Partitioning of halogens (F, Cl, Br, I) between hydrated silicates: analysis and first principles modelling

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Halogens are volatile elements of great interest for the study of fluid-rock interactions between minerals of metamorphic and mantle rocks. Constraining the partitioning of these elements between minerals is also key to understanding their deep geochemical cycle. Hydrous silicates such as micas, amphiboles, chlorites, epidotes or serpentines often contain minor to trace amounts of halogens incorporated by the OH⁻ = X⁻ (X⁻ = F⁻, Cl⁻, Br⁻ or I⁻) mechanism. Their abundance in metamorphic and mantle rocks grants them a major role in storing and transporting halogens through the subduction zone. However, low halogen concentrations hamper in situ analyses, and quantifying the partitioning of low-concentrated halogens remains then very challenging.

The present study focusses on incorporation of halogens (F⁻, Cl⁻, Br⁻, I⁻) into hydroxyl sites in phyllosilicates and amphiboles, on both analytical and theoretical grounds.

In situ measurements in minerals using electron probe microanalysis and LA-ICP-MS/MS have been carried out, allowing investigation of minor to ultra-trace halogen concentrations. Average detection limits with the electron probe are of 200 ppm for F and 35-40 ppm for Cl, Br and I. LA-ICP-MS/MS allowed simultaneous measurement of Cl, Br and I, reaching detection limits of about 50-100 ppm of Cl, 1-10 ppm of Br and well below 1 ppm for I. Calibrations have been carried out using international and house standards. Halogen ratios and partition coefficients between minerals have been measured.

Ab-initio modelling of the OH⁻ = X⁻ exchange in phyllosilicate end-members of interest (e.g. phlogopite, muscovite, clinochlore) is underway (CRYSTAL17, Dovesi et al., 2014). Halogen-bearing defects are modelled as diluted as much as possible in crystals (≤ 1 wt. %) to mimic trace concentrations. Crystal strain and energetic cost of the substitution as well as theoretical partition coefficients have been computed and compared between optimised structures. Comparison of F and Cl partitioning between Mg-biotite and muscovite shows that the effect of dioctahedral vacancies over the position of hydroxyl groups strongly influences halogen partitioning, where F and Cl distribute in favour of biotite. Forthcoming modelling will quantify the strain and energetic impact of halogen incorporation in chlorite and amphibole end-members.

Reference