



# Chalcophile element partitioning between sulfide phases and hydrous mantle melt: Applications to mantle melting and the formation of ore deposits



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## ABSTRACT

Understanding the geochemical behavior of chalcophile elements in magmatic processes is hindered by the limited partition coefficients between sulfide phases and silicate melt, in particular at conditions relevant to partial melting of the hydrated, metasomatized upper mantle. In this study, the partitioning of elements Co, Ni, Cu, Zn, As, Mo, Ag, and Pb between sulfide liquid, monosulfide solid solution (MSS), and hydrous mantle melt has been investigated at 1200 °C/1.5 GPa and oxygen fugacity ranging from FMQ–2 to FMQ+1 in a piston-cylinder apparatus. The determined partition coefficients between sulfide liquid and hydrous mantle melt are: 750–1500 for Cu; 600–1200 for Ni; 35–42 for Co; 35–53 for Pb; and 1–2 for Zn, As, and Mo. The partition coefficients between MSS and hydrous mantle melt are: 380–500 for Cu; 520–750 for Ni; ~50 for Co; <0.5 for Zn; 0.3–6 for Pb; 0.1–2 for As; 1–2 for Mo; and >34 for Ag. The variation of the data is primarily due to differences in oxygen fugacity. These partitioning data in conjunction with previous data are applied to partial melting of the upper mantle and the formation of magmatic-hydrothermal Cu–Au deposits and magmatic sulfide deposits.

I show that the metasomatized arc mantle may no longer contain sulfide after >10–14% melt extraction but is still capable of producing the Cu concentrations in the primitive arc basalts, and that the comparable Cu concentrations in primitive arc basalts and in MORB do not necessarily imply similar oxidation states in their source regions.

Previous models proposed for producing Cu- and/or Au-rich magmas have been reassessed, with the conclusions summarized as follows. (1) Partial melting of the oxidized ( $fO_2 > FMQ$ ), metasomatized arc mantle with sulfide exhaustion at degrees >10–14% may not generate Cu-rich, primitive arc basalts. (2) Partial melting of sulfide-bearing cumulates in the root of thickened lower continental crust or lithospheric mantle does not typically generate Cu- and/or Au-rich magmas, but they do have equivalent potential as normal arc magmas in forming magmatic-hydrothermal Cu–Au deposits in terms of their Cu–Au contents. (3) It is not clear whether partial melting of subducting metabasalts generates Cu-rich adakitic magmas, however adakitic magmas may extract Cu and Au via interaction with mantle peridotite. Furthermore, partial melting of sulfide-bearing cumulates in the deep oceanic crust may be able to generate Cu- and Au-rich magmas. (4) The stabilization of MSS during partial melting may explain the genetic link between Au–Cu mineralization and the metasomatized lithospheric mantle.

The chalcophile element tonnage, ratio, and distribution in magmatic sulfide deposits depend on a series of factors. This study reveals that oxygen fugacity also plays an important role in controlling Cu and Ni tonnage and Cu/Ni ratio in magmatic sulfide deposits. Cobalt, Zn, As, Sn, Sb, Mo, Ag, Pb, and Bi concentrations and their ratios in sulfide, due to their different partitioning behavior between sulfide liquid and MSS, can be useful indices for the distribution of platinum-group elements and Au in magmatic sulfide deposits.

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## 1. Introduction

Chalcophile elements in magmas can be used to constrain the nature of the mantle source region (Lee et al., 2012; Li and

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Audétat, 2012; Kiseeva and Wood, 2013) and can also form economically valuable deposits such as magmatic sulfide deposits and magmatic-hydrothermal deposits (Arndt et al., 2005; Li and Audétat, 2013; Audétat and Simon, 2013). The geochemical behavior of chalcophile elements in magmatic processes is largely controlled by the presence of sulfides. Previous studies have shown that sulfides are ubiquitous phases in mantle-derived samples (Peach et al., 1990; Wallace and Edmonds, 2011; Parat et al., 2011; Lee et al., 2012). Depending on pressure, temperature, and sulfide composition (e.g., Cu, Ni content), these sulfides can be crystalline monosulfide solid solution (MSS) and/or sulfide liquid (Kullerud et al., 1969; Bockrath et al., 2004a,b; Li and Audétat, 2012, 2013). To achieve a better understanding of the geochemical behavior of chalcophile elements in magmatic processes, the partition coefficients of chalcophile elements between sulfide phases and silicate melt are thus required.

Early studies on the partitioning of Cu, Ni, Co, Pb, Mo, and Zn between sulfide liquid and silicate melt were performed using simplified silicate melt without controlling of oxygen fugacity ( $f_{O_2}$ ) or sulfur fugacity ( $f_{S_2}$ ) (MacLean and Shimazaki, 1976; Shimazaki and MacLean, 1976; Rajamani and Naldrett, 1978). Later studies were performed in dry sulfide-silicate melt system either at atmospheric pressure (Gaetani and Grove, 1997; Ripley et al., 2002) or at highly reduced conditions with  $f_{O_2}$  below the Fe-FeO buffer (Lagos et al., 2008; Wood et al., 2008; Li and Agee, 2001). A few studies also investigated Cu, Au, Ag, W, and Mo partitioning between MSS (pyrrhotite) and felsic melts (Lynton et al., 1993; Jugo et al., 1999; Simon et al., 2008; Bell et al., 2009; Mengason et al., 2011). More recently, Zajacz et al. (2013) investigated the partitioning of Cu, Au, and Ag between pyrrhotite and silicate melt with compositions ranging from basalt to rhyolite at 2 kbar and temperatures below 1050 °C. Kiseeva and Wood (2013) determined the partition coefficients of Cu, In, Tl, Pb, Ag, Mn, Zn, Cr, Co, Ni, Sb, and Cd between sulfide liquid and anhydrous basaltic melt with different FeO contents synthesized in graphite capsule. However, in terms of pressure, temperature, melt composition, and  $f_{O_2}$  combined, none of the above studies was performed at conditions relevant to the upper mantle or the lower crust, and only the studies of Mengason et al. (2011) and Bell et al. (2009) included coexisting sulfide liquid and MSS in silicate melt.

Li and Audétat (2012) reported a coherent partition coefficient dataset of 15 elements (V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi) between sulfide liquid, MSS, and hydrous basanite melt at 1175–1300 °C/15–30 kbar and  $f_{O_2}$  ranging from FMQ–3 to FMQ+1. The same authors (Li and Audétat, 2013) further investigated Au solubility and partitioning between sulfide liquid, MSS, and hydrous basanite melt at 1200 °C/1.5 GPa and  $f_{O_2}$  ranging from FMQ–2 to FMQ+1. As a companion to Li and Audétat (2013), this contribution reports the partition coefficients of Cu, Ni, Co, Zn, Mo, As, Ag, and Pb between sulfide liquid, MSS, and hydrous mantle melt from the same set of experiments. More importantly, these new data combined with the previous partitioning data (Li and Audétat, 2012, 2013) are applied to understand partial melting of the upper mantle and the formation of magmatic-hydrothermal deposits and magmatic sulfide deposits.

## 2. Experimental methods

Detailed description of experimental methods can be found in Li and Audétat (2012, 2013). Below is a digested version.

### 2.1. High pressure experiments

The starting materials included a natural mantle rock, synthetic sulfide, pure metallic Au powder (0.3–3 μm), and reagent-grade

KCl and CaSO<sub>4</sub> (anhydrite). The natural mantle rock stems from a hornblende-rich, metasomatic vein in orogenic peridotite of the French Pyrenees (referred as AG<sub>4</sub> in Pilet et al. (2008)) and has a chemical composition of 2.38 wt% Na<sub>2</sub>O, 1.19 wt% K<sub>2</sub>O, 12.3 wt% CaO, 11.89 wt% MgO, 10.95 wt% FeO, 13.99 wt% Al<sub>2</sub>O<sub>3</sub>, 39.15 wt% SiO<sub>2</sub>, 5.39 wt% TiO<sub>2</sub>, 0.42 wt% P<sub>2</sub>O<sub>5</sub>, 0.2 wt% MnO, 1.75 wt% H<sub>2</sub>O, and 0.2 wt% CO<sub>2</sub>. The sulfide was synthesized in evacuated silica glass tubes at 1200 °C, with a chemical composition of 39.69 wt% S, 2.02 Cu wt%, 7.97 wt% Ni, and 50.32 wt% Fe. The studied elements Co, Zn, As, Mo, Ag, and Pb were not spiked in the starting material except in run FL02, but were mainly from the starting mantle rock. In run FL02, about 50–100 ppm Co, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi were doped in the starting synthetic sulfide.

Several combinations of capsule configuration and starting material were made to impose  $f_{O_2}$  ranging from FMQ–2.1 to FMQ+1 on the samples (see Table 1). In all experiments, a mixture of powdered mantle rock (~92–95 wt%) and sulfide (~5–8 wt%) was filled into a capsule made of single-crystal olivine from San Carlos. Gold was then added as a thin layer of Au powder (0.3–3 μm grain size) at the top of the olivine capsule. Reducing conditions were obtained by placing a sample-bearing olivine capsule into a graphite capsule which itself was sealed into a Pt<sub>95</sub>Rh<sub>05</sub> capsule (run Au01; Table 1). Intermediate conditions were obtained by placing an olivine capsule directly into a Pt<sub>95</sub>Rh<sub>05</sub> capsule (runs Au02, Au11a,b, Au12a,b; Table 1), with  $f_{O_2}$  buffered by the starting material itself, whereas oxidizing conditions were obtained by adding ~5 wt% anhydrite to the starting material (Au10a and Au10b; Table 1). Two runs (runs Au09 and FL02; Table 1) were performed with a double capsule technique (Chou, 1987). In these two runs, olivine capsules were sealed into inner Pt<sub>95</sub>Rh<sub>05</sub> capsules (3.7 mm O.D.; 3.2 mm I.D.; 7.5 mm length), which were then placed together with buffer materials (MnO–Mn<sub>3</sub>O<sub>4</sub> and Re–ReO<sub>2</sub>) and water into outer Pt<sub>95</sub>Rh<sub>05</sub> capsules (5.0 mm O.D.; 4.6 mm I.D.; 10.0 mm length).

All the experiments were conducted at 1200 °C and 1.5 GPa in an end-loaded, solid media piston cylinder apparatus at Bayerisches Geoinstitut, University of Bayreuth, using 0.5 in. diameter MgO–NaCl assemblies with stepped graphite heaters as have been used in a number of previous studies performed in this same laboratory (Huang and Audétat, 2012; Li et al., 2013; Li and Keppler, 2014). Temperature was measured using an S-type thermocouple with uncertainty of ±10 °C. Pressure was calibrated based on quartz–coesite transition. Experiments were brought down to below 100 °C within several seconds by switching off the electric power.

### 2.2. Analyses of run products

The major element composition of quenched sulfide liquid, solid MSS, and quenched silicate melt was measured with a JEOL JXA-8200 microprobe. Sulfides were analyzed with 20 kV acceleration voltage and 20 nA beam current, whereas quenched silicate melts were analyzed with 15 kV/10 nA. A defocused beam of 30 μm diameter was used for all the standardizations and sample measurements. Natural and synthetic standards were used for instrument calibration. Copper, Fe, S, Ni, Au, Co, Zn, Mo, Pb, and Ag concentrations in silicate melt, MSS, and sulfide liquid were analyzed by laser-ablation ICP-MS using a Geolas M193nm ArF Excimer laser (Coherent/Lambda Physik) attached to an Elan DRC-e quadrupole mass spectrometer (Perkin Elmer Instruments). Quenched silicate melt was analyzed with 10 Hz, 80 mJ and laser pit sizes of 50–80 μm, whereas sulfides were analyzed with 7 Hz, 70 mJ, and pit sizes of 10–20 μm. Isotopes <sup>23</sup>Na, <sup>25</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si, <sup>31</sup>P, <sup>32</sup>S, <sup>39</sup>K, <sup>42</sup>Ca, <sup>49</sup>Ti, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>59</sup>Co, <sup>62</sup>Ni, <sup>65</sup>Cu, <sup>75</sup>As, <sup>64</sup>Zn, <sup>98</sup>Mo, <sup>107</sup>Ag, and <sup>208</sup>Pb were measured with dwell times of 10 ms.

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