SIDEROPHILE ELEMENTS MAY NOT BE ENRICHED IN THE UPPER MANTLE: SPECULATIONS ON PROTOCORE SEPARATION, Robin Brett, U.S. Geological Survey 959, Reston, VA 22092

Measurements and calculations (1,2) indicate that the oxygen fugacity \( f_{O_2} \) of the upper mantle ranges roughly from the wüdite-magnetite buffer to the iron-wüdite (IW) buffer. Was this relatively high \( f_{O_2} \) regime typical of the upper mantle during core formation? The literature abounds in references to C-bearing species (graphite, diamond, CO, CO\(_2\)) in mantle-derived rocks, so C would also have been present in the mantle during core separation. Oxygen fugacity would, therefore, have been fixed by the "graphite surface" (C-CO-CO\(_2\) buffer in P-T-\( f_{O_2} \) space). For upper mantle conditions, this surface lies as much as 2 log units above IW (2). Under such redox conditions, pure metallic iron would not be a stable phase but would become stable at greater depths (2). We have little evidence to indicate whether or not metallic iron was an abundant phase in the later stages of accretion. This relatively high \( f_{O_2} \), a consequence of equilibrium processes in the upper mantle, may be the "late" oxidation invoked by several authors (3).

Stevenson (4) presented a calculation that indicates that chemical equilibrium can occur at low pressures, i.e., in the upper mantle where the protocore was percolating through a silicate matrix. Experimental partitioning data between metal and silicate suggest that such partitioning in the Earth took place under conditions more oxidizing than the redox state of the Moon and the eucrite parent body (5). A requirement for such relatively oxidizing conditions is that temperatures in the upper mantle were relatively low, so that widespread reduction of FeO to Fe did not occur. Such temperatures are consistent with protocore formation in a mainly solid mantle (4).

The composition of the protocore forming in the upper mantle would lie largely within the system Fe-S-O, and Ni would also be abundant. A rough estimate of the composition of the melt may be made from the work at 1 atm. of Naldrett (6) on the system Fe-S-O at 1200°C, at log \( f_{O_2} \) between -11 and -12 (straddling the \( f_{O_2} \) of IW at this temperature) and at log \( f_{S_2} \) between -5 and -6 (that for high-Fe pyrrhotite at this temperature (7)). Under such conditions, the melt consists of about 69% Fe, 23% S, and 8% O (by weight). This is a very rough estimate as the effects of pressure (say 30 kb) cannot be taken into account because of lack of data. Also the applicable temperature is not at all well known. Clearly this liquid would change markedly in its path through the mantle: the above composition by no means represents a postulated composition of the core.

Such liquids approximate natural immiscible sulfide liquids in mafic liquids (6), and relevant partition coefficients for Ni, Cu, Co, Ga, Ge, Au, and Ir may be used (8,9) to estimate elemental contents in the upper mantle after protocore separation. Solar abundances for the above elements (11), and a protocore mantle ratio of 31:69 were used, although wide latitude in this ratio produces similar results. A pyrolitic mantle was chosen (basalt: harzburgite = 5:1). Where partitioning data on olivine were lacking, data from analyzed samples on D basalt/harzburgite (11) were used. Calculations and analyses agree within a factor of 1.5 except for Cu (Table 1), however Cu in primitive ultramafic nodules varies by as much as a factor of 4.4 (12).

Jagoutz et al. (12) pointed out that Ni/Co for rocks of upper mantle origin is chondritic. If the present results have any credence, then this is a coincidence. Several authors (13) pointed out that the ratios for Ir, Os, Au, and Pd are chondritic and ascribe this to a late-stage meteoritic component. Clearly, to obtain partitioning data for these elements is of prime importance, so that the importance of the late-stage meteoritic
component can be evaluated. The present results for Au and Ir do not require a late-stage component, but they represent maximum values only.

The agreement between calculated and published mantle abundances of three of the four elements is remarkable. The calculated abundances of the three elements for which minimum distribution coefficients are available are consistent with mantle abundances. Either the simple model for core formation in the upper mantle is valid and available experimental distribution coefficients pertain to the conditions during such core separation, or else we are dealing with an extreme coincidence.

Jones and Drake (9) suggested that similar W/La ratios in lunar, terrestrial, and meteoritic basalts argue strongly for similar core-forming processes on all parent bodies and argue against a role for high pressures in determining partitioning. Their arguments are consistent with the present model which advocates that the partitioning between the protocore and mantle that has been sampled was solely a consequence of upper mantle processes.

Conclusions: 1) Protocore separation in the upper mantle may have been an equilibrium process within a P-T gradient, as elemental distributions are in the range of what would be expected by equilibrium separation of an Fe-S-O liquid from an upper mantle having $^{16}O_2$ in the vicinity of that of the IW buffer. After protocore separation, the upper mantle ceased to be in equilibrium with the protocore below it.

2) A late-stage bombardment of carbonaceous chondrites may not be the only possible explanation for elemental abundances in the upper mantle; more data on distribution coefficients are required to test this.

3) Because mantle abundances fit an equilibrium model for protocore separation, either the upper mantle has not been mixed very much with the rest of the mantle since the core formed, or else partition coefficients between protocore and mantle were similar for the whole mantle regardless of P, T, and $^{16}O_2$. The latter possibility seems unlikely over such a P-T range, especially because the composition of a protocore formed in the upper mantle would differ considerably from that of a protocore formed in the deep mantle.


Table 1. Upper mantle abundances of siderophile elements (in atoms/10^6 Mg)

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<tbody>
<tr>
<td>Ni</td>
<td>3600</td>
<td>3800</td>
<td>Ge</td>
<td>&lt;12</td>
</tr>
<tr>
<td>Co</td>
<td>190</td>
<td>190</td>
<td>Au</td>
<td>&lt;2.7x10^-4</td>
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<tr>
<td>Cu</td>
<td>2</td>
<td>47</td>
<td>Ir</td>
<td>&lt;6.3x10^-2</td>
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<tr>
<td>Ga</td>
<td>6.5</td>
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