

DIFFUSIVE REEQUILIBRATION OF QUARTZ HOSTED SILICATE MELT AND FLUID INCLUSIONS: ARE ALL METAL CONCENTRATIONS UNMODIFIED?

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Introduction

Quartz-hosted fluid inclusions (FI) and silicate melt inclusions (SMI) are commonly considered to preserve the composition of hydrothermal fluids and evolved silicate melts, allowing natural processes that lead to the generation of ore deposits and volcanic eruptions to be traced and characterized chemically. However, observations of anomalously Na-deficient SMI compositions in natural samples (Audétat et al., 2000; Audétat and Pettke 2003; Student and Bodnar, 2004; Zajacz et al., 2008) and modification of the Na, Cu and Ag content of natural SMI during experimental reheating (Kamenetsky and Danyushevsky, 2005; Zajacz et al., 2008) raise the question as to whether inclusions in quartz reliably represent the composition of fluids and silicate melts at the time of their entrapment.

Experiments and results

We conducted experiments to determine the extent and mechanism by which the composition of quartz-hosted silicate melt inclusions and aqueous fluid inclusions can undergo post-entrapment modification via diffusion. Quartz slabs containing assemblages of SMI and FI were reacted with synthetic HCl-bearing and metalliferous aqueous fluids at $T=500-720^{\circ}\text{C}$ and $P=150-200$ MPa in cold-seal pressure vessels. SMI and FI from single inclusion assemblages were analyzed by laser ablation inductively-coupled plasma mass spectrometry (LA-ICPMS) and electron probe microanalysis (EPMA) before and after the experiments. Inclusion bearing quartz crystals derived from both plutonic and volcanic rocks have been tested. Orders of magnitudes of changes were observed in the concentrations of Na, Li, Ag and Cu due to diffusion through the quartz during 24 h to 168 h long experiments (Fig. 1). Changes in the concentrations of these metals in the SMI and FI were reversible by varying the composition

of the external fluid phases that were reacted with the quartz slabs (HCl-bearing, metal-free, versus metalliferous, low HCl solutions). Concentrations of several other monitored elements with various ionic radii and valence states have not changed during the same experiments.

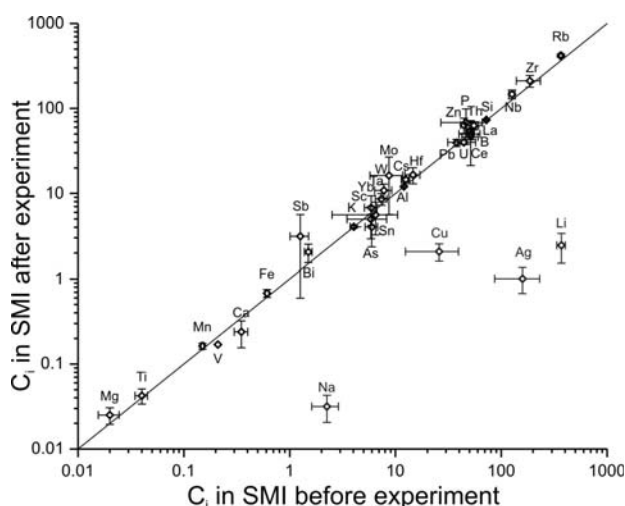


Figure 1. Comparison of the compositions of SMI in a miarolitic quartz crystal before and after reacting the quartz with 1 molal HCl solution for 24 hours at 710°C and 150 MPa. Concentrations of Na, Ag, Cu and Li decreased one to two orders of magnitude during the experiment, while other element concentrations remained unaltered. Note that Ag and Cu concentrations had been artificially raised in a previous experiment. Major elements are in wt%, trace elements are in $\mu\text{g/g}$.

Simultaneously to the modification of SMI and FI compositions, a change in the Li content of the host quartz was also observed. During interaction with HCl solution or pure water, Li leaves the quartz and 99 relative% of the Al content becomes charge balanced by H. During interaction with the doped salt solution Li^+ completely replaced H^+ again. Copper, Ag and Na concentrations were mostly below the limits of detection in the quartz.

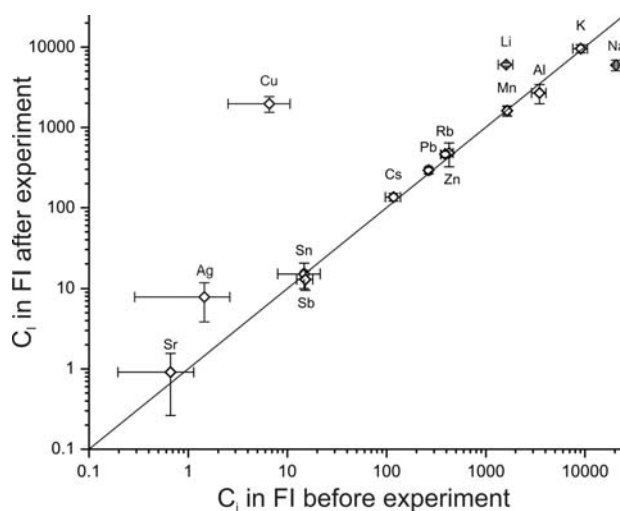


Figure 2. Comparison of the compositions of intermediate density FI along a single pseudosecondary trail in a miarolitic quartz crystal before and after the interaction of the host quartz with an aqueous solution of 5 wt% CuCl_2 , 6 wt% LiCl , 2wt% NaCl , and 1 wt% AgCl (added as solid). The experiment was conducted at 650 °C, 150 MPa for 72 h duration. All element concentrations are shown in $\mu\text{g/g}$.

Discussion

Consistent modification of the composition of the SMI and FI and their host quartz in equilibrium with various fluids points to bulk diffusion of H, Li, Na, Cu and Ag or their cations in the quartz. Considering the large number of studied elements with similar atomic and effective ionic radii (Shannon, 1976), concentration modification of only those elements that form cations in the univalent state suggests that these elements diffuse as charged species through the quartz structure, and that the tendency for rapid diffusion is valence-specific. If the effective ionic radii of known univalent cations are compared, it is apparent that the elements which rapidly diffused through quartz are the smallest (diffusing cations: Li^+ -0.59 Å < Cu^+ -0.60 Å < Na^+ -0.99 Å < Ag^+ -1.00 Å << non-diffusing cations: K^+ -1.37 Å < Rb^+ -1.52 Å < Cs^+ -1.67 Å). As Cl^- (the main anion present in the FI) is very unlikely to diffuse through quartz due to its very large effective ionic radius (1.81 Å), the diffusion of cations in and out of SMI and FI must have to be governed by exchange reactions involving cations that maintain charge balance. In experiments with pure aqueous HCl solutions (i.e., containing no

trace metal or alkali cations), the most likely candidate cation that replaced Na^+ and Li^+ in the SMI and FI is H^+ , the smallest and most rapidly diffusing univalent cation.

Conclusions

Our results show that Li/Na, Cu/Na and Ag/Na ratios in quartz hosted FI and SMI can readily readjust to equilibrate with subsequent generations of fluids or silicate melts that come into contact with the host quartz via cation exchange at P-T conditions characteristic of felsic magmas and related high-temperature hydrothermal systems. This may induce very significant post-entrapment modifications of the Li, Na, Cu and Ag concentrations in both silicate melt and fluid inclusions in quartz, and should be kept in mind during interpretation of this kind of compositional data.

References

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