ROEBLING MEDAL LECTURE

Trace element partitioning into sulfide: How lithophile elements become chalcophile and vice versa†

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ABSTRACT

Sulfides, although modally of low abundance in most igneous rocks, have strong influences on the geochemical behavior of many elements including Pb, Cu, Ni, and the PGEs. In a recent paper, we demonstrated a simple relationship between the sulfide-silicate partition coefficients \( D_{\text{m}}^{\text{sil}} \) of such elements and the FeO content of the coexisting silicate melt (Kiseeva and Wood 2013).

\[
\log D_{\text{m}}^{\text{sil}} = A - \frac{n}{2} \log [\text{FeO}]
\]

where \( n \) is the valency of element \( M \), \([\text{FeO}]\) is the concentration of FeO in the silicate in wt\%, and \( A \) is a constant that depends on temperature and pressure. Elements that closely obey the simple model are Pb, In, Sb, Cd, Co, Zn, and Cr. We show here, however, that the fitted slope \( n \) depends not only on the valency of element \( M \), but also on how \( M \) interacts with oxygen, the dissolution of which as FeO in the sulfide increases as the FeO content of the silicate melt increases.

To take account of interactions of trace element \( M \) with FeO dissolved in the sulfide we introduce an additional parameter \( \varepsilon_{\text{Fe}^{1/2}} \) (Wagner 1962), which represents the difference between the lithophile and chalcophile properties of \( M \) and those of Fe. If \( \varepsilon_{\text{Fe}^{1/2}} \) is positive, then element \( M \) is more chalcophile than Fe if negative more lithophile.

We performed experiments to investigate partitioning of lithophile Nb, Ta, Ce, and Ti between sulfide and simplified basaltic melt and find that they all exhibit, as expected, concave upward behavior on a plot of \( \log D \) vs. \( \log [\text{FeO}] \). New experiments on Cu at low FeO contents confirm that it is more chalcophile than Fe, yielding a concave-downward curve of \( \log D \) vs. \( \log [\text{FeO}] \). The combined results mean that nominally lithophile elements may partition more strongly into sulfide than nominally chalcophile elements at either very low or very high FeO contents of the silicate melt. For example, as the FeO content of the silicate melt declines below about 1 wt\%, the partition coefficient of Cu, \( D_{\text{Cu}}^{\text{sil}} \), declines to an unusually low value (\( D_{\text{Cu}}^{\text{sil}} \approx 80 \)), whereas those for Nb (\( D_{\text{Nb}}^{\text{sil}} \approx 600 \), and rare earths (REE’s) increase strongly. Under these conditions, Nb is, therefore, substantially more “chalcophile” than Cu in that it partitions much more strongly into sulfide.

The implications of these observations for the Earth are that under a wide range of conditions one would expect significant partitioning of REE, Nb, Ta, Ti, and other lithophile elements into sulfides. Wohlers and Wood (2015) have, for example, shown that the partitioning of U and the REE into sulfides at low FeO content of the silicate is sufficiently pronounced that addition of a reduced sulfur-rich body to the accreting Earth could generate observable fractionation of Nd from Sm and, together with S, transfer sufficient U to the core to provide a significant energy source for the geodynamo.

Keywords: Sulfides, chalcophile elements, partitioning behavior, trace elements, lithophile elements

INTRODUCTION

Although the concentration of sulfur in the silicate Earth is only about 250 ppm (McDonough and Sun 1995), sulfur and sulfides are major geochemical agents. Their impacts extend from immiscible droplets in basaltic melts, which control the concentrations of chalcophile elements such as Pb and Cu in differentiating magmas, through high-temperature hydrothermal deposits and low-temperature lead-zinc deposits. In the case of Pb, for example, the Ce/Pb and Nd/Pb ratios of N-MORB appear to be essentially constant at ~25 and ~20, respectively (Hart and Gaetani 2006; Hofmann et al. 1986). Since Pb is much more incompatible than Ce and Nd in mantle silicate minerals (Hart and Gaetani 2006), it seems that partitioning of Pb into volumetrically very small amounts of sulfide exerts the principal control on behavior of this element in partial melting and igneous differentiation. Similar arguments have
been made in favor of sulfide precipitation exerting the major control on the behavior of Cu (Lee et al. 2012) during generation and evolution of island arc basalts. Lee et al. (2012) found that Cu is strongly incompatible in most silicate phases and that with \( D_{\text{sil}} \) in the range 600–1200 the small amounts of sulfide present in the sub-arc mantle should control the Cu contents of magmas. Furthermore, they suggest that the low Cu concentrations in primitive arc basalts imply oxygen fugacities of ~FMQ (similar to MORB) and that some differentiated magmas reached about FMQ+1.3 log units before precipitating sulfide (Lee et al. 2012). Many other chalcophile elements (Cd, In for example) are economically important, which makes the interpretation and understanding of their geochemical behavior of considerable value.

In addition to economic importance, sulfide and chalcophile elements have frequently been proposed to have played important roles in the accretion and differentiation of the Earth. The strong depletion of S in the silicate Earth, relative to elements of similar volatility such as Zn is likely due to its strong partitioning into the core during accretion (Dreibus and Palme 1996). This may have been in the form of a late-added sulfide matte (O’Neill 1991; Wood and Halliday 2005). Both Wood and Halliday (2005) and Hart and Gaetani (2006) argue that partitioning of Pb into mantle sulfide and extraction of such sulfide to the core could be responsible for the “lead paradox,” the observation that silicate Earth lies to the right of the “geochron” on a \(^{207}\text{Pb}^{206}\text{Pb}\) vs. \(^{206}\text{Pb}^{204}\text{Pb}\) diagram.

**Theoretical development**

Given the importance of sulfides in controlling the geochemical behavior of many elements, we recently attempted to systematize trace element partitioning between sulfide melt and silicate liquid (Kiseeva and Wood 2013). We started with the simplest equilibrium describing partitioning of a chalcophile element, Ni, for example between the two liquid phases. This can be written as follows:

\[
\text{NiO} + 0.5\text{S}_2 = \text{NiS} + 0.5\text{O}_2 \tag{1}
\]

sulfide silicate

In that case, at fixed pressure and temperature the equilibrium constant is defined as:

\[
K_i = \frac{a_{\text{NiS}}}{a_{\text{NiO}}} \frac{f_{\text{S}^2}}{f_{\text{O}^2}} \tag{2}
\]

where \(K_i\) is the equilibrium constant and \(a_i\) and \(f_i\) are activity and fugacity of \(i\), respectively. Generally speaking, sulfide liquids in the Earth are FeS-rich so neither the activity of NiO (in silicate) nor that of NiS (in sulfide) is close to 1. To a good approximation, however, we can usually replace activity ratios by concentration ratios, which leads to:

\[
\frac{a_{\text{NiS}}}{a_{\text{NiO}}} \approx \frac{[\text{Ni}]}{[\text{Ni}]} = D_{\text{Ni}} = K_i^{0.5} f_{\text{S}^2} / f_{\text{O}^2} \tag{3}
\]

where \(K_i^{0.5}\) is a modified equilibrium constant in terms of concentration. Thus, the partition coefficients \(D_i\) must depend on the ratio of sulfur fugacity to oxygen fugacity. At one atmosphere pressure, oxygen and sulfur fugacities are fairly readily controlled using CO₂–CO–SO₂ mixtures, which enable \(K_i^{0.5}\) to be determined as a function of temperature. Many chalcophile elements are volatile, however, which means that experiments are most easily performed at high pressure. In that case, it is much more difficult to control sulfur fugacity and oxygen fugacity control requires the presence of a free fluid phase. However, as shown by Kiseeva and Wood (2013), we can dispense with sulfur and oxygen fugacity control if we consider partitioning of the elements of interest in terms of an exchange reaction with the major element Fe:

\[
\text{NiO} + \text{FeS} = \text{FeO} + \text{NiS} \tag{4}
\]

silicate sulfide silicate sulfide

At saturation of the silicate melt with sulfide the Ni partition coefficient \(D_{\text{Ni}}^{\text{sil}}\) can be expressed by a modified equilibrium constant \(K_i^{0.5}\) and the activities of iron species, which are much easier to measure and control than the fugacities of the gaseous species:

\[
D_{\text{Ni}}^{\text{sil}} = K_i^{0.5} \frac{a_{\text{FeS}}}{a_{\text{FeO}}} \tag{5}
\]

If we use a pure FeS liquid with trace Ni, then the activity of FeS is essentially 1.0, so we can take logarithms and rearrange Equation 5 to:

\[
\log D_{\text{Ni}}^{\text{sil}} = \log K_i^{0.5} - \log a_{\text{FeS}}^{0.5} \tag{6}
\]

More generally, where the trace element of interest \(M\) has a different valency from Fe and the activity of FeO in the silicate is a linear function of its concentration, Equation 6 may be expressed as:

\[
\log D_{\text{M}}^{\text{sil}} \approx A - \frac{n}{2} \log [\text{FeO}] \tag{7}
\]

In Equation 7, \(A\) and \(n\) depend on the equilibrium constant for the exchange reaction and valency, respectively, and [FeO] is the FeO concentration in the silicate in appropriate units. Kiseeva and Wood (2013) showed that, at fixed temperature and pressure, Equation 7 describes the sulfide-silicate partitioning behavior of several elements (notably Pb, In, Sb, Cd, Co, Zn, Cr) extremely well. These elements all show linear dependences of \(\log D_i\) on [FeO] if the sulfide is pure FeS. In nature, however, the major cations in magmatic sulfide liquids are generally mixtures of Fe with Ni and Cu. Kiseeva and Wood (2013) also found that, to a good approximation, one could assume ideal Fe-Ni-Cu solution so that the activity of FeS is reduced from 1.0 by the cation fraction of Fe in the sulfide. We incorporated this correction in the FeO term as follows:

\[
[\text{FeO}]_{\text{sulfide}} = \frac{[\text{FeO}]_{\text{silicate}} ([\text{Fe}]/([\text{Fe} + \text{Ni} + \text{Cu}])_{\text{sulfide}} \tag{8}
\]

Despite simple and predictable partitioning behavior for many elements, several important elements (Ni, Cu, Ag, Mn, Tl) show strongly non-linear dependences of \(\log D_i\) on [FeO] and we were unable to assign them to any one particular category in terms of affinity for sulfide. It is the purpose of this paper to expand on the ideas of Kiseeva and Wood (2013) and to test our
ideas on the potential roles of oxygen in the sulfide and of sulfur in the silicate on controlling partitioning of many elements.

**Oxygen and sulfur in sulfides and their influences on partitioning**

As observed by Kiseeva and Wood (2013), there is an excellent correlation between the FeO content of the silicate melt and the oxygen content of the coexisting sulfide. At 1.5 GPa and 1400 °C this corresponds to:

\[ O(\text{sulf}) \approx 0.24 \text{FeO(sil)} \]  

(9)

where O and FeO are both in wt%. (Note that with more data the slope has been updated from the original 0.23.) At 10 wt% FeO in the silicate, therefore, the O content of the sulfide is 2.4 wt% approximately, which corresponds to an \( O/(S+O) \) of about 0.13 in sulfide. Thus, at 10% FeO in the silicate, 13% of the anions in the sulfide are oxygen rather than sulfur and the FeO content of the sulfide is about the same as that in the silicate:

\[ \text{[FeO]}(\text{sulf}) \approx \text{[FeO]}(\text{sil}) \]  

(10)

We hypothesized that this significant replacement of S by O would affect partitioning of both chalcophile and lithophile elements into sulfide.

Figure 1 shows idealized and “non-ideal” partitioning behavior based on Equation 7. Ideal behavior (Fig. 1a) yields, of course, a straight line of slope \( n/2 \) where \( n \) is the valency of the trace ion. We show in Figure 1a that Pb closely approximates “ideal” partitioning behavior. Figure 1b shows the situation when the trace ion is slightly more lithophile than Fe. A linear correlation
is observed but the slope is less negative if the element, like Zn, is more lithophile than Fe. Similar behavior is exhibited by Ga, V, and Ge. If the element is more chalcophile than Fe (e.g., Co), the slope is more negative than the “ideal” slope. Figure 1c shows the expected partitioning behavior for elements that are much more chalcophile than Fe and that exhibit downward curvature on the plot of logD vs. log[FeO]. The example shown is Cu, but Ni and Ag behave similarly. Strongly lithophile elements should show upward curvature on a plot of logD vs. log[FeO] (Fig. 1d), but since partitioning of lithophile elements into sulfide is not generally regarded as important, this behavior has not previously been explored. One of our purposes here is to show that some important lithophile elements do partition into sulfides in the manner depicted in Figure 1d. A second purpose is to investigate partitioning of both chalcophile and lithophile elements into sulfide at very low FeO content of the silicate. As will be shown, the results are surprising and would have been very difficult to predict. We continue with a description of partitioning experiments aimed at studying the lithophile elements Ti, Ce, Nb, and Ta together with additional results on chalcophile Cu.

### EXPERIMENTAL AND ANALYTICAL PROCEDURES

#### Experimental methods

Starting materials consisted of mixtures of ~50% FeS and ~50% synthetic silicate, by weight. The silicate constituent was a composition close to the 1.5 GPa eutectic composition in the system anorthite–diopside–forsterite (An$_{50}$Dis$_{28}$Fo$_{22}$) (Presnall et al. 1978) (Table 1). The end-members anorthite, diopside, and forsterite were pre-synthesized from mixtures of analytical-grade SiO$_2$, Al$_2$O$_3$, and MgO, combined with CaCO$_3$. The oxide mixes were decarbonated at 950 °C for 2 h, pelleted, and fired twice for 5 h at 1150 °C with grinding and re-pelletizing in between each firing. Iron oxide (as Fe$_3$O$_4$) was added after firing in some experiments to increase FeO activity. In other cases FeSi$_2$ was added to consume the oxide layer that forms on powdered FeS (in the bottle) and to drive the FeO content of the silicate to as low a value as possible. Occasionally this leads to precipitation of a second immiscible Fe-Si liquid in addition to the sulfide. Fortunately in such cases the two liquids are physically separate from one another. Small amounts of Ni (as NiS ≤1%) and/or Cu (as oxide) were sometimes added to the sulfide starting mixture to provide a second internal standard for laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis of the metallic phase. Ti, Nb, and Ta were added as 1–2% oxides to the silicate mix. Ce was present as a contaminant. The starting materials were ground under acetone before being dried prior to the experiment.

Starting mixtures were loaded into 3 mm O.D., 1 mm I.D. graphite capsules and experiments performed in an end-loaded piston-cylinder apparatus. The experimental assembly consisted of a 12.7 mm O.D. calcium fluoride cylinder with inner graphite heater of 8 mm O.D. and 6 mm I.D. At temperatures above 1450 °C the outer sleeve was replaced by an outer thin-walled barium carbonate sleeve and inner silica glass sleeve. Internal (to the heater) spacers were of 6 mm O.D. machineable MgO. The capsule was surrounded and separated from the graphite furnace by a 6 mm O.D. ring of machineable MgO. The experimental pressure was based on the calibration of McCauley et al. (2002).

Temperature was controlled and measured using a C-type (W$_8$Re$_6$–W$_8$Re$_6$) thermocouple separated from the capsule by a 0.5 mm alumina disk. Based on our previous work (Kiseeva and Wood 2013) experiment durations of 30 min are sufficient to approach equilibrium at 1400 °C. All experiments were therefore performed for 30 min or longer. After quenching, products were mounted in acrylic resin, individually sectioned and hand-polished using water-based lubricants and diamond pastes. During the experiment the sulfide segregates into large blobs, several hundred micrometers across, while the silicate glass also generally exhibits large sulfide-free areas (Fig. 2). This good physical separation enables analysis of both phases under the methods described below.

The experimental products were analyzed using a JEOL JXA8800 electron microprobe at the Department of Archaeology at the University of Oxford. WDS analyses were conducted using a 15 kV accelerating voltage and 20 to 100 nA beam current with a defocused 10 μm spot to improve averaging of both silicate and sulfide phases. At least 25 repeat analyses were collected for the silicate and sulfide parts of each charge. Counting times were as follows: 30 s peak and 15 s background for major elements (e.g., Si, Al, Ca, Mg), 60–120 s peak and 30–60 s background for minor elements (Ti, Cu, Ni, Nb, Ta). The peak count time for Fe was adjusted from 30–60 s on peak (half of this time on background) depending on anticipated concentration. A range of synthetic and natural standards was used for calibration. Standards for sulfide analysis were galena (Sn), Nb, Ta, Ni, and Cu metals, rutile (Ti), and hematite (Fe, O). Standards for silicate glass analysis were wollastonite (Ca, Si), periclase (Mg), rutile (Ti), albite (Na, Al), fowlerite (Mn), orthoclase (K), and hematite (Fe). Natural almandine was used as a secondary standard for the silicate phases. Oxygen in the sulfide was determined using the Ka peak and a LDE pseudocrystal as described by Kiseeva and Wood (2013). Results are given in Tables 2 and 3.

#### Table 1. Experimental conditions

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Starting composition</th>
<th>Duration (h)</th>
<th>Trace elements</th>
<th>T (°C)</th>
</tr>
</thead>
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<tr>
<td>390</td>
<td>CMAS+FeS</td>
<td>1</td>
<td>TR2</td>
<td>1400</td>
</tr>
<tr>
<td>395</td>
<td>CMAS+FeS</td>
<td>1</td>
<td>TR2</td>
<td>1400</td>
</tr>
<tr>
<td>1321</td>
<td>MORB+FeS+NiS(tr)</td>
<td>2</td>
<td>TR2</td>
<td>1400</td>
</tr>
<tr>
<td>1322</td>
<td>MORB+FeS+NiS(tr)</td>
<td>2</td>
<td>TR2</td>
<td>1400</td>
</tr>
<tr>
<td>1323</td>
<td>(MORB+30%FeO)+FeS+NiS(tr)</td>
<td>2</td>
<td>TR2</td>
<td>1400</td>
</tr>
<tr>
<td>1324</td>
<td>(MORB+20%FeO)+FeS+NiS(tr)</td>
<td>2</td>
<td>TR2</td>
<td>1400</td>
</tr>
<tr>
<td>1325</td>
<td>(MORB+40%FeO)+FeS+NiS(tr)</td>
<td>2</td>
<td>TR2</td>
<td>1400</td>
</tr>
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</tr>
<tr>
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<td>CMAS+FeS+4%NiS+15%FeSi$_2$</td>
<td>0.5</td>
<td>TR</td>
<td>1460</td>
</tr>
</tbody>
</table>

Notes: All experiments performed in graphite capsules. NiS(tr) = less than 0.5% added in the bulk started mixture. MORB = from Falloon and Green (1987) (column 2). CMAS = Fo$_{22}$Di$_{28}$An$_{50}$. TR contains Cu, In, Ti, Pb, Ag, Zn, Cr, V, Co, Sb, and Cd as oxides with Cu$_2$O double that of other oxides. TR2 contains Nb and Ta.

#### FIGURE 2. Backscattered electron image of products of experiment 1323. Slight “speckling” of sulfide surface is due to polishing imperfections.
WOOD AND KISEEVA: LITHOPHILE ELEMENTS IN SULFIDE

Although lithophile elements are not conventionally considered of interest in sulfide behavior, Figure 1d suggests that, at high and low FeO contents of the silicate melt, there should be significant partitioning of many lithophile elements into the sulfide phase. Figure 3 shows partitioning results for Ce, Ti, Nb, and Ta at 1.5 GPa and temperatures of 1400–1460 °C. As can be seen, all three elements show the predicted behavior for lithophile elements sketched in Figure 1d, which suggests a U-shaped dependence of logD_E on [FeO]. These elements follow oxygen and partition more strongly into sulfide as FeO contents of sulfide and silicate increase. At low FeO contents, the low activity of FeO in the silicate forces contents of sulfide and silicate increase. At low FeO contents, follow oxygen and partition more strongly into sulfide as FeO contents were discarded.

LITHOPHILE ELEMENT PARTITIONING INTO SULFIDE

In the manner predicted from Equation 7 with a negative slope of 0.5 times the valency. In principle, then, the concave-upward behavior implies that lithophile elements such as these may partition strongly into sulfide and become “chalcopyrite” under conditions of either very low or very high FeO content. We discuss this in more detail below.

The dependence of D_E^38 to 107% for these lithophile elements on the oxygen content of sulfide may be parameterized using the ε-model of non-ideal interactions in metallic liquids (Ma 2001; Wagner 1962). For the case of highly dilute trace element M this model yields, for MS3, dissolved in, as shown by Kiseeva and Wood (2013), an approximately ideal FeS-FeO matrix:

### Table 2. Major element compositions of the sulfide (wt%)

<table>
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<tr>
<th>Exp. no.</th>
<th>n</th>
<th>SiO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>Nb2O5</th>
<th>Ta2O5</th>
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<td>16.54</td>
<td>4.07</td>
<td>d.b.d.</td>
<td>15.94</td>
<td>16.08</td>
<td>d.b.d.</td>
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<td>101.80</td>
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<td>12.67</td>
<td>n.m.</td>
<td>n.m.</td>
<td>10.91</td>
<td>103.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 3. Major element compositions of the sulfide (wt%)

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>n</th>
<th>O</th>
<th>S</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Ti</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>390</td>
<td>41</td>
<td>1.14</td>
<td>36.89</td>
<td>62.88</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>n.m.</td>
<td>100.91</td>
</tr>
<tr>
<td>395</td>
<td>33</td>
<td>1.23</td>
<td>35.93</td>
<td>62.29</td>
<td>0.14</td>
<td>n.m.</td>
<td>99.60</td>
<td></td>
</tr>
<tr>
<td>1321</td>
<td>15</td>
<td>1.49</td>
<td>36.64</td>
<td>62.65</td>
<td>n.m.</td>
<td>n.m.</td>
<td>0.0077</td>
<td>100.59</td>
</tr>
<tr>
<td>1322</td>
<td>42</td>
<td>3.08</td>
<td>33.61</td>
<td>64.37</td>
<td>n.m.</td>
<td>n.m.</td>
<td>0.0135</td>
<td>101.08</td>
</tr>
<tr>
<td>1323</td>
<td>44</td>
<td>5.55</td>
<td>30.60</td>
<td>65.04</td>
<td>n.m.</td>
<td>n.m.</td>
<td>0.0254</td>
<td>101.22</td>
</tr>
<tr>
<td>1324</td>
<td>38</td>
<td>4.03</td>
<td>32.45</td>
<td>64.67</td>
<td>n.m.</td>
<td>n.m.</td>
<td>0.0225</td>
<td>101.18</td>
</tr>
<tr>
<td>1325</td>
<td>63</td>
<td>7.19</td>
<td>28.62</td>
<td>64.86</td>
<td>b.d.l.</td>
<td>n.m.</td>
<td>0.0434</td>
<td>100.71</td>
</tr>
<tr>
<td>1412</td>
<td>12</td>
<td>0.81</td>
<td>30.99</td>
<td>63.96</td>
<td>0.39</td>
<td>0.11</td>
<td>0.3013</td>
<td>96.56</td>
</tr>
<tr>
<td>1418</td>
<td>15</td>
<td>1.03</td>
<td>36.13</td>
<td>59.27</td>
<td>0.28</td>
<td>n.m.</td>
<td>0.0072</td>
<td>96.71</td>
</tr>
<tr>
<td>1419</td>
<td>15</td>
<td>1.00</td>
<td>35.83</td>
<td>60.33</td>
<td>n.m.</td>
<td>0.16</td>
<td>n.m.</td>
<td>97.32</td>
</tr>
<tr>
<td>1425</td>
<td>63</td>
<td>1.21</td>
<td>30.55</td>
<td>67.09</td>
<td>0.03</td>
<td>n.m.</td>
<td>0.0063</td>
<td>98.88</td>
</tr>
<tr>
<td>KK38-1</td>
<td>28</td>
<td>0.17</td>
<td>32.57</td>
<td>60.78</td>
<td>1.58</td>
<td>0.86</td>
<td>n.m.</td>
<td>95.97</td>
</tr>
</tbody>
</table>

Notes: Besides listed results, sulfides contain trace elements Cu, Pb, Zn, Cd, Ga, Ge, Ag, Sb, Mn, Co, In, Tl, Cr in the following total amounts: 1412 (0.92 wt%), 1418, 1419 (0.8 wt%), 1425 (2.05 wt%), KK38-1 (4.6 wt%).

Notes: The high totals accompanying high S contents are due to calculation of all cations as oxides. b.d.l. = below detection limit. n.m. = not measured. Values for Ta and Nb for experiments 1321, 1322, 1323, 1324, and 1325 were obtained by LA-ICP-MS.
Table 4. Trace element compositions of silicate and sulfide liquids (ppm)

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Ti</th>
<th>Ce</th>
<th>Nb</th>
<th>Ta</th>
<th>Cu</th>
<th>Ti</th>
<th>Ce</th>
<th>Nb</th>
<th>Ta</th>
<th>Cu</th>
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<td>390</td>
<td>0.0087</td>
<td>0.0149</td>
<td>0.0089</td>
<td>0.0008</td>
<td>0.0008</td>
<td>0.0087</td>
<td>0.0149</td>
<td>0.0089</td>
<td>0.0008</td>
<td>0.0008</td>
</tr>
<tr>
<td>395</td>
<td>0.0008</td>
<td>0.0012</td>
<td>0.0009</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0008</td>
<td>0.0012</td>
<td>0.0009</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>1321</td>
<td>0.0009</td>
<td>0.00052</td>
<td>0.0009</td>
<td>0.0004</td>
<td>0.0004</td>
<td>0.0009</td>
<td>0.00052</td>
<td>0.0009</td>
<td>0.0004</td>
<td>0.0004</td>
</tr>
<tr>
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<td>0.00004</td>
<td>0.00010</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0007</td>
<td>0.00004</td>
<td>0.00010</td>
<td>0.0001</td>
<td>0.0001</td>
</tr>
<tr>
<td>1333</td>
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<td>0.00003</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.001</td>
<td>0.00003</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1324</td>
<td>0.0022</td>
<td>0.00065</td>
<td>0.0025</td>
<td>0.001</td>
<td>0.0010</td>
<td>0.0022</td>
<td>0.00065</td>
<td>0.0025</td>
<td>0.001</td>
<td>0.0010</td>
</tr>
<tr>
<td>1325</td>
<td>0.0001</td>
<td>0.00005</td>
<td>0.0001</td>
<td>0.0004</td>
<td>0.0004</td>
<td>0.0001</td>
<td>0.00005</td>
<td>0.0001</td>
<td>0.0004</td>
<td>0.0004</td>
</tr>
<tr>
<td>1412</td>
<td>0.0048</td>
<td>0.0012</td>
<td>0.0035</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.0048</td>
<td>0.0012</td>
<td>0.0035</td>
<td>0.0015</td>
<td>0.0015</td>
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<tr>
<td>1418</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
</tr>
<tr>
<td>1419</td>
<td>0.0009</td>
<td>0.05</td>
<td>0.68</td>
<td>0.93</td>
<td>0.93</td>
<td>0.0009</td>
<td>0.05</td>
<td>0.68</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>1425</td>
<td>0.0046</td>
<td>0.05</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
<td>0.0046</td>
<td>0.05</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
</tr>
<tr>
<td>KK38-1</td>
<td>0.0020</td>
<td>0.20</td>
<td>0.58</td>
<td>0.58</td>
<td>0.58</td>
<td>0.0020</td>
<td>0.20</td>
<td>0.58</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>K33-1</td>
<td>0.0004</td>
<td>0.40</td>
<td>0.76</td>
<td>0.76</td>
<td>0.76</td>
<td>0.0004</td>
<td>0.40</td>
<td>0.76</td>
<td>0.76</td>
<td>0.76</td>
</tr>
</tbody>
</table>

\[ \log \frac{\gamma_{MSn/2}}{\gamma_{MSn/2}} \equiv \log \frac{\gamma_{FeO_{sulf}}} {\gamma_{FeO_{sulf}}} - \frac{1}{2} \log \left( \frac{\gamma_{FeO_{sulf}}} \right) \log \left( 1 - \frac{x_{FeO_{sulf}}} \right) \]  \hspace{1cm} (11)

In Equation 11, \( \gamma_{MSn/2} \) is the activity coefficient of MSn/2 in the sulfide, \( \gamma_{MSn/2} \) is the activity coefficient of MSn/2 component at infinite dilution in FeS and \( e_{FeO_{sulf}} \) is the ε-parameter describing interactions between MSn/2 and FeO dissolved in the sulfide.

Adding activity coefficients for MSn/2 components to Equation 7 gives us a predicted form of \( D^\text{silicate}_M \) of (Kiseeva and Wood 2015):

\[ \log D^\text{silicate}_M \equiv A' - \frac{1}{2} \log \left[ \frac{\gamma_{FeO_{sulf}}} \right] \frac{1}{2} \log \left( 1 - \frac{x_{FeO_{sulf}}} \right) \]  \hspace{1cm} (12)

In Equation 12, A’ is a constant incorporating end-member properties, [FeO] is, before the FeO content of the silicate melt and n is the valency of element M.

We assumed valencies of +5 for Nb and Ta, +4 for Ti, and +3 for Cu.

**FIGURE 3.** Measured partitioning of Ce, Ti, Nb, and Ta between sulfide and silicate at 1.5 GPa and 1400–1460 °C from this study and Kiseeva and Wood (2013, 2015). Curved lines correspond to fits to Equation 12 with assumed oxidation states of +3 for Ce (a), +4 for Ti (b), and +5 for Nb and Ta (c).
for Ce to construct fits to the sulfide-silicate partitioning data for these lithophile elements. As can be seen in Figure 3, despite the strongly non-linear behavior, Equation 12 fits the partitioning results extremely well with the addition of the single ε-parameter describing the effects of adding FeO to the sulfide.

At low FeO content the partition coefficient is predicted to converge to the “ideal” slope and this prediction is met reasonably well for Ti$^{4+}$, Ce$^{3+}$, and Ta$^{5+}$ (Fig. 3). Note, however, that the likely change of oxidation state of Ti to Ti$^{3+}$ at low FeO content (Mallmann and O’Neill 2009) will tend to “flatten” the slope of log$D_{Ti}$ vs. log[FeO] and hence cause underestimates of $D_{Ti}$ at low [FeO]. A similar phenomenon is observed for Nb because $D_{Nb}$ increases much more steeply than that of the “ideal” slope for Nb$^{5+}$ as log[FeO] is decreased below 0 (Fig. 3c). These observations lead us to consider whether there are additional effects, which apply at very low FeO content of the silicate melt.

LOW FeO ACTIVITY AND ITS EFFECTS ON SULFUR AND TRACE ELEMENT PARTITIONING

In a study of metal-silicate partitioning of trace elements at very low oxygen fugacity it was observed that, at very low FeO contents of the silicate melt, the sulfur partitioning into the silicate increases dramatically (Kilburn and Wood 1997). This observation is consistent with replacement of O (formally O$^{2-}$) in the silicate melt by S$^{2-}$ in accordance with the equilibrium (O’Neill and Mavrogenes 2002):

$$\text{FeS} + \text{O}^{2-} = \text{FeO} + \text{S}^{2-}$$  \hspace{1cm} (13)

sulfide melt melt melt

From the equilibrium constant $K_{13}$ it can readily be seen that, at sulfide saturation ($a_{FeS} = 1$), lowering the activity of FeO must raise the activity of S$^{2-}$ in the silicate melt and hence the solubility of sulfur in the melt. We tested this hypothesis by adding FeSi$_2$ to our starting mixes to drive the FeO contents of the silicate to very low values.

Figure 4a shows the results of our measurements of S solubility at sulfide saturation as a function of FeO content of the silicate melt. As can be seen (Fig. 4, Table 2) sulfur concentrations in the silicate reach 10.9 wt% as the FeO content declines well below 1 wt%. In such cases the S/(O+S) ratio of the silicate is around 0.1–0.15, which suggests that the sulfur concentration in the silicate may be an important factor in partitioning. It is logical to think that, as the S content of the silicate increases at sulfide saturation the partitioning of chalcophile elements into the sulfide will become less strong as they become more compatible in the S-rich silicate. Similarly, strongly lithophile elements might be expected to be “repelled” by high S contents of the silicate and to partition more strongly than anticipated into coexisting sulfide.

Figure 4a shows partition coefficient $D_{Cu}^{sulfsal}$ data from this and earlier studies (Kiseeva and Wood 2013, 2015) at 1400–1460 °C and 1.5 GPa. It can clearly be seen that $D_{Cu}$ decreases dramatically, as expected, as the sulfur content of the silicate melt increases in the region of low FeO concentration. Figure 4b shows results for $D_{Sm}^{sulfsal}$ at 1.5 GPa and 1400–1500 °C (Wohlers and Wood 2015). As suggested above, the pronounced increase in the solubility of sulfur in the silicate as FeO decreases below 1 wt% is accompanied by a dramatic increase in $D_{Sm}^{sulfsal}$. The effects of increasing S solubility in the silicate are, therefore, the surprising but intuitively reasonable ones of decreasing the partitioning of chalcophile elements and increasing the partitioning of lithophile elements into sulfide relative to silicate.
DISCUSSION AND IMPLICATIONS

Figures 1, 3, and 4 summarize our current understanding of trace element partitioning between sulfide and silicate melts. Many elements (e.g., Pb, In, Sb, Cd, Co, Zn, Cr) approximate “ideal” behavior, albeit with slopes slightly different from n/2 (Fig. 1b). Strongly lithophile elements such as Nb, Ti, and the REE become chalcophile at very high and very low FeO contents of the silicate due, respectively, to the increasing oxygen content of the sulfide and the increasing sulfur content of the silicate. The corollary is that chalcophile elements such as Cu, Ag, and Ni become more lithophile at both high FeO and low FeO contents of the silicate melt. Thus, one can envision a situation where lithophile Nb partitions more strongly into sulfide than chalcophile Cu because of either the high S content of the silicate or the high oxygen content of the sulfide. Indeed, our data set shows that experiment 1412 with 4 wt% S and 0.28 wt% FeO in the silicate melt has D_{l/s} of 604 while 1425 with 6.9 wt% S and 0.42 wt% FeO has D_{l/s} of 84. Under these, admittedly extreme conditions, Nb is clearly more “chalcophile” than Cu in that it partitions more strongly into sulfide relative to silicate.

Given that nominally lithophile elements can partition strongly into sulfide at low FeO activity, we now consider whether this has any implications for the Earth and other planets. Moderately siderophile (e.g., Ni, Co, Mo, W) and weakly siderophile (e.g., V, Cr, Nb, Si) refractory elements (those that condense at high temperatures from a solar gas) are depleted to varying extents in the bulk silicate Earth relative to lithophile elements of similar volatility (McDonough and Sun 1995). By comparing the Solar System abundances of siderophile with lithophile elements we may calculate the approximate core-mantle partition coefficients of the former (Wade and Wood 2005). These can then be used in conjunction with experimentally determined metal-silicate partition coefficients to construct possible pressure-temperature-oxygen fugacity paths of accretion and core segregation (Wade and Wood 2005). When subsets of the elements of interest are considered it is possible to model core segregation at a single high pressure, temperature, and oxygen fugacity consistent with the current FeO content of bulk silicate Earth. When, however, data for all refractory elements are considered the most consistent solution involves a prolonged period of planetary growth under strongly reducing conditions with low FeO content of the mantle followed by addition of FeO-rich material to bring the oxidized iron content of the mantle up to its current value of 8 wt% (Rubie et al. 2011; Wade and Wood 2005; Wade et al. 2012). Asteroids and planetesimals that may have contributed to an Earth accreting under reducing conditions could have been similar in composition to the enstatite-chondrite meteorites or perhaps to the planet Mercury, which is metal-rich, probably with a S-rich core and has a low FeO, sulfur-rich outer silicate layer (Nittler et al. 2011). In such cases one would anticipate that nominally lithophile elements would be partitioned to some extent between core and mantle, disturbing the expected ratios in the outer silicate part.

The implications of accreting a reduced S-rich body to Earth have been explored in our laboratory by Wohlers and Wood (2015). We found strong partitioning of REE and U into sulfide at low FeO content (Fig. 4b) with the following order of sulfide-silicate partition coefficients for all experiments at 1.5 GPa: D_{l/s} > D_{l/s} > D_{l/s} > D_{l/s} (Wohlers and Wood 2015). In general, D_{l/s} ≈ 1.4D_{l/s} and D_{l/s} ≈ 0.1D_{l/s}.

The implications are that, in a reduced S-rich body such as Mercury, addition of sulfide to the core would carry U with it together with strong fractionation of Nd relative to Sm. Addition of a similar body to Earth during accretion could provide significant energy in the form of U and Th added to the core to drive the geodynamo (Wohlers and Wood 2015). Furthermore, the silicate part of such a body would have superchondritic Sm/Nd with, as observed (Boyet and Carlson 2005) a positive 273Nd anomaly relative to chondritic meteorites. It appears, therefore, that addition of reduced, S-rich bodies to the accreting Earth provide a possible explanation both for slow cooling of the core and for the non-chondritic Sm/Nd ratio of the silicate Earth.

Given our observations and considering the ubiquitous nature of both quenched sulfide melts and solid sulfides in igneous rocks it is clear that there is much more to be discovered about the geochemical behavior of sulfides in igneous petrogenesis. As yet, we have only scratched the surface.

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REFERENCES CITED


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