Chalcophile elements in the mantle

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Introduction

The elements V, Ga, Ge, As, Mo, Ag, Cd, In, Sn, Sb, W, Tl, Pb, and Bi show variable geochemical behavior between Earth's different reservoirs. All of these elements, with the exception of V, W and Ga, have been shown experimentally or observationally to partition into sulfides to varying extents in the bulk silicate earth (Li and Audetat, 2012; Kiseeva and Wood, 2015). However, these elements can also exhibit siderophile (V, Ga, Ge, As, Mo, Ag, Sn, Sb, W) and lithophile (V, Ga, Ge, As, Mo, Cd, In, Sn, Sb, W, Tl, Pb) behavior based on studies of mantle peridotites (Witt-Eickschen et al., 2009), and mantle-derived magmas (Greaney et al., 2017; Patten et al., 2013; Yi et al., 1995; Jochum et al., 1993; Jochum and Hofmann, 1997; McDonough and Sun, 1995). Many of these studies infer geochemical behavior based on element ratios in the whole rock or glass and do not directly measure the abundance of these variably chalcophile elements in sulfides themselves.

By measuring the abundances of variably chalcophile elements in situ, their mineralogical hosts and partitioning behavior can be directly determined. These data serve as a comparison to experimental data and will allow for greater accuracy in determining the behavior of these elements during partial melting and fractional crystallization. Additionally, we aim to determine more accurate BSE abundances for the highly volatile elements (Cd, In, Sn, Tl) than those calculated by element ratios in basalts and komatiites from McDonough and Sun (1995).

We have analyzed preserved sulfides in lherzolite and harzburgite xenoliths from the North China Craton for the aforementioned elements. While most peridotite xenoliths have lost their sulfides due to metasomatism or alteration during/post-eruption (Lorand, 1990; Liu et al., 2010), the xenolithic peridotites hosted in the Hannuoba basalts from the Trans-North China Orogen preserve them surprisingly well. The sulfides are predominately pentlandite with associated MSS1, pyrrhotite, and chalcopyrite. Textural and chemical evidence suggests that there are multiple generations of sulfides between the samples. The distinctly metasomatised samples (noted by distinct LREE patterns and incomplete Sm-Nd and Rb-Sr mass balance) fall off a Re-Os isochron, however Re and Os have not been significantly disturbed by metasomatism in most samples (Gao et al., 2002).

Using LA-ICP-MS, we analyzed 48 sulfides and many olivine, clinopyroxene, orthopyroxene, and spinel from eight peridotites. Whole rock data was collected using standard addition solution ICP-MS.

Mineralogical Hosts

The LA-ICP-MS data are shown in Fig. 1 where elements are ordered based on their median primitive-mantle-normalized abundance in sulfides. All of the elements are more enriched in the sulfides than the silicates and spinel, except for Ga and V, which substitute for Al and Fe or Cr, respectively. Despite this, mass balance reveals that silicates are the dominant hosts for all of the elements studied here except for Ag and Bi, which are primarily hosted in sulfides, and Mo, Sn, and W, for which mass balance consistently falls short (up to 90% missing, indicating that they may be hosted along grain boundaries or in an unidentified phase). A predominate silicate host is somewhat in agreement with the results of Witt-Eickschen et al. (2009), however sulfides still contribute a significant proportion of the mass balance ($> 20\%$) for the elements As, Cd, In, and Pb. Molybdenum seems to be significantly affected by metasomatic processes, where it is likely carried in fluids in its soluble, hexavalent state and subsequently reduced and deposited in secondary sulfides. The metasomatised sample DMP-60 shows an overabundance of Mo relative to the melt depletion trend (Fig. 2) and the sulfides within this sample contain an order of magnitude more Mo (mean $[\text{Mo}]_{\text{metasomatised}} = 650$ ppm) than in other un-altered samples (mean $[\text{Mo}]_{\text{primary}} = 56$ ppm).
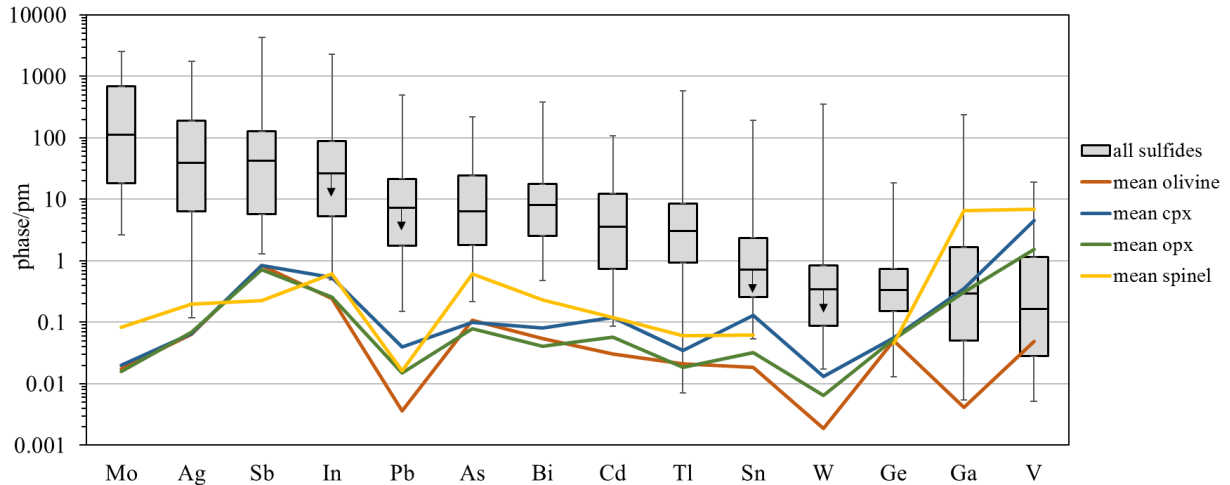
Figure 1. Primitive mantle-normalized LA-ICP-MS data of all phases with the sulfide data represented by box and whisker plots (error bars plot the max. and min. values measured). Elements are ordered by their median concentration in the sulfide with Mo having the highest median abundance in sulfide and V having the lowest. Several sulfides contained less than the detection limit (~0.01 ppm) of Sb, In, Sn, and W. These sulfides were not included in the analysis, so the plotted data are skewed to slightly higher values (hence the arrows).

Bulk Silicate Earth Abundances

Melt depletion trends are observed for a subset of elements (Fig. 2).
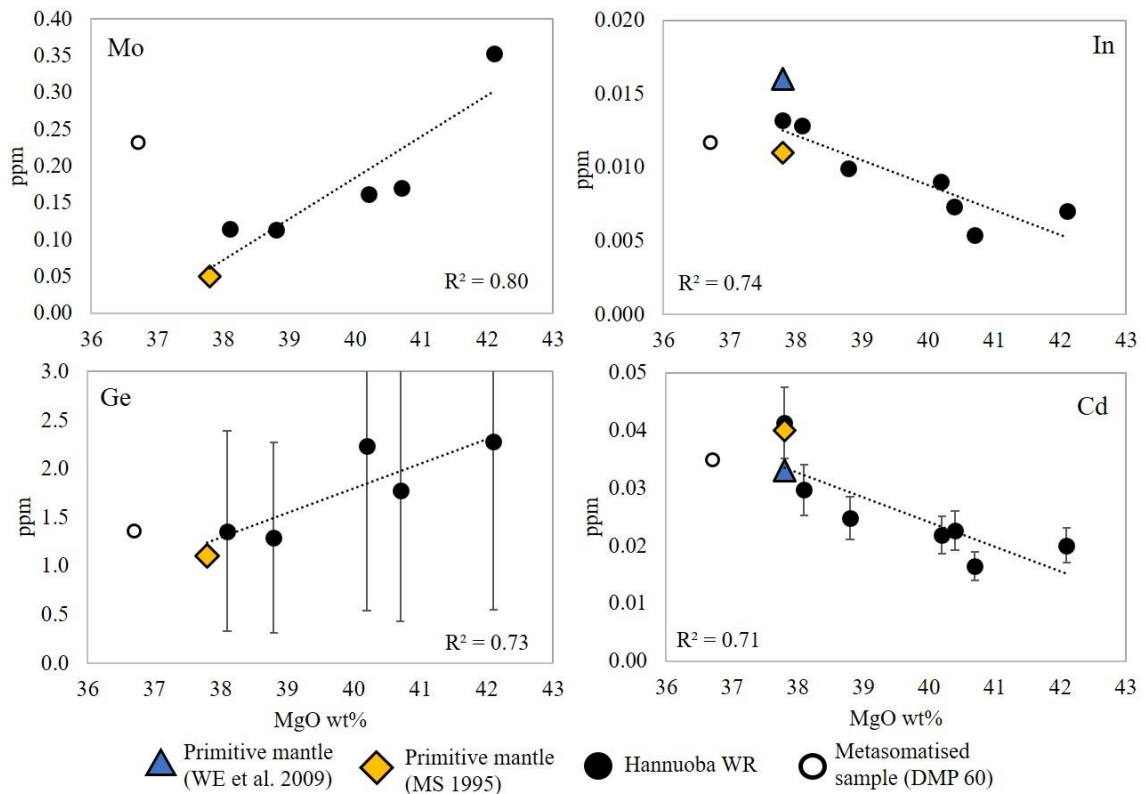

Figure 2. Melt depletion trends for Mo, Ge, In, and Cd; the regressions are through the DMP samples (excluding DMP 60). The large error bars on Ge reflect a high, unstable background signal created after a synthetic Ge-glass was run on the ICP-MS. The 2σ error bars for Mo and In are within the data point.

The refractory element Mo and moderately volatile element Ge show compatible behavior during mantle melting with estimated primitive mantle values of Mo = 62 ppb (± 50) and Ge = 1240 ppb (± 280). This estimate for [Mo] is slightly higher than the basalt-derived estimates of McDonough and Sun

(1995) (50 ppb) and Palme and O'Neill (2014) (47 ppb), however there is a large error associated with the Mo regression, given the scatter in the data. This higher mantle estimate supports the observations of Liang et al. (2017) who found that Mo is enriched in peridotites relative to previous estimates, suggesting that Mo may be slightly more compatible in the mantle than initially thought, or that Mo may be selectively enriched from mantle metasomatism. Both Mo compatibility and metasomatic enrichment are observed in this study. Liang et al. propose that Mo may be retained in mantle sulfides, which is seemingly supported by this data given Mo's high abundance in the sulfides measured here (1.8 to 2000 ppm). However, sulfides are exhausted during mantle melting and Mo mass balance is incomplete in these samples, so another unknown phase may be needed to explain Mo's compatibility.

The volatile elements Cd and In are incompatible during mantle melting, with primitive mantle values estimated at Cd = 32 ppb (± 5.1) and In = 12 ppb (± 1.4), in good agreement with values calculated by Witt Eickschen et al. (2009) and McDonough and Sun (1995), respectively. The data collected for the remaining elements V, Ga, As, Ag, Sn, Sb, W, Tl, Pb, and Bi form rough melt depletion trends against MgO or Al_2O_3, but there is too much scatter for a BSE estimate to be reliably calculated.

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