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Core formation and core composition from coupled geochemical and geophysical constraints

James Badro, John P. Brodholt, Hélène Piet, Julien Siebert, and Frederick J. Ryerson

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 physicochemical 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% 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.

Earth formed ~4.56 billion years ago (1–3), over a period of several tens of millions of years, through the accretion of planetary embryos and planetesimals (4). The energy delivered by progressively larger impactors maintained Earth’s outer layer as an extensively molten (4) magma ocean. Gravitational segregation of metal and silicate within the magma ocean resulted in the primary differentiation of the planet characterized by a metallic core and silicate mantle. Although numerous accretion/core formation models have been proposed (5, 6), perhaps the simplest in terms of quantitative testability postulates that the molten metal and silicate maintained chemical equilibrium (7–11), allowing phase relations and partitioning constraints to be applied in modeling their chemical evolution. This scenario couples the chemical evolution of the mantle and core with the evolving conditions (depth, pressure, temperature, composition) in the magma ocean that directly influence partitioning behavior and the resulting composition of metal and silicate.

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 (fO₂) 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–fO₂ 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–fO₂ 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–fO₂ 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

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 consistent 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 place during Earth’s accretion. As accretionary material 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 magma ocean depth, which is a free parameter. Finally, the FeO content (oxygen fugacity, or composition) of the magma ocean is calculated at each step to follow a given redox path, which is the last free parameter of the model. At each accretion step, P, T, and X\text{FeO} are used to calculate the composition (Ni, Co, Cr, V, and Si) of the metal equilibrated 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 mantle and redox path) were tested over the broadest possible range. The main parameters of the model (magma ocean depth, geotherm, and redox path) were tested over the broadest possible range. The main parameters of the model (magma ocean depth, geotherm, and redox path) were tested over the broadest possible range.
solid phase equilibrium (31, 32) in the metal. In a silicon-

Fig. 1. The evolution of FeO concentration in the magma ocean, over the
course of accretion, for 14 redox models. The final FeO content is fixed at the
present-day value for the primitive upper mantle, 5.9% FeO (all fractions in
mol%). Path 5 is the constant redox path, where FeO concentration is main-
tained at 5.9% throughout accretion. Paths 1–4 start more reduced than the
present-day mantle, and the magma ocean oxidizes throughout accretion.
Paths 6–14 all start more oxidized than the present-day mantle, and the magma
ocean becomes more reduced over the course of accretion. Some paths have
initial FeO concentrations similar to the silicate fractions of common meteorite
groups: paths 1 and 2 are similar to that of EH chondrites, but path 1 has a
constant low FeO until 28% accretion as proposed in ref. 15; path 9 is similar to
that of H chondrites; path 10 is similar to that of HED meteorites; paths 11
through 14 are similar to that of L, LL, CV, and G chondrites, respectively. The
paths span four orders of magnitude in initial fO₂ ranging from IW-4.5 (paths
1 and 2) to IW-0.6 (path 14), so as to cover the entire plausible range of redox
conditions found in Earth’s accretionary building blocks.

collection is (0%). 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
delineates all possible oxygen and silicon concentrations that fit the seismological data, for any plausible carbon and sulfur con-
centration; it therefore defines the broadest possible oxygen and silicon concentration range that can produce a seismologically con-
sistent 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-oxi-
dizing conditions, which have O–Si concentrations higher than geo-
physically allowable. Only geochemically consistent cores with initial
magma ocean FeO content ranging between 10 mol% (path 7) and
26 mol% (path 12) have Si–O contents that match seismology. These
models define a very narrow pressure range, 57–62 GPa, corres-
ponding 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% 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). As-
suming 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>Path</th>
<th>Initial Redox</th>
<th>Initial FeO (mol%)</th>
<th>Magma Ocean Composition</th>
<th>Magma Ocean Pressure Range (at base, at end of accretion), GPa</th>
<th>Magma Ocean Temperature Range (at base, at end of accretion), K</th>
<th>Core Oxygen Concentration Range, wt%</th>
<th>Core Silicon Concentration Range, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Solidus</td>
<td>Cool Liquidus</td>
<td>Average Liquidus</td>
<td>Hot Liquidus</td>
<td>Solidus</td>
</tr>
<tr>
<td>1</td>
<td>IW-4.5</td>
<td>0.6</td>
<td>49 - 75</td>
<td>48 - 74</td>
<td>46 - 71</td>
<td>43 - 65</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>2</td>
<td>IW-4.5</td>
<td>0.6</td>
<td>66 - 75</td>
<td>54 - 74</td>
<td>45 - 71</td>
<td>43 - 64</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>3</td>
<td>IW-3.3</td>
<td>2</td>
<td>73 - 73</td>
<td>73 - 73</td>
<td>73 - 73</td>
<td>42 - 64</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>4</td>
<td>IW-2.7</td>
<td>4</td>
<td>63 - 69</td>
<td>63 - 69</td>
<td>48 - 64</td>
<td>48 - 64</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>5</td>
<td>IW-2.3</td>
<td>5.9</td>
<td>3514 - 4012</td>
<td>3714 - 4012</td>
<td>3766 - 4336</td>
<td>3766 - 4336</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>6</td>
<td>IW-2.3</td>
<td>5.9</td>
<td>3516 - 4012</td>
<td>3714 - 4012</td>
<td>3766 - 4336</td>
<td>3766 - 4336</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>7</td>
<td>IW-1.9</td>
<td>10</td>
<td>4153 - 4335</td>
<td>4153 - 4335</td>
<td>4175 - 4292</td>
<td>4175 - 4292</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>8</td>
<td>IW-1.7</td>
<td>12</td>
<td>4232 - 4292</td>
<td>4232 - 4292</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>9</td>
<td>IW-1.4</td>
<td>17</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>10</td>
<td>IW-1.3</td>
<td>18</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>11</td>
<td>IW-1.2</td>
<td>22</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>12</td>
<td>IW-1.0</td>
<td>27</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>13</td>
<td>IW-0.8</td>
<td>34</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>0.5% - 1.0%</td>
</tr>
<tr>
<td>14</td>
<td>IW-0.6</td>
<td>43</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>4264 - 4264</td>
<td>0.5% - 1.0%</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, and 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 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 H2O 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 obtained from the equilibrium conditions (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 SiO2.3% density contrast with respect to the oxygen-free constituent. These results are consistent with seismology.

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