**Title**: Crystal chemistry and partitioning of halogens in hydrous silicates

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Understanding the crystal chemistry of halogens and their distribution in usual hydrous silicates in the lithosphere is important to constrain their deep geochemical cycle and has implications for studies of fluid-rock interactions. Hydrous silicates are abundant in metamorphic and mantle rocks and often contain minor to trace amounts of halogens incorporated via substitution with hydroxyl groups. However, measuring and modelling these halogens remains challenging because their absolute abundance may be very low.

The energetic cost of the substitution of hydroxyl groups by halogens (F-, Cl-, Br-) in hydrous silicates including mica, chlorite, serpentine, amphibole, epidote, and carpholite is quantified using *ab initio* simulations based on the density functional theory. The computations are performed in large systems where halogens are treated as point defects, in minor to trace concentrations. First estimations in brucite show that F-bearing defects must be separated by at least 9 Å (i.e., less than about 12000 ppm in brucite) from one another to reproduce trace element behaviour. This value increases to at least 10 Å for Cl and Br (i.e. less than about 12000 ppm and 26000 ppm in brucite, respectively).

In silicates, the results highlight the competition between the effects of electrostatic interactions and steric hindrance for the incorporation of halogens, where steric hindrance becomes the controlling parameter for heavy halogens. Interaction with alkalis, along with octahedral site occupancy, plays a major role in controlling halogen incorporation, especially in mica and amphibole. Other parameters such as Si/Al ratio of neighbouring tetrahedral sites and the nature of alkalis in amphibole and mica (K or Na) appear to play subordinate roles.

Partition coefficients are estimated in mineral assemblages which are representative of subduction zone metamorphism. All halogens partition in favour of pargasite, biotite and lizardite, followed by clinochlore, tremolite and carpholite. The energetic cost of incorporating halogens into dioctahedral phyllosilicates and epidote is comparatively higher, and partitioning is predicted to be unfavourable to these minerals.

Fractionation between halogens in subduction zones is predicted by the evolution of mineral assemblages and partition coefficients, a consequence of the influence of crystal chemistry over halogen incorporation in hydrous silicates.

**Reference**: Figowy, S., Dubacq, B., & d’Arco, P. (2021). Crystal chemistry and partitioning of halogens in hydrous silicates. *Contributions to Mineralogy and Petrology*, 176, 1-20. <https://doi.org/10.1007/s00410-021-01860-y>