

The structure and lability of Re(VII)-sodalite

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⁹⁹Tc (Tc), a long-lived radionuclide, is one of the most widespread contaminants within the Hanford subsurface with an estimated inventory of 5.31×10^3 curies. For example, Tc contamination has been found in the sediments beneath the C, S, SX, T, and TX Tank Farms as a result of high-level waste (HLW) solutions that have leaked or spilled from Hanford Tanks. The HLW solutions are characterized as highly alkaline (hydroxide ion concentration > 8.5 M) and high ionic strength solutions (up to saturation with respect to NaNO₃). Previous research focused on ⁹⁰Sr and ¹³⁷Cs has demonstrated that these elements are incorporated into feldspathoid minerals, such as sodalite [Na₈(Al₆Si₆O₂₄)Cl₂], that formed as a result of the contact between Hanford sediments and the HLW solutions [1, 2]. The desire to immobilize Tc in aluminosilicate minerals through the application of subsurface amendments for contaminated sediments as well as the production of mineralized wasteforms further emphasizes the need to understand the long-term stability and release of Tc from aluminosilicate minerals, specifically the feldspathoid mineral sodalite.

In an attempt to determine the structure and reactivity of Re-sodalite (as a chemical analogue for Tc-sodalite), a combination of spectroscopy analyses along with single-pass flow-through experiments were performed under dilute and near saturated conditions at pH (23°C) = 9.0 and 40°C. These initial experimental results suggest the release of elements from Re-sodalite is complex; the saturation state of the solution changes and this behavior may be associated with the formation of other mineral phases.

[1] Chorover, J. Choi, S. Rotenberg, P. Serne, R.J. Rivera, N. Strepka, C. Thompson, A. Mueller, K.T. O'Day, P.A. (2008) Silicon control of strontium & cesium partitioning in hydroxide-weathered sediments. *Geochimica Et Cosmochimica Acta* **72**, 2024–2047. [2] Deng, Y. Harsh, J.B. Flury, M. Young, J.S. & Boyle, J.S. (2006) Mineral formation during simulated leaks of Hanford waste tanks. *Applied Geochemistry* **21**, 1392–1409.

Long term chemical variations in stream waters draining a granitic catchment (1986-2010). Link between hydrology and weathering (Strengbach catchment, France)

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The forested Strengbach catchment is an experimental site for which hydrological, geochemical and meteorological data have been collected since 1986. It is located in the Vosges massif on a granitic bedrock with temperate oceanic mountainous climate. The site suffered from acid rains and tree decline was acknowledged in the 1980s.

At the end of the 1980s, in parallel with the decrease of the acid atmospheric depositions, the pH of surface waters increased. At the same time, the chemical composition of the stream water evolved to significant lower cation (Ca, Mg) and anion (SO₄, NO₃) concentrations. Similarly, soil solutions show a decrease in Ca and Mg concentrations since 1986.

The decreasing sulfate concentrations are related to the reduction of anthropogenic acidic rain depositions as well as combination of sorption/desorption in soils. The variations of nitrate concentrations, which are not continuous over time, might be related to extremely dry periods causing modification of the N biogeochemical cycle at the catchment scale.

The decreasing cation concentrations cannot be explained by diminishing atmospheric wet and dry depositions. Similarly, hydrological processes do not explain these compositional changes. But the annual chemical fluxes out of the catchment are strongly correlated to the annual water fluxes, which were highly variable during the past 25 years.

Only changes in water-rock interaction and in the nature of the weathered sources might explain the Ca, Mg and K concentration variations at the catchment scale. The mechanisms involved include the formation of secondary soil minerals (mainly clays), cation exchange processes as well as weathering of primary, granite-derived and secondary minerals with resulting cation depletion in soil and saprolite.

Therefore, the long term monitoring of rain, throughfalls, spring and stream waters allows to follow the geochemical evolution of the ecosystem over time in response to changes in atmospheric pollution and forest management.