



## Distribution of halogens during fluid-mediated apatite replacement

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Apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$ ) is one of the most abundant halogen-containing minerals in the crust. It is present in many different rock types and stable up to P-T conditions of the mantle. Although probably not relevant for the halogen budget of the mantle, apatite is potentially a carrier phase of halogens into the mantle via subduction processes and therefore important for the global halogen cycle. Different partitioning behavior of the halogens between apatite and melt/fluids causes fractionation of these elements. In hydrothermal environments apatite reacts via a coupled dissolution-precipitation process that leads to apatite halogen compositions which are in (local) equilibrium with the hydrothermal fluid. This behavior enables apatite to be used as fluid probe and as a tool for tracking fluid evolution during fluid-rock interaction.

Here, we present a combined experimental and field related study focused on replacement of apatite under hydrothermal conditions, to investigate the partitioning of halogens between apatite and fluids. Experiments were conducted in a cold seal pressure apparatus at 0.2 GPa and temperatures ranging from 400-700°C using halogen-bearing solutions of different composition (KOH, NaF, NaCl, NaBr, NaI) to promote the replacement of Cl-apatite. The halogen composition of reacted apatite was analyzed by electron microprobe (EMPA) and secondary ion mass spectrometry (SIMS). The data was used to calculate partition coefficients of halogens between fluid and apatite. Our new partitioning data show that fluorine is the most compatible halogen followed by chlorine, bromine and iodine. Comparison between partition coefficients of the apatite-fluid system and coefficients derived in the apatite-melt system reveals values for F that are one to two orders of magnitude higher. In contrast, Cl and Br show a similar partition behavior in fluid and melt systems. Consequently, apatite that formed by fluid-rock interaction will fractionate F from Cl more efficiently than apatite crystallizing from a melt. Although F concentrations in apatite correlate strongly with F concentrations in fluids, a correlation between Cl concentration of apatite and salinity of the fluid is not observed. Therefore, we interpret the apatite composition in saline environments being rather controlled by the pH of the fluid than by the NaCl concentration. Consequently, the compatibility of OH in apatite is higher than that of Cl, which is in contrast with findings in apatite-melt-fluid systems.

Based on the experimental results we interpret the halogen composition of natural apatite of two metasomatized gabbros from different localities and pressure regimes (i.e. amphibolitic vs eclogitic) to be the result of extensive fluid-rock interaction and a compositional evolution of the fluid.