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The role of continental crust in the global halogen cycle: Insights from halogen concentrations (F, Cl, Br, and I) of ancient glacial deposits

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The concentrations of halogens (F, Cl, Br, and I) in the continental crust are poorly known [1], hindering better understanding of the continental crust in Earth's halogen cycle. We present halogen data (F, Cl, Br, and I) for twenty-four glacial diamictite composites that derive from the upper continental crust (UCC) and were deposited during discrete glacial events at ~2.9 Ga, ~2.4–2.2 Ga, 0.75–0.58 Ga, and ~0.30 Ga.

The good correlation between Cl and the highly soluble Na ($R^2 = 0.70$), together with low and scattered Cl concentrations in the diamictites (2–279 ppm), indicates significant Cl loss during chemical weathering. The other halogens (F, Br, and I), however, correlate well with less soluble elements like K, Nd, and Lu, suggesting that their concentrations in the diamictites are not strongly affected by chemical weathering. Increasing concentrations of F, Br, and I in the diamictites through time may reflect the evolving composition of the UCC. Using linear regressions of halogens versus other elements, the estimated minimum halogen concentrations of the present-day unweathered UCC are 394 ± 67 ppm F, 83 ± 24 ppm Cl, 0.413 ± 0.042 ppm Br, and 0.031 ± 0.005 ppm I (with 2σ uncertainties). These values are all depleted relative to elements of similar incompatibility, which may reflect their loss via magmatic exsolution/degassing and/or chemical weathering during formation of the continental crust.

The distinct behavior of Cl compared to Br and I during continental weathering leads to strongly fractionated Br/Cl (2–265 * 10^{-3}) and I/Cl (122–197,952 * 10^{-6}) ratios. The calculated weathering flux of Cl from the continents is quite limited (< 8–34 %) compared to the total Cl content of seawater, which suggests that Cl in seawater is mainly derived from outgassing of the mantle and/or late volatile accretion. On the other hand, the significantly higher Br and I contents in terrigenous organic-rich sediments than those of crystalline bedrocks require that significant amounts of Br and I were transported from the oceans to continents.

[1] Rudnick & Gao (2003), *Treatise on Geochemistry, The crust* 3, 1-64.