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Title: Determining the speciation and solubility of copper in synthetic and natural fluid inclusions by XAS from ambient to homogenisation temperatures

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Aims:

The majority of the World's copper resources are found in hydrothermal ore deposits. A major controversy aroused concerning the formation of World-class porphyry-copper deposits. Current models -and all available experimental data- suggest that copper should partition strongly into high-density hypersaline brines upon phase separation. This view has been challenged in the last decade by analyses of natural fluid inclusions showing that Cu, and Au, may partition preferentially in low-density vapours coexisting with the brines. If confirmed, this would have major implications for our understanding of the formation of many important ore deposits, but also for ore processing and metal recycling technologies. In recent experiments at FAME we investigated the speciation of Cu in brines and vapours in S-bearing solutions at T to 600˚C using an autoclave (report EC 324), but found that Cu was preferrentially partitioned in a fluid even when it exists as a Cu-bisulfide complex.

The main aim of the present experiment was to investigate the nature of the speciation change affecting Cu upon heating of the vapour inclusions from the Mole Granite (Australia). We aimed to take advantage of recent advances of the new microprobe set-up at FAME (report 30 02 812) to collect high quality XANES as well as EXAFS from single fluid inclusions up to homogenization temperature. In addition, we aimed to compare the results obtained on these natural fluid inclusions with results from synthetic S-bearing fluid inclusions, grown under conditions similar to those inferred during the formation of the Mole Granite porphyry deposit, and with the results of measurements obtained using an autoclave system (report EC 324).

Results:

Working with natural and synthetic fluid inclusions if very challenging indeed. Finding objects buried in a 3-dimentional matrix is not trivial, and obtaining good quality spectroscopic data is made difficult by varying concentrations in different fluid inclusions, absorption by the matrix (quartz), and beam damage. We successfully collected XANES and a few EXAFS data on Cu Ka edge in fluid inclusions from 3 porphyry copper deposits. Amazingly, our results are very different from those obtained by previous researchers: while they observe Cu(II) are room-T and a linear Cu(I) complex at higher temperature, we observed that in all inclusions most of the copper is contained in a chalcopyrite inclusion, that remains to high temperature (~500˚C). This result is most probably related to the much smaller beam flux density used in our experiments (i.e., reduced beam damage).

We are using ab-initio XANES calculation using the FDMNES program to demonstrate that, in principle, we could have seen the different between chalcopyrite (in which Cu is coordinated by 4 S in tetrahedral arrangement) and an aqueous [CuS4] complex.

We did not succeed in getting any useable information from the synthetic fluid inclusions, which were quite small (<10 µm, compared to a 25µm beam-size) and usually tube-shaped.

Publications

Since we basically obtained mainly ‘negative’ results in this experiment, publication is a challenge. We’re hoping that this data can help to support a review of the chemistry of liquid-vapour partitioning of copper, emphasizing the experimental difficulties. Fingers crossed!