

## THE STUDY OF VOLATILE/MELT PARTITIONING IN INTERMEDIATE/MAFIC MAGMATIC SYSTEMS: ENTRAPMENT OF SYNTHETIC FLUID INCLUSIONS

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### Introduction

The efficiency of extraction and transfer of Cu and Au by primary magmatic volatile phases (MVP) has been in the main focus of research over the past decades. Experimental studies and natural observations indicate that besides chlorine, sulfur plays an important role in the complexation of Cu and Au in magmatic volatiles (Heinrich et al., 1999; Simon et al., 2006; Pokrovski et al., 2008; Zajacz and Halter, 2009). Most of these data, however, represent P-T conditions typical of felsic magmas and related hydrothermal systems. A link between the formation of porphyry type ore deposits and some felsic volcanic eruptions characterized by excess amounts of degassed sulfur (e.g. Mt. Pinatubo, El Chichon) has been suggested, and underlying mafic magma has been recommended as the most likely source of sulfur, and potentially Cu and Au, which are transported by the exsolving MVP (Hattori and Keith, 2001; Klemm et al., 2007).

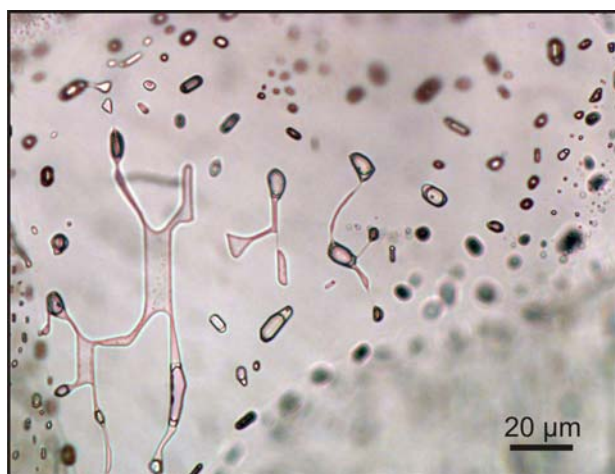
### Experiments and results

The major goal of our experimental study is to determine the partition coefficients of S, Cu, Au and Mo between intermediate to mafic silicate melts and MVP. In order to evaluate the role of Cl and S, experiments were performed in Cl-bearing S-free and S-bearing Cl-free systems. The Cl concentration (in Cl-bearing experiments),  $fS_2$  and alkali chloride to HCl ratios) were varied in order to place constraints on the potential contribution of mafic magmas to the S and metal budget of porphyry ore deposits. To sample the volatile phase at the experimental run conditions, we developed a technique to trap synthetic fluid inclusions (SFI) in orthopyroxene. Coarse-grained orthopyroxene crystals from the Bushveld complex (Mg#~85), and gem-quality enstatites from Tanzania and Burma (Mg#>90) have been tested for the purpose of trapping SFI. Rectangular prism-shaped slabs of pyroxene (~ 1 mm x 4 mm x 5-10 mm long) were cut by using a small diamond saw, pre-

fractured and placed into the capsule together with a natural andesitic glass and an aqueous solution. To avoid disequilibrium caused by loss of Cu to the capsule by alloying, we use in-house synthesized  $Au_{98}Cu_2$  alloy capsules as a Cu-source. By design, this buffers the Cu-activity over the duration of the experiment. Efficient pre-fracturing of the pyroxene crystals requires a much larger thermal shock than that needed to fracture quartz. Optimal fracture density and width was achieved by dropping the pyroxene slabs, heated to 1050-1200 °C, into cold distilled water. To avoid significant cooling of the pyroxene before reaching the water, procedures were performed to either heat the pyroxenes in an air-natural gas flame 5 to 10 cm above the water bath or heat them in a tube furnace and move them to the water bath on a thermal ballast. At these conditions a very dense network of randomly oriented fractures develops in the pyroxene and the slab remains in one piece.

The experiments were conducted in a rapid-quench TZM pressure vessel apparatus at 1000 °C and 150 MPa. The thermal gradient was reduced below 8 °C over the length of the capsule (typically ~16 mm) with the use of a special furnace design developed in-house. The  $fO_2$  was maintained between -0.3 and +0.1 log units relative to the Ni-NiO buffer by the addition of  $CH_4$  to the Ar pressure media. Fracture healing times depend on the composition of the volatile phase and positively correlate with the concentration of Cl. The concentration of Cl in the starting solution was kept below 0.9 molal to stay in the one-phase field at run condition, and close to the compositional range relevant for natural systems. Low-chlorinity fluids (0.5 or 0.9 molal starting Cl concentrations added as alkali-chloride or HCl) resulted in effective healing, isolation of most fractures, and formation of numerous near isometric or elongated SFI with diameters up to 20  $\mu m$  (Fig. 1). In the enstatites from Tanzania and Burma, however, a large number of unhealed fractures are still

present and a transition between the healed and unhealed part of the fractures is observable even after 64 h long experiments.



**Figure 1.** Synthetic fluid and melt inclusions along a healed fracture in an enstatite crystal from Tanzania.

Observation of such features is essential to ensure that inclusions that isolated shortly before the end of the experiment (thus equilibrated with the silicate melt) can be selected for LA-ICPMS analyses. In the same enstatites, Cl-free solutions yield a large number of unhealed fractures and only small (<10 μm in diameter) SFI are produced. This situation is somewhat improved by the addition of enstatite gel to the charge. In the pyroxenes from the Bushveld complex, fracture healing is significantly faster and all fractures were isolated after 24 h and 48h experiments, forming SFI mainly under 12 μm in diameter. Quantification of the fluid compositions from LA-ICPMS analyses is a challenge in these systems because some experiments are conducted with Cl-free volatile phases, thus microthermometry cannot be used to obtain an internal standard. We use the concentration of B (doped in starting fluid) and Mo (doped in starting glass) for this purpose, since these elements do not alloy with the capsule (positively tested) and show large fluid/melt partition coefficients that allow precise estimation of their concentration in the volatile phase by mass balance calculation. LA-ICPMS data on the FI in pyroxenes from the Bushveld complex (with all fractures isolated and healed) have shown that most SFI isolated before the achievement of equilibrium, thus not useful for the determination of partition coefficients. This is research in progress and LA-ICPMS data on

metal and sulfur concentrations in the SFI in the enstatites from Tanzania and Burma will be available by the time of the conference. Verification of the achievement of equilibrium before fracture healing will be assessed by comparing the composition of the SFI to the volatile phase trapped by an alternative method in the same experiments.

## References

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