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# First-principle modelling of the partitioning of halogens between hydrated silicates

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Halogens are volatile elements whose deep cycle remains poorly constrained. Hydrated silicates may contain trace to minor amounts of halogens incorporated via substitution with hydroxyl groups, therefore they may represent a significant reservoir of halogens in subduction zones. The partitioning of halogens between usual hydrated silicates remains mostly restricted to F (and Cl to a lesser extent) in amphibole, micas and serpentine. The very low Br and I content of these phases hampers the measurement of their partitioning at natural amounts. Modelling brings then crucial constraints to study the behaviour of halogens.

In this work, the partitioning of F, Cl and Br has been modelled *ab initio* via exchange with OH groups using the CRYSTAL17 program. Hydrated silicates representative of subduction zone minerals have been selected (brucite, carpholite, end-members for phyllosilicates, amphibole, epidote, for a total of 16 minerals) to estimate partitioning varying with metamorphic facies and understand how crystal-chemistry influences halogen uptake.

Calculations of the Gibbs free energy for the halogen = OH exchange confirm the importance of biotite, amphibole and lizardite in incorporating F, Cl and Br. F is also favourably trapped in clinochlore and talc, whereas carpholite and kaolinite are potentially important Br-hosts. Fractionation effects appear due to competition between steric hindrance (e.g. favouring Br incorporation in the cage-like structure of carpholite) and electrostatic effects (e.g. $K^+$-$F^-$ interactions in micas, inducing compaction along the c axis after the F = OH exchange).

Partition coefficients are computed from the Gibbs free energy of partitioning reactions, accounting for the contribution of all OH sites. Estimated partition coefficients for three representative assemblages show that the partitioning of halogens evolves with metamorphic facies in subduction zone. In the high-grade assemblage of pargasite-phlogopite-clinozoisite (c.a. 700 °C), halogens are more favourably hosted by pargasite, and also by phlogopite for F. Clinozoisite contains virtually no halogen. In the tremolite-muscovite-paragonite assemblage (c.a. 500 °C), tremolite is systematically favoured. For the clinochlore-pyrophyllite-carpholite assemblage (c.a. 400 °C), F and Cl are mostly hosted by clinochlore, and Br by carpholite.