Chalcophile Elements and Sulfides in the Upper Mantle

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Sulfides are among the most important petrogenetic agents in magmatic systems. They are ubiquitous in most upper-mantle rock types, common as inclusions in diamonds and they host significant amounts of geochemically and economically important chalcophile ('sulfur-loving') elements, such as Cu, Ni, Pb, In, Au and the platinum-group elements. Despite their low abundance (<< 1% of the bulk rock), residual sulfides have a disproportionate control over the chalcophile element budget in upper mantle lithologies, as well as that of melts derived from the Earth's mantle.

KEYWORDS: chalcophile, element partitioning, upper mantle, sulfides

INTRODUCTION

Sulfides are minerals that contain the sulfide anion, S^{2-}, as the major structural component. Sulfides are common accessory minerals in the Earth's interior. They are observed in upper-mantle peridotites and oceanic basalts, in mantle xenoliths, and are also the most common mineral inclusion in diamonds. Despite sulfur being a minor component in the mantle – present at concentrations of ~150–300 parts per million (ppm) S in the bulk silicate Earth (e.g. Palme and O'Neill 2013) – sulfides are, nonetheless, very important phases because many elements have a strong affinity for sulfur. These sulfur-loving elements are termed 'chalcophiles' (FIG. 1), and they are concentrated in sulfide minerals. Thus, sulfides control the behaviour of the chalcophile elements during magmatic processes.

Most chalcophile elements (some of which are also siderophile, or 'iron-loving') are economically important metals; ten of these are the most valuable metals in the world [In, Re, Au, Ag and the platinum-group elements (PGEs)]. In Earth's crust, these elements are typically found associated with base-metal sulfides, and sulfide deposits are mined extensively as a result. In addition to their economic importance, residual sulfides exert a strong control on the budget of chalcophile elements during partial melting and crustal differentiation and, hence, have a profound effect on the trace-element concentrations found in erupted magmas.

In this article, we explore the occurrence of sulfides in the Earth's mantle, the role of sulfides in the partitioning of chalcophile elements in magmatic systems, and the abundance of chalcophile elements in mantle-derived silicate melts.

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SULFIDES IN THE UPPER MANTLE

Sulfides are ubiquitous accessory phases in all types of mantle xenoliths. The major sulfide phases present in mantle rocks are pentlandite, pyrrhotite and chalcopyrite (Vaughan and Corkhill 2017 this issue). Also present are the 'monosulfide solid solution' (mss) and 'intermediate solid solution' (iss) phases. The observed mineralogy of mantle sulfides, however, likely represents low temperature (<300 °C) re-equilibration of high-temperature mss or, possibly, sulfide melt. Therefore, most recent studies have concentrated on reporting the bulk chemistry of polyphase inclusions (e.g. Bulanova et al. 1996), and this will be the focus of this discussion.

The compositions of sulfides from mantle xenoliths and diamond inclusions are shown in FIGURE 2. Sulfides observed in mantle xenoliths are dominantly Fe-rich with minor amounts of Ni and Cu. Peridotite xenoliths generally contain sulfides with ~20 wt% Ni and 4–5 wt% Cu, on average. Eclogitic sulfides are generally similar with respect to their Cu content compared to peridotite-hosted sulfides, but are consistently lower in Ni, with average concentrations ~3 wt% Ni.

Even though sulfides are accessory phases in mantle xenoliths (<0.1%) they are the most common mineral inclusions found in diamonds, accounting for 35%–46% of all diamond inclusions in the Finsch, Koffiefontein and Premier kimberlite pipes of South Africa (Harris and Gurney 1979). The Ni and Cu concentrations in sulfide inclusions in both peridotite- and eclogite-type diamonds are broadly similar compared to intergranular sulfides in peridotite and eclogite xenoliths, respectively. The marked difference in Ni concentrations between peridotite- and eclogite-hosted sulfides has been used as a paragenetic discriminator (Bulanova et al. 1996). Pearson et al. (1998) also noted that Ni concentrations of diamond-hosted sulfide inclusions correlate broadly with Os, and that Re/Os may be a more robust petrogenetic indicator for differentiating between peridotitic and eclogitic sulfides. Of course, how the concentrations of these elements in sulfides may be used as petrogenetic indicators hinges on our understanding of their partitioning behaviour between sulfide and silicate melt during mantle melting.

FIGURE 1 Periodic table showing chalcophile elements (highlighted in yellow). Note that many of these elements, according to Goldschmidt's classification, are also siderophile.

THEORETICAL CONSIDERATIONS ON PARTITIONING OF CHALCOPHILE ELEMENTS INTO SULFIDES

Because sulfides have the ability to concentrate economically important elements, several studies have been aimed at quantifying the chalcophile character of ore-forming metals. Most experimental studies have focused on PGEs (see review by Brenan et al. 2016) and, to a lesser extent, on the chalcophile elements, such as Cu, Ag, Sb, Tl, As and others (e.g. Kiseeva and Wood 2013; Li and Audétat 2012).

The most obvious way to investigate the behaviour of chalcophile elements in magmatic systems is through studying the partitioning of trace elements between sulfide and silicate liquids. The partition coefficient (D) for an element M is defined as the concentration of this element in a sulfide liquid divided by its concentration in a silicate liquid.

$$D_M^{\text{sulfide/silicate}} = \frac{C_M^{\text{sulfide liquid}}}{C_M^{\text{silicate liquid}}}$$

The higher the D, the more element M prefers to go into a sulfide phase, hence the more chalcophile it is. Determining D can be tackled using two different experimental approaches, both, as shown below, being similarly effective.

The first approach uses oxide–sulfide equilibria at controlled oxygen and sulfur fugacity conditions. The exchange of a chalcophile element, such as Pb, between sulfide and silicate melt can be described by the following reaction:

$$\text{PbO}_{x/2} + \frac{x}{4}\text{S}_2 = \text{PbS}_{x/2} + \frac{x}{4}\text{O}_2 \qquad (1)$$
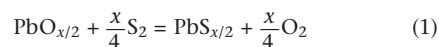
where x corresponds to the valence of Pb in silicate and sulfide melts. Assuming Pb is present in dilute concentrations, we can express Equation (1) in terms of the equilibrium constant (Brenan et al. 2016) and relate the $D_{\text{Pb}}^{\text{sulf/sil}}$ with oxygen and sulfur fugacity according to:

$$\log D_{\text{Pb}}^{\text{sulf/sil}} \propto -\frac{x}{4}\log\left(\frac{f\text{O}_2}{f\text{S}_2}\right) \qquad (2)$$

An essential conclusion to be drawn from Equation (2) is that the partition coefficient of a chalcophile element between sulfide and silicate melts is a function of the ratio between sulfur and oxygen fugacity. In other words, higher $f\text{S}_2$ values will favour the partitioning of Pb to a sulfide melt (i.e. higher $D_{\text{Pb}}^{\text{sulf/sil}}$), whereas high values of $f\text{O}_2$ will drive Pb into silicate melt (i.e. lower $D_{\text{Pb}}^{\text{sulf/sil}}$). In nature, however, because sulfur is a redox-sensitive element, $f\text{O}_2$ and $f\text{S}_2$ are inversely proportional, and as a result, do not vary independently.

In the more oxidising conditions prevalent during arc magmatism, sulfide is not stable and sulfate becomes the preferred S species (e.g. Jugo et al. 2010). When this occurs, $f\text{S}_2$ will drop considerably, while $f\text{O}_2$ can increase unabated. However, it is desirable to evaluate how $f\text{O}_2$ and $f\text{S}_2$ affect trace-element behaviour individually, because different trace elements will respond to changes in these parameters in different ways depending on how chalcophile they are.

A large number of experimental studies of silicate melts at 1 atm pressure were carried out during the 1980s and 1990s, in which $f\text{O}_2$ and $f\text{S}_2$ were controlled either by gas mixing or by the use of redox buffers (see review by Brenan et al. 2016). Unfortunately, some of these studies turned out to be compromised by contamination of their silicate glasses by the noble metals that the experiments were doped with. The so-called micronugget contaminants, which are sub-micrometer particles of metal and/or sulfide present in the silicate melt, are not dissolved species and can easily (wrongly) be included into the glass composition when experimental products are analysed. This has resulted in a widespread underestimation of the melts $D_M^{\text{sulf/sil}}$, in particular at more reducing conditions (cf. Ertel et al. 2008).

Only over the last couple of decades has the micronugget contamination issue been overcome by either measuring the solubilities of individual chalcophile elements in sulfide melt and silicate melt independently (e.g. Fonseca et al. 2011), or by measuring sulfide–silicate equilibria directly (Mungall and Brenan 2014). As a result, more recent studies now show $D_M^{\text{sulf/sil}}$ increasing with decreasing $f\text{O}_2/f\text{S}_2$, as expected from Equation (2).

A good illustration of the dependence of the partitioning behaviour of a given trace element with $f\text{O}_2/f\text{S}_2$ is given by Os. Older data obtained from experiments that did not consider micronugget contamination (grey symbols in FIG. 3A) are completely at odds with more recent Os partitioning data, in that they show the opposite dependence on $f\text{O}_2/f\text{S}_2$ expected from Equation (2). More recent
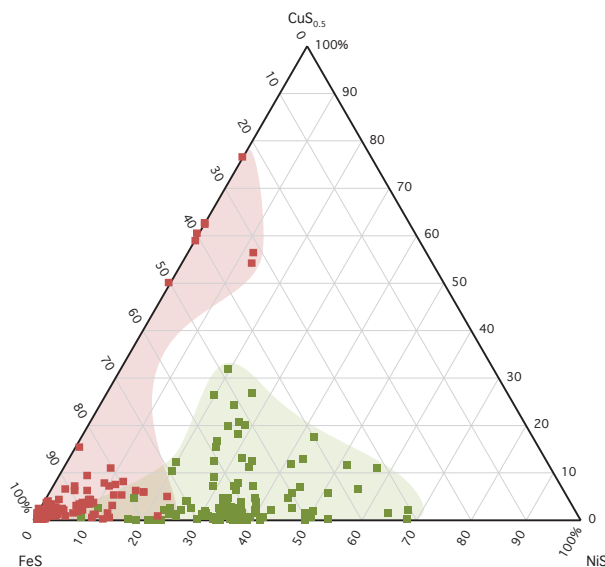
FIGURE 2 Ternary diagram ($CuS_{0.5}$, FeS and NiS) showing the major element composition of the mantle sulfides (in weight %). Green (peridotite); red (eclogite and pyroxenite). Data from Efimova et al. (1983), Bulanova et al. (1996), Pearson et al. (1998), Guo et al. (1999), Richardson et al. (2001), Westerlund et al. (2006).

studies (blue symbols in FIG. 3A), where efforts were made to avoid micronugget contamination, agree with the prediction of Equation (2). This contrast is a good illustration of the strides that have been made in investigating the chalcophile nature of trace elements over the last 25 years.

One other complexity that arises from the experimental approach described above is that the partition coefficient for a chalcophile element is related to sulfur and oxygen fugacities, which are easily controlled in laboratory experiments but that can be difficult to measure or estimate for natural systems. To overcome this problem, Kiseeva and Wood (2013, 2015) proposed an alternative second approach.

Following the study by Haughton et al. (1974), who related fS_2 to FeS and fO_2 to FeO, Kiseeva and Wood (2013) derived an expression that substitutes the fO_2/fS_2 ratio from Equation (2) with the FeO content of the silicate liquid (provided that the silicate melt is in equilibrium with the FeS sulfide), considering the exchange reaction:

$$MO_{x/2 \text{ (silicate)}} + (x/2)FeS_{\text{ (sulfide)}} = MS_{x/2 \text{ (sulfide)}} + (x/2)FeO_{\text{ (silicate)}} \quad (3)$$
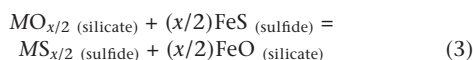
Again, if we use divalent Pb as an example, Equation (3) will become:

$$PbO_{\text{ (silicate)}} + FeS_{\text{ (sulfide)}} = PbS_{\text{ (sulfide)}} + FeO_{\text{ (silicate)}} \quad (4)$$

As for Equation (1), Equation (4) can be rearranged so that the partition coefficient $D_{Pb}^{\text{sulf/sil}}$ relates to the equilibrium constant and the activity of FeO in silicate melt (Kiseeva and Wood 2013). This leads to the very simple statement that when a magma is sulfide-saturated (where the activity of FeS will be approximately unity), $D_{Pb}^{\text{sulf/sil}}$ mainly depends on the FeO content of the silicate liquid:

$$\log D_{Pb}^{\text{sulf/sil}} \approx A + \frac{x}{2} \log[FeO] \quad (5)$$

where A is a constant related to the free energy of the Fe–Pb exchange between sulfide and silicate liquids; x is a constant related to the valence of the element; [FeO] is the

FeO content of the silicate melt in mole fraction or weight %. In theory, $-x$ will be the valence of the chalcophile element being studied (FIG. 3B).

Relationships between partition coefficients and FeO content of the silicate melt, summarised by Equation (5), have been successfully tested on a large number (>15) of chalcophile and moderately chalcophile elements and have proved to be valid for a broad range of temperatures and sulfide and silicate melt compositions. Moreover, the method outlined in Equation (5) allows the partition coefficient of a given chalcophile element to be described in terms of the easily measurable FeO content of silicate magma, precluding the need to account for oxygen and sulfur fugacities.

The two experimental approaches aimed at determining the partitioning relationships between the sulfide and silicate liquids are essentially addressing the same equilibrium, and they provide similar results for chosen T–fO_2 conditions, most notably when applied to melting of Earth's mantle.

To illustrate the equivalence of the approaches, we applied the two methods to the same dataset using data from Gaetani and Grove (1997). These authors controlled fO_2 and fS_2 and they synthesised silicate glasses over a range of FeO concentrations. In FIGURE 4, $D_{Ni}^{\text{sulf/sil}}$ is plotted as a function of $\log(fO_2/fS_2)$ and $\log[FeO]$ and shows an excellent correlation.
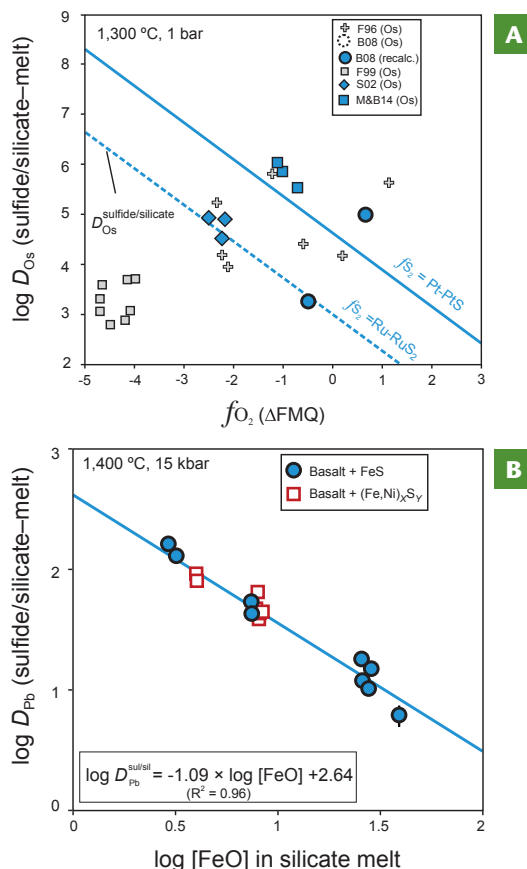

FIGURE 3 (**A**) Compilation of literature sulfide–melt/silicate–melt partition coefficients for Os, given as a function of oxygen fugacity (here given relative to the fayalite–magnetite–quartz redox equilibrium – ΔFMQ) and at different sulfur fugacities (dashed and solid blue lines). Data sources include studies with micronugget contamination that was not taken into account (grey cross symbols). Blue symbols represent experiments where micronugget contamination was avoided. Data from Fonseca et al. (2011) and Mungall and Brenan (2014). (**B**) Sulfide–melt/silicate–melt partition coefficients for Pb versus log[FeO] content (wt %) of the silicate glass. Modified from Kiseeva and Wood (2013).
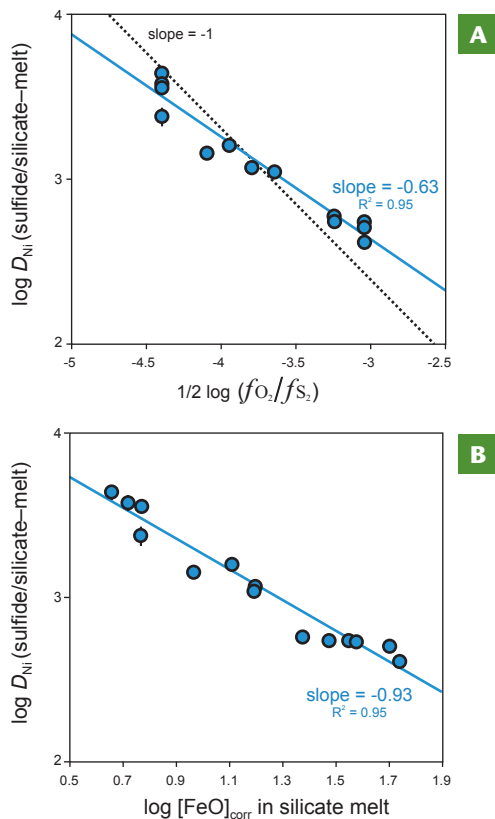
FIGURE 4 Sulfide–melt/silicate–melt partition coefficients for Ni. (**A**) Values of log $D_{Ni}^{sulf/sil}$ plotted as a function of ½ log(fO_2/fS_2). (**B**) Values of log $D_{Ni}^{sulf/sil}$ plotted as a function of log[FeO]. The log[FeO] values have been corrected for the activity of FeS (see Kiseeva and Wood 2013). It is notable that the model using the relationship shown in Equation 5 (panel B) provides the slope (–1) predicted by the reaction stoichiometry. In contrast, the model using the relationship in Equation 2 (panel A), yields a substantially non-stoichiometric dependency (–0.63 slope). This could potentially be due to the uncertainties in the fS_2 measurements or due to the deviation from ideality in the Fe–Ni–Cu–S system. Additional discussion can be found in Gaetani and Grove (1997). Data from Gaetani and Grove (1997).

The method described in Equation (5) enables us to compile partition coefficients for a number of chalcophile elements in typical magmas (TABLE 1).

CHALCOPHILE ELEMENT BEHAVIOUR DURING MANTLE MELTING

The behaviour of chalcophile elements during mantle melting is summarised in FIGURE 5. Elements with a very strong chalcophile affinity ($D_M^{sulf/sil}$ of 10^4–10^6) (TABLE 1), such as Pt, Ir and Au, are extremely depleted in the silicate liquids due to their retention in the residual mantle sulfide. Only when sulfide is almost exhausted from the mantle source (~16% of aggregate fractional melting, assuming 140 ppm S in the mantle source), will highly chalcophile elements partition into the silicate melt. The concentration of chalcophiles that are incompatible in silicate phases, such as Pt and Au, decrease with continued melting as they become diluted by the silicate melt, while Ir, which is likely retained by olivine (Brenan et al. 2016), remains at constant concentrations.

The moderately chalcophile elements, such as Ni, Cu, In, and Pb have $D_M^{sulf/sil}$ values of ~10–1,000. Both In and Pb are incompatible elements in mantle silicates, so their concentrations continually decrease with increased melting. Copper, which is only moderately incompatible,

is relatively constant during fractional melting and shows only a small increase in concentration when approaching sulfide exhaustion. Despite being strongly chalcophile, Ni is also compatible in olivine (D ~2–6), and this dominates its partitioning. Thus, sulfide exerts little or no control on Ni concentration during the melting of peridotite.

THE ROLE OF SULFIDES IN CONTROLLING THE RE–OS ISOTOPE SYSTEM

Rhenium and osmium were scavenged into the Earth's core during terrestrial accretion, leaving the silicate mantle highly depleted in these elements. Although they share this particular geochemical property, Re and Os have contrasting geochemical behaviours during partial melting of the mantle: Re is thought to be mildly incompatible, whereas Os is thought to be compatible (e.g. Fonseca et al. 2011). This fundamental difference is unique among commonly used isotope chronometers (e.g. K–Ar, Rb–Sr, Sm–Nd, Lu–Hf, and U–Th–Pb–He systems) where both parents and daughters are highly incompatible elements. The fact that Re is mildly incompatible and Os is compatible causes large variations of Re/Os ratios in oceanic basalts. Mid-ocean ridge basalts, for example, have Re/Os ratios
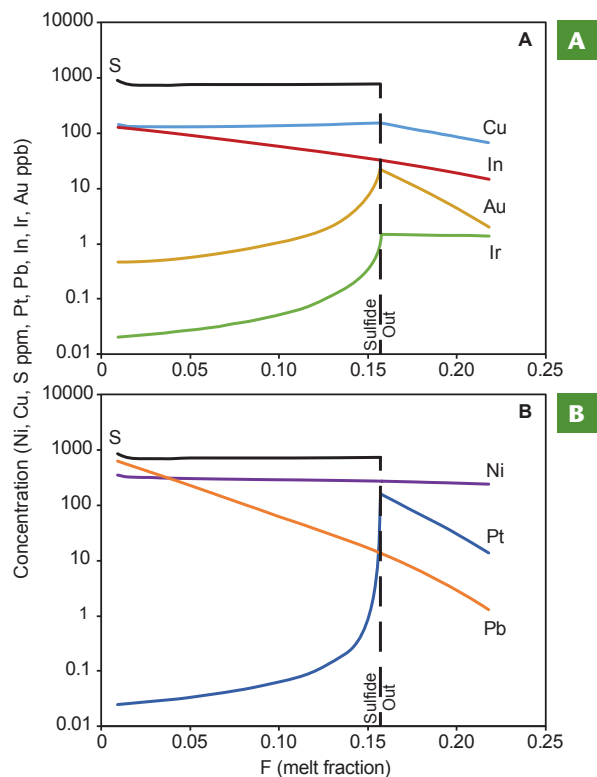
FIGURE 5 Instantaneous concentration of chalcophile elements (**A**) Ni, Cu, In, and Ir. (**B**) Pt, Au, and Pb] in basaltic melt during fractional melting of a depleted mantle source, following the method of Mungall and Brenan (2014). The elements are grouped as shown for clarity. Major element chemistry of the melts and phase proportions were modelled using pMELTS (Ghiorso et al. 2002); sulfur solubility was calculated using the model of Smythe et al. (2017). Assuming 140 ppm sulfur in the mantle, sulfide becomes exhausted at approximately 16% melting (denoted as "sulfide out"), which allows highly chalcophile elements to partition into the silicate melt. As the chalcophile base metals have smaller sulfide melt/silicate melt partition coefficients relative to the PGEs (Kiseeva and Wood 2013; Mungall and Brenan 2014) they are less sensitive to the presence of sulfide in the residue. Partition coefficients and depleted mantle concentrations are shown in TABLE 2.

	Andesite	Basalt	Komatiite
	6–9 wt % FeO	8–11 wt % FeO	10–14 wt % FeO
Tl	14–18	13–15	11–13
In	14–24	11–17	8–12
Sb	22–39	17–26	13–20
As	29–36	25–31	22–27
Pb	41–62	33–46	25–37
Co	56–86	45–63	34–50
Cd	65–98	53–73	42–59
Cu	420–560	360–460	290–390
Ag	530–700	460–580	370–490
Se	550–850	450–650	350–500
Ni	770–1,160	630–870	500–690
Bi	1000–1250	900–1,100	800–950
Te	3,000–3,800	2,600–3,200	2,300–2,800
Re	22–22,377 (3,100)		
Au	4,100–11,200 (6,300)		
Pd	$6.70 \times 10^4 - 5.36 \times 10^5$ (1.89×10^5)		
Rh	$5.72 \times 10^4 - 5.91 \times 10^5$ (2.05×10^5)		
Ru	$3.03 \times 10^5 - 4.85 \times 10^5$ (4.19×10^5)		
Ir	$4.80 \times 10^4 - 1.90 \times 10^6$ (4.58×10^5)		
Os	$3.52 \times 10^5 - 1.15 \times 10^6$ (7.49×10^5)		
Pt	$4.38 \times 10^3 - 3.45 \times 10^6$ (8.45×10^5)		

Notes: Partition coefficients for elements Tl through Te (1.5 GPa, 1,400°C, and in equilibrium with FeS) are from Kiseeva and Wood (2015) and Kiseeva (unpubl). Values are derived according to Equation (5), and partition coefficients decrease with increasing FeO content of the silicate liquid. To determine partition coefficients at different temperatures, the reader is referred to the electronic appendix of Kiseeva and Wood (2015). The highest and the lowest partition coefficients for elements Re through Pt are given, with the average value in brackets. Values for Re (0.1–1.5 GPa and 1,200–1,250°C) are from Brenan (2008). Values for Au–Pt (1 atm and 1,200°C) are from by Mungall and Brenan (2014).

ranging between 10 and 2,000 (Shirey and Walker 1998). This variability makes the Re–Os isotopic system a useful geochemical tool for understanding mantle evolution.

The experimental literature has provided some detailed insights into the geochemical behaviour of Re during partial melting of the mantle. Rhenium is the least chalcophile of all the highly siderophile elements (e.g. Mungall and Brenan 2014), and it has been shown to partition into other mantle phases such as clinopyroxene, orthopyroxene, garnet, and spinel (Mallmann and O'Neill 2007), particularly under more reducing conditions. At oxidising conditions, however, Re will become hexavalent and will behave as a highly incompatible element during partial melting of the Earth's mantle. Osmium, on the other hand, is strongly

compatible in sulfide (e.g. Mungall and Brenan 2014): about 97% of the Os budget in source peridotites is controlled by sulfide (Luguet et al. 2007).

Effectively then, residual sulfide is the primary phase in the Earth's mantle that confers on the Re–Os isotope system its unique ability to date episodes of mantle melting. Mantle sulfides efficiently retain the entirety of the Os budget of a peridotite during partial melting, while Re, owing to its high incompatibility, is efficiently removed from the mantle. At high degrees of partial melting (10%–20%), alloys are expected to form from a host sulfide (Luguet et al. 2007; Fonseca et al. 2011), and, because of this, Os will further fractionate from Re.

If melt-depleted peridotites can be presumed to have lost all their Re during partial melting, then their ^{187}Os/^{188}Os can potentially be used to derive model ages that ostensibly track melt extraction events (reviewed in Lorand and Luguet 2016). This approach can be applied at both the whole-rock and mineral (i.e. sulfide) scale to date ancient melting events in the Earth's mantle (e.g. Wainwright et al. 2015). However, the same thing that makes the Re/Os system so useful in dating ancient melt events is also responsible for its biggest caveat. For example, metasomatic sulfides, which can be introduced to a mantle peridotite through basaltic melt percolation and/or fluid infiltration, will typically introduce Re into a virtually Re-free peridotite. Because of this, these metasomatic sulfides will develop more radiogenic ^{187}Os/^{188}Os over time, which will mix into the whole-rock signature and obscure the actual age of melt depletion of that peridotite. This difficulty can be partly circumvented by carrying out studies at the mineral scale to identify different generations of mantle sulfide, each with their own ^{187}Os/^{188}Os (cf. Wainwright et al. 2015). Sulfides are, thus, unique in their ability to fractionate Re from Os in magmatic systems and to control the Os isotope systematics during melting of the Earth's mantle.

CONCLUDING THOUGHTS AND FUTURE DIRECTIONS

The role of sulfides in igneous processes is not limited to the examples listed above. For instance, the Cu/Ag ratios of erupted magmas are fully controlled by the distinctive partitioning of Cu and Ag into solid and liquid sulfides (Wang and Becker 2015). Furthermore, the precipitation of sulfide may be responsible for the decline in Cu concentration of arc lavas during the evolution of volcanic systems at convergent margins (Lee et al. 2012). Sulfide also plays a significant role in the mysterious behaviour of Pb (Hart and Gaetani 2006) during mantle melting, which includes the nearly constant Ce/Pb (~25) and Nd/Pb (~20) ratios of mid-ocean ridge basalts and of ocean island basalts and the 'lead paradox', whereby all major Pb reservoirs appear to be substantially younger than the silicate Earth.

TABLE 2 PARTITION COEFFICIENTS USED FOR MODELLING THE CURVES IN FIGURE 5.

	Olivine	Clinopyroxene	Orthopyroxene	Spinel	Sulfide	Depleted mantle
Ni	5	1	1	0.001	980–1,140	1,960 ppm
Pb	0.003	0.1	0.009	0.001	61–74	23.2 ppb
Cu	0.05	0.043	0.15	0.22	540–635	30 ppm
In	0.04	0.3	0.02	0.001	23–28	12.2 ppb
Pt	0.009	–	–	–	850,000	6.2 ppb
Au	0.01	–	–	–	7,000	1 ppb
Ir	2	–	–	–	520,000	2.9 ppb

The Pd/Cu ratio may be an indicator of sulfide saturation in magmatic systems (Park et al. 2013), a parameter of fundamental importance in volcanic degassing. Ultimately, the precipitation of sulfides that act as a reservoir for the chalcophile and highly siderophile elements, such as Cu, Ag, Pb and the PGEs, is one of the key triggers that eventually leads to the formation of porphyry ore deposits and are key for the formation of magmatic sulfide deposits.

Thus, given that a typical peridotite will have sulfide phases present at less than 600 ppm (or 220 ppm S), such phases could certainly be said to "punch well above their weight".

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