Preferential partitioning of copper into the vapor phase: An artifact?

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Studies on natural assemblages of coexisting vapor and brine inclusions revealed that Cu (± Au, As, Mo) commonly occurs at higher concentrations in the vapor phase, which has been interpreted to be due to the formation of stable hydrosulfide-bearing complexes. Although several experimental studies proved the existence of such complexes, none of them has succeeded in reproducing conditions under which Cu fractionates into the vapor phase (i.e. $D_{Cu}^{vap/brine} > 1$). An exception seemed to be the study of Nagaseki and Hayashi [1] who claimed to have obtained $D_{Cu}^{vap/brine}$ values up to 30. However, mass balance constraints and results of identical experiments performed in our laboratory suggest that these values are wrong and in fact are below unity.

In view of recent studies demonstrating that quartz-hosted fluid inclusions can diffusively loose or gain Cu after their formation we wanted to check whether the evidence from natural fluid inclusions could be compromised. For this purpose we synthesized vapor and brine inclusions from a Cu-H_2O-NaCl-S fluid at 800 °C/1.3 kbar and reequilibrated them in a second experiment with similar fluid at 800 °C/700 bar. After each step some of the inclusions were analyzed by LA-ICP-MS. Vapor inclusions indeed experienced a dramatic increase in their Cu content (from 0.3 ± 0.04 to 5.7 ± 3.3 wt% Cu) during this procedure, while brine inclusions remained unmodified, leading to a change in $D_{Cu}^{vap/brine}$ from a true value of 0.4 ± 0.05 to an apparent value of 8.3 ± 4.9. Subsequent experiments showed that the requirements for diffusional gain of Cu in fluid inclusions are a change in pH from ≤ 1 to a more basic value in the surrounding fluid, and the presence of S in the inclusions. These requirements are also fulfilled in nature: Cooling magmatic-hydrothermal fluids experience a change from acidic to more neutral pH due to buffering along the feldspar-mica join, and natural vapor inclusions typically contain significant amounts of S. $D_{Cu}^{vap/brine}$ values >1 observed on natural boiling assemblages could thus be a secondary feature, with original values being closer to 0.1. If true, then the role of vapor transport in the formation of magmatic-hydrothermal copper deposits has been severely overestimated.

[1] Nagaseki H. & Hayashi K. I. (2008) *Geology* **36**, 27–30.

Mineralogical heterogeneities in the Earth's mantle: Constraints from Mn, Co, Ni and Zn partitioning during partial melting

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The first-row transition elements (FRTE; Sc to Zn) are compatible to moderately incompatible during melting in mafic and ultramafic systems. Thus, because FRTE are sensitive to changes in mineralogy and major element composition, they are promising tracers of lithological heterogeneities in the mantle source regions of basalts. However, the partitioning behaviors of some FRTE at mantle conditions are still lacking despite growing interest in the application of these tracers to magmatic systems. Here we present mineral-melt partitioning experiments at 1.5-2.0 GPa and 1300-1500 °C for divalent FRTE – Zn, Fe, Mn, Co, and Ni. Our study, for the first time, provides Zn and Zn/Fe fractionation data between peridotitic olivine, orthopyroxene, clinopyroxene and basaltic melt. Using our new partition coefficients and combining multiple ratios (Zn/Fe, Ni/Co, Mn/Fe, Mn/Zn) we assess the role of FTRE as tracers of mineralogical composition of the mantle. We show that, during melting, olivine and orthopyroxene do not significantly fractionate Mn, Fe, and Zn from each other, and melts from peridotite would be expected to have similar Mn/Fe, Co/Fe and Zn/Fe as the source. In contrast, our results for clinopyroxene and published results for garnet show strong fractionations, such that melts of pyroxenites or eclogites would be expected to have low Mn/Fe, Co/Fe, Ni/Co, Mn/Zn and high Zn/Fe compared to peridotite partial melts. We compare Zn, Fe, Co, Mn and Ni contents of natural oceanic basalts to modeled compositions of peridotitic and pyroxenitic partial melts. Most MORB and near-ridge OIB can be explained by shallow melting of peridotite, but most OIB away from ridges deviate from predicted peridotite melt compositions. We use melting and mixing models of FRTE ratios in peridotite and in MORB-like eclogite to illustrate the potential contribution of eclogite- and peridotite derived melts in individual MORB and OIB lavas. We also present a melt-melt mixing model that estimates, under the assumptions of the present model, the amount of eclogite in the source of mantle end-members HIMU, EM1, and EM2.