

## Mg isotopes in natural waters: what do they mean?

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It has been known for decades that river water elemental or isotopic ratios are controlled by mixtures of end-members with differing compositions. The compositions of such end-members are either inherited from heterogeneity in the original lithological sources (e.g., carbonate, silicate and evaporite) or from process-related fractionation of elemental or isotopic ratios during weathering. Distinguishing process-related variations from lithological mixing trends is a problem fundamental to partitioning weathering fluxes between different sources, and are a fundamental problem for quantifying the carbon consumption associated with silicate weathering. In most catchments, distinguishing chemical signatures in river waters related to lithology from those related to weathering processes is complex because of heterogeneous lithology.

New isotopic tracers such as the isotope ratios of Mg therefore have the potential to help deconvolve the extent to which rivers reflect mixing, or the extent to which rivers have compositions which are chemically evolved by physicochemical processes. In a geological context this is similar to distinguishing fractionational crystallisation from magma mixing. The stable isotopes of Mg offer important advantages over more common place isotope ratios such as Sr, that have been used for decades. This is because they have the potential to trace both source and process effects of one the major cations in solution rather than just source effects of a trace cation. It is now more than a decade since Mg isotope ratios have been published on natural waters, but progress in using them to place constraints on the origin of solutes requires careful calibration before the data can be successfully applied.

Almost all published Mg isotope data on natural waters falls between the end-member  $\delta^{26}\text{Mg}$  values of the carbonate and silicate rocks that are drained. This could suggest that waters simply reflect mixing between end-members, but coherent relationships with elemental ratios that have typically been used to infer mixing relationships are rare. This leads to a catch22 scenario: Is it possible to infer a mixing relationship using an X/Mg ratio when  $\delta^{26}\text{Mg}$  doesn't show the same relationship?

In simple mono-lithological catchments where there is inferred to be a single source of Mg,  $\delta^{26}\text{Mg}$  is apparently fractionated and covaries with Li isotopes. The relationship between Mg and Li is complex. Li isotopes are thought to be strongly influenced by clay, but the precise relationship between Mg, Li and clay is not yet known. The mixing versus process problem will be discussed with examples, illustrating what we have learned so far from Mg isotopes in natural waters, and the many things that Mg isotopes still have to tell us about.

## Immobilisation of hexavalent actinides in cementitious materials: Evidence for structural incorporation in calcium-silicate-hydrates

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### Abstract

Cementitious materials are an important component of the multi-barrier concepts developed in many countries for the safe disposal of low and intermediate level radioactive waste in deep geological repositories. Studies of the retention of radionuclides by cementitious materials have focused predominantly on adsorption as the relevant uptake process. However, other immobilization processes, such as incorporation in the solid matrix, may take place and, thus, exert a beneficial effect on radionuclide retardation. Calcium silicate hydrates (C-S-H), the major cement constituent, are characterized by high recrystallisation rates making them an ideal system for the incorporation of radionuclides present in cement-based repositories.

In the present study, wet chemistry and luminescence spectroscopy experiments have been performed under high pH conditions, with the aim of determining the speciation of hexavalent actinides (An(VI)), U(VI) and Np(VI), in C-S-H. Batch sorption experiments have been carried out with C-S-H and titanium dioxide, a solid phase stable under high pH conditions and often used as a model material for surface complexation studies. Comparison of the sorption of U(VI) and Np(VI) on both solids allows the influence of incorporation processes on the immobilisation of hexavalent actinides by C-S-H to be determined.

The An(VI) sorption behaviour on TiO<sub>2</sub> and on C-S-H phases appeared to be nearly identical; R<sub>d</sub> values were found to decrease with the increasing predominance of negatively charged species in the aqueous phase suggesting the weaker sorption of these actinyl anions. Uranyl-doped C-S-H exhibited inhomogeneously broadened luminescence bands following non-selective laser excitation at liquid helium temperature (4K). Luminescence spectra following selective resonant laser excitation showed these broad band structures to consist of a superposition of many overlapping narrower bands associated with slightly different non-interacting uranyl luminescence centers in a disordered environment indicating incorporation in the amorphous C-S-H structure. The characteristics of the luminescence spectra provided information on the local coordination geometry of the incorporated uranyl moiety leading to the conclusion that it is incorporated in the C-S-H interlayers. The study shows that, under high pH conditions, the wet chemical behaviour (pH dependence and effect of aqueous Ca concentration) is similar for An(VI) incorporated in the interlayers of C-S-H and uranyl bound on the surface of TiO<sub>2</sub>.