The distribution of halogens between fluids and upper-mantle minerals

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The behavior of halogens in subduction zones controls the exchange of chlorine and fluorine between the Earth´s mantle and the oceans. The distribution of halogens between aqueous fluids and mantle minerals will have a strong effect on the ability of these fluids to transport trace elements as well. So far, there are no experimental data on the behaviour of halogens in subduction zones and their fate during dehydration metamorphic reactions and fluid migration across the slab-mantle interface are not known.

In this study we investigate the incorporation of chlorine and fluorine in forsterite, enstatite and pyrope under upper-mantle conditions. Experiments were performed with oxide-hydroxide mixtures, synthetic glasses, and chlorides, fluorides, and halogen-bearing aqueous fluids as halogen sources. Runs were carried out in a piston cylinder apparatus at 1100 °C and 2.6 GPa, and major-element and halogen concentrations were determined by electron microprobe.

Runs in the system MgO-SiO_2-H_2O-$MgCl_2$ produced a three or four-phase assemblage of pyrope or forsterite and enstatite, Cl-bearing hydrous silicate melt and aqueous fluid (brine). Our results demonstrate that (1) solubility of chlorine in forsterite, enstatite and pyrope at 1100 °C and 2.6 GPa is low and it ranges between 60-400 ppm; (2) partition coefficients for chlorine between aqueous fluid (brine) and silicate minerals are high, $5 \cdot 10^3$ to $3 \cdot 10^4$, and those between hydrous melt and minerals range from $1.4 \cdot 10^2$ to $4.8 \cdot 10^2$. Therefore, both the aqueous fluids and silicate melts efficiently sequester chlorine from anhydrous silicate minerals; (3) halogens promote the stability of hydroxyphases which can act as storage sites of halogens.

The use of compound-specific isotope analysis to quantify biodegradation of RDX in groundwater

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Compound-specific isotope analysis (CSIA) was used to examine the extent of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) biodegradation in groundwater along a ca. 1.35-km contamination plume.

Isotope analysis of RDX in the groundwater samples revealed apparent enrichment in $\delta^{15}N$ values further away from the contamination sources. The extents of biodegradation and first-order degradation rate constants along the plume were calculated based on this shift in isotopic composition.

The rate constants of RDX biodegradation were generally found to be of the same order of magnitude for different wells at different locations. An exception was observed in a three-well cluster, in which a clear correlation was observed between the depth of the well's screen and RDX-biodegradation rate. In a borehole that penetrates the complete depth of the aquifer, the range of calculated half-life values was more than one order of magnitude greater than the values calculated for all other boreholes. The decrease in degradation rate was found to be correlated with a decrease in dissolved oxygen concentrations, suggesting that the relatively low dissolved oxygen concentrations in the deep subsurface limit the rate of aerobic biodegradation of RDX. However, the possibility that this decrease is the result of other factors that were not studied in this work, such as nutrient availability, cannot be ruled out.

Our study shows that CSIA is a suitable tool for the detection of RDX biodegradation in the environment. Our findings indicate that RDX is naturally biodegraded in the contaminated aquifer and that biodegradation rates decrease with depth.