



# A simple model for chalcophile element partitioning between sulphide and silicate liquids with geochemical applications



Ekaterina S. Kiseeva\*, Bernard J. Wood

Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, UK

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## ABSTRACT

We have determined the partitioning of the elements Cu, In, Tl, Pb, Ag, Mn, Zn, Cr, Co, Ni, Sb and Cd between FeS-rich sulphide liquids and anhydrous basaltic melts at high pressures and temperatures. The sulphide liquids were found to have oxygen contents which are linearly related to the FeO contents of the silicate melts. We also found simple relationships between the FeO contents of the silicate melts and the sulphide–silicate partition coefficients  $D_M^{sulph/sil}$  for the individual trace elements. These relationships can be generally represented as follows:

$$\log D_M^{sulph/sil} \approx A + \frac{n}{2} \log[\text{FeO}]$$

where  $A$  is a constant related to the free energy of Fe–M exchange,  $n$  is a constant related to the valence of the element and  $[\text{FeO}]$  is the FeO content of the silicate melt in mole fraction or weight %. This simple relationship effectively removes the need to define the fugacity ratio  $f_{\text{O}_2}/f_{\text{S}_2}$  when considering partitioning and hence greatly simplifies application of partitioning data to natural systems. In theory  $n$  should approximate  $-1$  for  $1+$  ions,  $-2$  for  $2+$  ions and so on. Regressed values of  $n$  are generally close to those expected, although deviations occur for some elements. The deviations can be understood in terms of the relative chalcophile and lithophile characteristics of the element of concern.

For cases in which the sulphide is an FeS–NiS–Cu<sub>2</sub>S liquid we obtain excellent agreement with results for pure FeS by correcting the FeO content of the silicate melt as follows:

$$[\text{FeO}]_{\text{corrected}} = \frac{[\text{FeO}]_{\text{silicate}}}{[\text{Fe}/(\text{Fe} + \text{Ni} + \text{Cu})]_{\text{sulphide}}}$$

We tested our model on data from the literature in which sulphide–silicate partition coefficients for Cu, Co, Ni and Mn were determined. Literature data for these elements follow the predicted linear dependence of  $\log D_M^{sulph/sil}$  on  $\log[\text{wt}\% \text{FeO}]$ . Furthermore, differences between the absolute values of  $D_M^{sulph/sil}$  obtained by us and those in the literature are quantifiable in terms of temperature and matrix effects such as the Ni/Fe ratio of the sulphide.

We used our results for Pb partitioning to calculate Ce/Pb and Nd/Pb ratios of basalts generated by partial melting of the mantle followed by fractional crystallization. Calculated Nd/Pb is essentially constant over wide ranges of partial melting and fractional crystallization with a value of  $\sim 18.6$  if we assume that depleted mantle contains 65 ppb of Pb. Calculated Ce/Pb varies slightly during batch partial melting from 21 to 29 with the canonical value of 25 being achieved at  $\sim 10\%$  partial melting. These trends are in excellent agreement with measurements of oceanic basalt glasses.

Finally, we used our partitioning relationships to calculate the concentrations of a number of the incompatible chalcophile trace elements in depleted mantle. These are as follows: 32 ppm Cu, 65 ppb Pb, 7.6 ppb Ag, 12 ppb In, 23 ppb Cd, 1.7 ppb Sb and 1.3 ppb Tl.

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## 1. Introduction

Despite the concentration of sulphur in the silicate Earth being only about 250 ppm (McDonough and Sun, 1995), sulphur and sulphides are known to be very important geochemical agents in all petrogenetic environments. The presence of immiscible sul-

\* Corresponding author.

E-mail addresses: kate.kiseeva@earth.ox.ac.uk (E.S. Kiseeva), berniew@earth.ox.ac.uk (B.J. Wood).

phide globules in basaltic magmas indicates, for example, sulphide saturation at the time of eruption (Mathez, 1976; Wallace and Carmichael, 1992) and the decreasing solubility of S in silicate melts with increasing pressure (Holzheid and Grove, 2002) implies that MORB are generally at sulphide saturation throughout their path of ascent to the surface. The ability of sulphides to concentrate chalcophile elements is economically important in the context, for example, of high temperature copper porphyry deposits and low temperature lead–zinc deposits. Many other chalcophile elements (Cd, In, for example) are economically important, which makes the interpretation and understanding of their geochemical behavior of considerable value. There are, however, few data on the partitioning of these elements into sulphides under high temperature petrogenetic conditions.

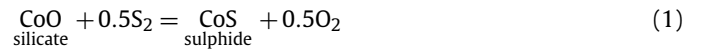
In addition to economic importance, sulphide and chalcophile elements have played important roles in the accretion and differentiation of the Earth. The relatively low abundance of S in the silicate Earth is probably due to its strong partitioning into the core during accretion (Dreibus and Palme, 1996) plausibly as a late-added sulphide matte (O'Neill, 1991; Wood and Halliday, 2005). The effects of such a matte would be to remove large fractions of chalcophile elements such as the platinum group elements (PGE) Pb, Cu and Ag to the Earth's core with corresponding increase in ratios such as U/Pb in the silicate Earth (Hart and Gaetani, 2006; Wood and Halliday, 2005). Wood and Halliday (2005) suggested that Pb partitioning into such a matte would be so strong that removal of < 1% by mass would be sufficient to shift  $\mu$  ( $^{238}\text{U}/^{204}\text{Pb}$ ) of the silicate Earth from the CI chondrite value (0.7) to the current value of  $\sim 9$ . Hart and Gaetani (2006) suggested that continuing dissolution of such a mantle sulphide into the core could be responsible for the “lead paradox”, the observation that silicate Earth lies to the right of the “geochron” on a  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  diagram. The latter indicates that U/Pb fractionation occurred on Earth considerably later than the time of core formation given by Earth's  $^{182}\text{W}$  anomaly (relative to chondrites) either in a single late core addition event (Wood and Halliday 2005, 2010; Rudge et al., 2010) or through progressive Pb extraction through geologic time (Hart and Gaetani, 2006). In either case, accurate modeling of the effects of sulphide extraction has been hampered by insufficient data on  $D_{\text{Pb}}^{\text{sulph/sil}}$ , the partition coefficient for Pb between sulphide and silicate melt. The importance of sulphide in controlling the behavior of Pb in the mantle is emphasized by data showing that silicates from a selectively leached peridotite contained only about 10% of the total expected amount of Pb, with the inference that the remainder resides in sulphide (Meijer et al., 1990). This conclusion was confirmed by recent studies showing the presence of significant amounts of unradiogenic lead, with  $^{207}\text{Pb}$ – $^{206}\text{Pb}$  age of about 2 Gyr in sulphides from abyssal peridotites (Burton et al., 2012; Warren and Shirey, 2012). The latter lie well to the left of the geochron and could provide a major part of the reservoir complementing the Pb–isotope compositions of crust and MORB source regions.

Since the Ce/Pb and Nd/Pb ratios of N-MORB are essentially constant at  $\sim 25$  and  $\sim 20$  respectively, it is generally assumed that lead behaves in a similar manner to these rare earths during partial melting and fractional crystallization (Hart and Gaetani, 2006; Hofmann et al., 1986). However, almost all measurements of silicate crystal–melt partition coefficients show that Pb is much more incompatible than Ce and Nd (Hart and Gaetani, 2006), which means that partitioning of Pb into sulphide exerts the principal control on behavior of this element during melting and differentiation. As noted above, however, lack of reliable sulphide/silicate partition coefficients hinders understanding of the relationship between Pb, Nd and Ce. A summary of available data on  $D_{\text{Pb}}^{\text{sulph/sil}}$  demonstrates, for example, a measured range from 1.3

to 40 (Hart and Gaetani, 2006) with a possible dependence on the oxygen content of the sulphide melt.

Lee et al. (2012) argue for an important role of sulphide precipitation in controlling the behavior of Cu during generation and evolution of island arc basalts. Their summary of literature data indicates that Cu is strongly incompatible in most silicate phases and that with  $D_{\text{Cu}}^{\text{sulph/sil}}$  in the range 600–1200 the small amounts of sulphide present in the arc mantle control the Cu contents of magmas. Furthermore, they suggest that the low Cu concentrations in primitive arc basalts imply oxygen fugacities of  $\sim \text{FMQ}$  (similar to MORB) and that some differentiated magmas reach about  $\text{FMQ} + 1.3$  before precipitating sulphide (Lee et al., 2012). In contrast to these conclusions, a recent experimental study of silicate crystal–melt partitioning of Cu (Fellows and Canil, 2012) indicates greater compatibility of this element in silicate and a conclusion that sulphide is much less important in controlling Cu concentrations in magmas than was supposed by Lee et al. (2012). More accurate measurements of  $D_{\text{Cu}}^{\text{sulph/sil}}$  for basaltic magmas would help resolve this issue.

To date, a large proportion of sulphide–silicate partitioning studies have concerned themselves with the platinum group elements (Bockrath et al., 2004; Crocket et al., 1997; Fleet et al., 1996, 1991) and relatively few with the chalcophile elements such as Cu, Co, Pb, Sb, Bi and Ag discussed above (Gaetani and Grove, 1997; Li and Audétat, 2012; Wood et al., 2008). In order to address their geochemical behavior, Li and Audétat (2012) recently made a comprehensive study of partitioning of a large number of elements (V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, Bi) between solid and liquid sulphides and hydrous basanite melt at high pressure. These authors followed Gaetani and Grove (1997) in recognizing the importance of oxygen fugacity in determining sulphide–silicate partitioning. This can be appreciated from the equilibrium of an element such as Co between silicate and sulphide phases:



The equilibrium constant for reaction (1) can be written as:

$$K_1 = \frac{a_{\text{CoS}}^{\text{sulph}} \cdot f_{\text{O}_2}^{0.5}}{a_{\text{CoO}}^{\text{sil}} \cdot f_{\text{S}_2}^{0.5}} \quad (2)$$

where  $K_1$  is the equilibrium constant and  $a_i$  and  $f_i$  are activity and fugacity of  $i$  respectively. In general, the activity of a component is closely related to its concentration in the phase of interest, so, to a good approximation we can simplify (2) as follows:

$$\frac{a_{\text{CoS}}^{\text{sulph}}}{a_{\text{CoO}}^{\text{sil}}} \approx \frac{[\text{Co}]^{\text{sulph}}}{[\text{Co}]^{\text{sil}}} = D_{\text{Co}}^{\text{sulph/sil}} = K'_1 \cdot \frac{f_{\text{S}_2}^{0.5}}{f_{\text{O}_2}^{0.5}} \quad (3)$$

where  $K'_1$  is a modified equilibrium constant in terms of concentration  $[\text{Co}]^{\text{sulph}}$  and  $[\text{Co}]^{\text{sil}}$ . Thus, the partition coefficients  $D_i$  must depend on the ratio of sulphur fugacity to oxygen fugacity. To account for these dependences Li and Audétat attempted to control oxygen fugacity in piston–cylinder experiments using external buffers such as Ni–NiO with a hydrous fluid. They then calculated sulphur fugacity after the experiment from the ratio  $\text{FeO}^{\text{sil}}/\text{FeS}^{\text{sulph}}$ . The principal difficulties and uncertainties in this approach are firstly that diffusion of hydrogen through the inner metal capsule caused reaction and loss of sulphide as  $\text{H}_2\text{S}$  and  $\text{FeO}$  in experiments of more than 2 h duration. Secondly, changing water and  $\text{FeO}$  contents of the silicate with time makes it difficult to ensure that equilibrium is approached. Since many of the elements of interest are volatile, the alternative approach of performing the experiments at 1 bar with controlled  $f_{\text{O}_2}$  and  $f_{\text{S}_2}$  may not be productive. However, in sulphide-saturated experiments at

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