} + \ln \gamma_{i0} - \varepsilon_i^i \ln(1 - X_i)
\]

\[
- \sum_{j=1}^{N-1} \varepsilon_j^j X_j \left( 1 + \frac{\ln(1 - X_j)}{X_j} - \frac{1}{1 - X_i} \right)
\]

\[
+ \sum_{j=1}^{N-1} \varepsilon_j^j X_j^2 X_i \left( \frac{1}{1 - X_i} + \frac{1}{1 - X_j} + \frac{X_j}{2(1 - X_j)^2} - 1 \right)
\]

\( (\text{Eqn. 4}) \)

Values of the \( \varepsilon_i^j \) and are reported at a reference temperature of 1873 K (Table 1) and extrapolated to any temperature according to:

\[
\varepsilon_i^j(T) = \frac{T}{T_i} \cdot \varepsilon_i^j(T_i)
\]
Table S1 below lists all the regression parameters used in our model along with their uncertainties. The regressions are from (2, 3), and were regressed on a large set of previously published data obtained from piston-cylinder press, multi-anvil press, and laser-heated diamond anvil cell experiments.

<table>
<thead>
<tr>
<th>Element (i)</th>
<th>a</th>
<th>b (K)</th>
<th>c (K/GPa)</th>
<th>( \varepsilon_i^0 ) (T_0)</th>
<th>( \varepsilon_i^{sl} ) (T_0)</th>
<th>\ln \gamma_i^0 ) (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.304 (0.162)</td>
<td>2916 (344)</td>
<td>-60 (5)</td>
<td>1.40</td>
<td>1.16</td>
<td>-0.42 * 1873/T</td>
</tr>
<tr>
<td>Co</td>
<td>0.287 (0.141)</td>
<td>1360 (286)</td>
<td>-35 (5)</td>
<td>1.89</td>
<td>0</td>
<td>-0.60 * 1873/T</td>
</tr>
<tr>
<td>Cr</td>
<td>0.082 (0.097)</td>
<td>-3379 (220)</td>
<td>0</td>
<td>-7.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>V</td>
<td>-1.238 (0.141)</td>
<td>-5288 (408)</td>
<td>0</td>
<td>-21.1</td>
<td>2.00</td>
<td>-2.53 * 1873/T</td>
</tr>
<tr>
<td>Si</td>
<td>0.364 (0.28)</td>
<td>-16520 (716)</td>
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<td>12.41</td>
<td>-6.65 * 1873/T</td>
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<tr>
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<td>11439 (387)</td>
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**b. Accretion and Magma Ocean**

The Earth was iteratively (discretely) accreted in N=1000 steps, each amounting to 0.1% of Earth’s total mass. At each step, the mass and accreted fraction are calculated:

\[
M_i = M_{i-1} + \delta M_i \quad \text{and} \quad f_i = \frac{M_i}{M_E} \quad \text{(Eqn. 5)}
\]

and \( M_i \) is the mass of the proto-Earth at step \( i \), \( \delta M_i \) the mass flux at step \( i \), and \( M_E \) the final mass of the Earth. We used \( N=1000 \) and a constant \( \delta M_i = 0.001 \) \( M_E \).

As accretion proceeds, the pressure and the temperature at the base of the magma ocean increase. The pressure at the base of the magma ocean is calculated according to:

\[
P_i = P_{final} \cdot f_i^{2/3} \quad \text{(Eqn. 6)}
\]

where \( P_{final} \) is the pressure at the base of the magma ocean at the end of accretion \( (f_N=1) \), or in other words, the final pressure of the magma ocean. \( P_{final} \) is an adjustable parameter of the model.

At the base of the magma ocean, the top molten part is in equilibrium with the bottom solid part. Therefore, the temperature at the base of the magma ocean has to lie above the solidus and below the liquidus of pyrolite. We have chosen 4 geotherms based on experimental melting data: the solidus (Eqn. 7) and liquidus (Eqn. 8) from Fiquet et al 2010, the liquidus (Eqn. 9) of Andrault et al 2011, and an intermediate liquidus (Eqn. 10) obtained from the arithmetic mean of the (Eqn. 8) and (Eqn. 9).
Finally, at each step, FeO content of the magma ocean is calculated along \textit{ad hoc} models shown in the main article, Figure 1.

c. Core and Mantle Composition

At each accretion step, the pressure, temperature and FeO content of the magma ocean are calculated at its base (eqs. 2–5 and figure 1). These parameters, $P_i$, $T_i$, and $X_i^{FeO}$ are the used to calculate the composition of the metal and that of the silicate at equilibrium. The metal is added to the pre-existing core, the silicate magma ocean grows and changes, and the process is repeated.

The concentrations of Ni, Co, Cr, V, Si and O in the metal and silicate are calculated at each step using published partition coefficients and thermodynamical models. The metal is then extracted and added to the pre-existing core, thus changing its composition. The magma ocean composition is also modified, and a new accretion step proceeds.

It is clear that all parameters have associated uncertainties that can be fairly large. It was recently argued that if these uncertainties are properly propagated, core formation can take place in almost any accretion scenario, an even in a single stage! We therefore forward-propagated all uncertainties on the thermodynamic parameters governing the partitioning equations, using Monte Carlo simulation. At each accretion step $i$, $10^5$ partition coefficients are calculated according to equation 7, where the parameters $a$, $b$, and $c$ are sampled from a normal distribution around their mean and standard deviation. This means that we obtain the full statistical dispersion for each partition coefficient, which is only possible with the use of Monte Carlo Simulations. The average partition coefficient and its (1-\sigma) standard error are then obtained from the statistics on those $10^5$ values of D, effectively propagating the uncertainties in thermodynamic parameters on the metal-silicate partition coefficients. Then the 1-\sigma values were used to obtain the figure in the main article, and can be compared with the same plot obtained by using 2-\sigma is shown in Fig. S1. It is clear that the solution spaces naturally occupy a larger extent, but the message is the same. Highly reduced models (paths 1-5) still cannot yield core compositions that are consistent with seismology, whereas the most oxidized models (path 13 and 14) can be made consistent at the lower end of the P–T range of equilibration. At any rate, relaxing the uncertainties cannot help reconcile the seismic models with cores produced under reducing conditions in the magma ocean.
Figure S1: (Left) The same plot as Fig. 2 in the main text. The points represent the spread of the solutions obtained by propagating all uncertainties in the partition coefficients to 1-σ. The seismologically consistent composition space consists of the area delimited by the black dashed line; the grayed sub-area corresponding to the O and Si solutions if the core contains no C and no S, and the rest of the polygon corresponding to the O and Si solutions with a core containing up to 2% S and 5% C. (Right) A similar plot obtained by propagating all uncertainties in the partition coefficients to 2-σ instead of 1-σ. The spreads are naturally larger, but the highly reduced models (paths 1-5 in fig. 1) still cannot produce core compositions that satisfy seismology. The main difference is that the most oxidized paths (13 and 14) that couldn’t produce geophysically acceptable cores now do.

d. Model Output

The model’s output is the evolution of partition coefficients (Ni, Co, Cr, V) and Si and O content in the metal, as a function of accreted fraction. Figure S3 below shows a typical example of such a multi-stage core formation model, for a final magma ocean pressure of 65 GPa, a warm liquidus, and accretion path 6 (initial FeO concentration in the magma ocean is 8 mol%) from Figure 1.

The next step is to focus solely on the final values, reached at the end of accretion, since these are the ones that will be used to constrain the model. We successively ran 136 simulations such as the one described above, varying $P_{\text{final}}$ between 0 and 135 GPa, by 1 GPa increments. The final values (Ds and core compositions) at the end of accretion are then plotted as a function of final magma ocean pressure, as shown in figure S3. Again, the solid lines are the Monte Carlo averages of the D distributions, and the dashed lines are the 1-sigma envelopes.
Figure S2: Evolution of thermodynamic parameters in the magma ocean and core. The top 4 panels represent the evolution of thermodynamic conditions in the magma ocean as a function of accreted fraction: pressure (blue), temperature (red), redox (green), and O/Si concentration in the core. The bottom 4 panels show the evolution of the core-mantle partition coefficients of the four siderophile elements (Ni in red, Co in blue, Cr in violet, V in green) as a function of accreted fraction; the solid line corresponds to the Monte Carlo average and the dashed lines to the 1-sigma envelope. The vertical bar corresponds to the observed core-mantle partition coefficient (with its uncertainty), and represents the value, or range of values, that must be reached at the end of accretion for the model to match the observation.
Figure S3: The result of a series of multi-stage core formation models where the final magma ocean depth (or pressure) was varied from 0 to 135 GPa, scanning the whole possible range of plausible magma oceans pressure in the Earth. We used the same redox path ad geotherm as in the example shown in figure S2. Each point in this graph corresponds to the endpoint of the graphs in figure S2, computed for different final pressures. Note that the same numbers are found at the end of accretion in figure S2 and at 65 GPa in this figure. Notice that the x-axis (except for the redox model on the top left) is now labeled in GPa, corresponding to final magma ocean depth. The Ds and core concentrations are the final values reached at the end of accretion. The horizontal shaded areas correspond to the terrestrial observables, and these are the same as the bars in figure S2. The vertical bar corresponds to the pressure range for which all four partition coefficients match the observables, and therefore constrains the locus of plausible magma ocean depths for a given redox and geotherm.
For a given geotherm and a given composition, this allows constraining the depth range of the magma ocean that would be consistent with the geochemical observables (horizontal colored range). Since all four partition coefficients need to be satisfied simultaneously, the allowable P range (vertical gray range) corresponds to the intersection of all four pressure ranges. Each one of those simulations provides an acceptable pressure (or depth) range for the magma ocean, as well as a concentration range for O and Si in the core; these satisfy Ni, Co, Cr, and V abundances in the mantle, for a given geotherm and a given redox path.

Taking this idea one step further, all geotherms and all redox paths were tested. We now solely focus on the O and Si concentrations in the core within the gray vertical bar (top right panel in figure S3), i.e. in P–T–fO$_2$ conditions that satisfy the mantle concentrations for Ni, Co, Cr, and V. These values of Si and O are plotted one against another for various geotherms and redox paths, and these are reported in the main text in figure 2.

Table S1: Model outputs of multi-stage core formation model for which Ni, Co, V, and Cr concentrations in the mantle match the present-day geochemical observables. The table is similar to Table 1 in the main text but has additional info. The data is given for each redox path (Fig. 1) and each geotherm, and empty cells indicate that there is no solution for the relevant redox/geotherm pair. Final pressure (top left), temperature (top center), and depth (top right) range of the magma ocean at the end of accretion. Average pressure (center left) and temperature (center) averaged over accretion. Final oxygen (bottom left) and silicon (bottom center) concentrations in the core; along with total light element concentration (bottom right) at the end of core formation.
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2. Core Light-Element Content

It is obvious that any proposed compositional model for the core must (at the very least) match – within uncertainties – the seismically observed density and sound velocity of the core. The idea here is to rule out core composition models based on their Si and O concentration; for this we need to define the broadest O–Si solution space that is compatible with seismology. This analysis has only been possible recently possible (4) thanks to first principles molecular dynamics simulation, offsetting the lack of density and velocity data on (Fe–Ni)–C–O–Si–S liquid alloys under core conditions. Measuring bulk sound velocities and densities in molten Fe alloys at core conditions lies currently beyond the capability of experimentation. An alternative is to use *ab initio* simulations to interpret seismic observations in terms of outer core composition. We can, therefore, calculate the density and bulk sound velocity of liquid alloys in the (Fe–Ni)–C–O–Si–S system using *ab initio* molecular dynamics. We then compare the properties of the molten alloys directly with the primary geophysical observations, e.g. density and bulk sound velocity obtained from radial seismic models (5, 6); keeping only the ones that satisfy seismology. This subset of compositions defines a seismologically constrained compositional model of the Earth’s core.

![Figure S4](image)

*Figure S4: The three panels show plots of the Si–O concentration range that is consistent with the AK135 seismological model, for three fixed S- and C- concentrations. At the left is the end-member with no S nor C. In the middle, a model with 1 wt% S and 1wt% C. At the right a model with 2% S and 2% C.*

We chose the AK135 (6) radial seismic model, and corrected the velocity profile to avoid artifacts from the F-layer and the low-velocity layer at the CMB. In all simulations, the Ni content was fixed (7) at 4.2%. First we calculated the O–Si solution maps for fixed amounts of S and C, according to (4). Figure S4 shows three such solution maps.

As we said earlier, ruling out core composition models based on their Si and O concentration requires defining the broadest O–Si solution space. For this, we need to superpose the individual O–Si solution maps calculated for all possible/plausible S and C concentrations. This superposition map is shown in figure S5, and has been calculated for all C and S concentrations between 0 and 7 wt% and 0 and 3 wt%, repectively. The 3% sulfur limit was taken from the cosmochemical arguments put forth in (8).

To give the readers a more granular perception of the distinctive effects of S and C on figure S5, we plotted O–Si core concentrations for four core concentrations of sulfur: 0%, 1%, 2% and 3%.
The results are reported in figure S6, and the area in each subplot represents the broadest O–Si solution space for its associated sulfur concentration, with the C concentration indicated by the color of the symbol. One can see figure S5 as the superposition of individual figures similar to the ones in figure S6, calculated for a discrete range of S concentrations.

**Figure S5:** The O–Si concentration range consistent with the AK135 radial seismic model, for any sulfur concentration between 0 and 3% and any carbon concentration. The symbol color is mapped to carbon concentration with the scale in the color bar to the right.
Figure S6: The O–Si–C concentration range consistent with the AK135 radial seismic model, for four sulfur concentrations: 0% (upper left), 1% (upper right), 2% (lower left), and 3% (lower right). Symbol color is mapped to carbon concentration with the scale in the color bar to the right of each graph.

3. References