Partitioning of Cu between vapor and brine – An experimental study based on LA-ICP-MS analysis of synthetic fluid inclusions

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Studies on natural fluid inclusion assemblages trapped from two-phase ('boiling') fluids systems have shown that Cu has a higher affinity to the vapor phase than other base metals, commonly occurring at higher concentration in the vapor than in the coexisting brine. It is believed that this behavior is due to complexation of Cu by reduced sulfur in the vapor phase (e.g., Heinrich *et al.* [1]). To test this hypothesis we have produced synthetic fluid inclusions in quartz at controlled pressure, temperature, pH, fluid salinity and fO_2 in cold-seal pressure vessels. Quartz cores were filled together with a buffer mineral assemblage, fluid and SiO_2 glass into gold capsules, and subjected to 500-1000 bar and 600-700°C for 10-21 days. In some runs, the formation of fluid inclusions was initiated after 7 days of pre-equilibration by *in situ* thermal fracturing. The resulting fluid inclusions were analyzed by microthermometry and LA-ICP-MS.

In a first set of experiments it was tried to reproduce the environment during early stages of porphyry-Cu ore formation by using a buffer assemblage consisting of biotite, magnetite, bornite, chalcopyrite, orthoclase, andalusite ± albite ± anhydrite, and fluids containing variable amounts of KCl, $FeCl_2$, HCl ± NaCl. In all cases Cu was found to partition into the brine, with $D^{Cu}_{vap/brine}$ values determined by LA-ICP-MS of 0.1-0.2.

In two other experiments the number components was greatly reduced by using elementary sulfur, anthracene as a reducing agent, and a fluid consisting of CuCl, $ZnCl_2$, NaCl and HCl as starting material, added in similar amounts as in Nagaseki & Hayashi [2]. Partial (to full ?) conversion of elementary sulfur and anthracene to H_2S and CO_2 was confirmed by Raman spectroscopy of the produced fluid inclusions. $D^{Cu}_{vap/brine}$ values are ≤0.39 and ≤0.18, in contrast to the findings of [2]. It has to be noted, however, that in our experiments a substantial amount of Cu was lost to the Au-capsule, whereas some experiments of [2] appear to have experienced no Cu-loss.

[1] Heinrich *et al.* (1999) *Geology* **27**, 755-758. [2] Nagaseki & Hayashi (2008) *Geology* **36**, 27-30.

In situ lithium isotope analysis by LA-MC-ICP-MS

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Geochemical studies using Li stable isotopes are limited due to difficult and tedious chemical preparation required for TIMS and solution MC-ICP-MS analys, or the cost and time required for SIMS analysis [1, 2]. Precise (<1‰ 2σ), *in situ* B isotope data have been obtained on natural glasses (<1ppm B) by laser ablation coupled to a MC-ICP-MS [3]. Results are presented here for a similar approach to obtain *in situ* Li isotope (<1‰ 2σ) compositions of glasses.

A 213nm NewWave LA unit coupled to a NuPlasma HR (operating at 6kV) at the AEON EarthLAB, and a selection of glasses with known Li concentrations and isotope composition [1, 2] are employed. All unknowns and standards are epoxy mounted, polished, cleaned by ultrasonication in milliQ water and wiped with ethanol. After rapid surface cleaning of a 500µm line with a 150µm laser spot (10Hz, ±1.25mJ/cm^2) at 25µm/sec, this line is sampled at 3µm/sec using a 125µm laser spot (10Hz, ±10.5mL/cm^2) defocussed ±250µm below the surface.

Depending on the Li concentration of the glass sampled, either an all-Faraday (>30ppm Li; total Li signal >0.3V) or Faraday(^{7}Li)-IC(^{6}Li) (±3-30ppm Li; total Li signal 0.3-0.005V) detector combination is used. Time resolved analysis (TRA) is used, with a 30 second initial background measurement (typically <10 000cps ^{7}Li; <1000 ^{6}Li) followed by ±165seconds of data acquisition.

Three to four analyses of an unknown are corrected for instrumental mass fractionation and drift using two bracketing standard analyses. Analysis of NIST glasses resulted in significant buildup on the cones, leading to signal loss, drift and degraded reproducibility. Using BCR-2G as the bracketing standard, example analyses of BIR-1G (±3ppm Li) yield δ^7Li of 5.8±0.6‰ (n=3, 2σ) and MPI GOR128-G (±10ppm Li) yield δ^7Li of 12.9±0.3‰ (n=2, 2σ) in agreement with published values [1, 2].

Li isotope analysis by LA-MC-ICP-MS is rapid, inexpensive, *in situ* and with external precision comparible to established techniques [1, 2].

[1] Kasemann *et al*. (2005) *Anal. Chem.* **77**, 5251-5257.
[2] Jochum *et al*. (2006) *G3*, doi:10.1029/2005GC001060.
[3] le Roux *et al*. (2004) *CG* **203**, 123-138.