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Fluorine, Cl, Br & I in serpentinites

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The abundance of F, Cl, Br and I in serpentinites were examined to evaluate their behaviour in subduction zones. Samples include (1) unmetamorphosed, obducted hydrated abyssal peridotites, (2) subducted abyssal peridotites to depth of ~30 km, (3) forearc mantle serpentinites from shallow depth (<30 km) and (4) mantle wedge serpentinites from ~140 km depth in the Himalayas. Samples (1,2,3) from Dominican Republic are composed of lizardite (low temp. serpentine). The Himalayan samples consist of antigorite (high temp. phase). Abyssal peridotites contain high (<530 ppm) Cl but they lose Cl during their subduction. In the mantle wedge, elevated (<880 ppm) Cl in shallow serpentinites suggests transfer of Cl from subducting slab to the overlying mantle wedge. Lower Cl values (≤50 ppm) in deep mantle wedge serpentinites indicate loss of Cl either by pressure increase or transition from lizardite to antigorite. The Br/Cl ratios for obducted abyssal peridotites are comparable to that of seawater, confirming their serpentinization on or near the ocean floor. Bromine appears to mimic Cl in its behaviour; abyssal peridotites partially lose Br during subduction and there is high Br content in shallow mantle wedge serpentinites. However, the degree of Br loss is less than that of Cl with increasing depth, as illustrated by the elevated Br/Cl ratio (<12 $x10^{-3}$) in the deep mantle wedge. Hydrated abyssal peridotites contain relatively high I/Cl ratios up to 240 times seawater. Our results are consistent with data from sea floor serpentinites [1]. The content of I remains relatively constant during their shallow subduction. In the mantle wedge, shallow and deep forearc serpentinites contain similar amounts of I, indicating retention of I during the lizardite to antigorite phase transition.

Fluorine shows significantly different behaviour from the other halogens. The content of F is low (≤20 ppm) in abyssal peridotites, as expected from low F content in seawater. Upon shallow subduction, F content increases in hydrated abyssal peridotites, likely incorporated from shallow water sediments. Similar F-enhancement is observed for shallow forearc peridotites. Fluorine is further enriched in deep mantle wedge peridotites (<160 ppm) by incorporating F released from slabs and sediments.

Serpentinites likely contribute to the transfer of F and I into the deep mantle, whereas Br and Cl have shallow cycles in subduction zones.

[1] Kendrick *et al.* (2013) *Earth Planet Sc. Lett.* **365**, 86-96.