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Studying the pseudomorphic replacement of olivine by silica at acidic conditions

Helen E. King (1), Thorsten Geisler (1,2), and Andrew Putnis (1)

(1) Institut für Mineralogie, University of Münster, Münster, Germany (hking_01@uni-muenster.de), (2) Mineralogisch-Petrographisches Institut, Universität Hamburg, Hamburg, Germany

Silicification is an important reaction occurring in volcanic environments that aids the neutralisation of the extremely acidic fluids produced. Replacement of the original minerals by silica results in the reacting fluid becoming enriched in cations that can be subsequently transported through the hydrothermal system (Varekamp et al., 2000). In some examples olivine and pyroxene phenocrysts within the reacted layers are pseudomorphically replaced by silica (Africano and Bernard, 2000). We have performed unstirred batch experiments using sulphuric acid and whole olivine crystals to explore the parameters that control phase precipitation and the pseudomorphic replacement of forsteritic olivine. The experiments were conducted in Teflon-lined steel autoclaves at temperatures between 80 and 120 ˚C. In lower temperature experiments the reaction of olivine with 0.1 M sulphuric acid produced a red precipitate coating the olivine surface. The red phase was too low in concentration to be identified but is expected to be hematite (Fe_2O_3). In contrast, experiments conducted in sulphuric acid between 1 and 3.6 M produced an amorphous silica pseudomorph of olivine. The dependence of phase precipitation on pH was tested using a sulphuric acid solution neutralised to pH 2 with a resulting ionic strength equivalent to 1 M. At low temperatures the olivine reacted to produce amorphous silica and a yellow fluid indicating that Fe remained in solution, possibly as a complex with sulphate. Higher temperatures allowed the iron to be liberated from the fluid and precipitated as hematite in association with amorphous silica. Elemental content microprobe data for the olivine and silica rim from pseudomorphic replacement reactions suggests that the majority of cations from olivine dissolution remained in solution. This observation was confirmed by inductively coupled plasma-mass spectroscopy, which showed a high content of Mg and Fe in the fluid. The variation of replacement products at different reaction conditions highlights the sensitivity of olivine replacement in acidic conditions to factors such as pH. We used an ^{18}O-enriched fluid to trace the mechanism of the pseudomorphic replacement. Raman spectroscopy of the silica layer showed that the ^{18}O was taken into the silica rim in enough concentration to produce a shift in the Raman peaks resulting from ^{18}O-Si bonding within the silica network. The products from experiments with different sulphuric acid concentrations showed that as concentration was reduced the silica layer became increasingly fragile until it no longer precipitated as a pseudomorph. This observation and the incorporation of ^{18}O into the amorphous silica structure indicate that the formation of a pseudomorph occurs via an interface-coupled dissolution-reprecipitation mechanism (Putnis and Putnis, 2007).

References

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