Bridging the 'gap' between laboratory dissolution and natural chemical weathering

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Mineral surfaces play a primordial role in controlling the transfer of matter and energy between minerals and the surrounding environment. In order to understand the mechanisms of chemical weathering reactions, both in the laboratory and in the field, we are carrying out nanoscale investigations of altered layers that develop on silicate mineral surfaces. Specifically, we are investigating the chemical and physical evolution of fluid-mineral interfaces at the molecular level using various analytical techniques, in particular high resolution and energy filtered TEM. A series of silicate minerals (orthoclase, albite, labradorite, anorthite, wollastonite, diopside, pyrope garnet, olivine) have been altered in the laboratory at acid pH conditions. In addition, one sample of naturally weathered K-feldspar was investigated. In all cases, the mineral surfaces developed a near-surface altered layer that is chemically and structurally distinct from the unaltered mineral. The structural and chemical interfaces between the altered layers and the corresponding minerals are always spatially coincident and extremely sharp. The chemical depth profiles, which are measured directly in cross section on FIB-prepared electron transparent ultrathinsections, are very sharp (chemical gradients on the order of 5-10 nm) and therefore were most likely not created by a diffusional process. This finding suggests that altered surface layers represent the precipitation of a new secondary phase. This hypothesis stands at odds with the commonly accepted 'leached layer' theory based on surface altered layers created by preferential leaching and interdiffusion. Most importantly, our preliminary results suggest that the intrinsic dissolution process is the same for laboratory and natural weathering processes.

U(VI) uptake by calcium silicate hydrates

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The uptake of U(VI) by calcium silicate hydrate (C-S-H) phases has been investigated using batch sorption experiments and time-resolved laser fluorescence spectroscopy (TRLFS). C-S-H phases are secondary minerals formed by the interaction of hyperalkaline groundwater escaping from a cementitious nuclear waste repository, with Si-containing host rocks.

The U(VI) uptake by C-S-H phases with varying composition was investigated in a series of batch sorption experiments in the pH range of 10.0 to 13.3. The distribution of ^{233}U(VI) between solid and liquid phase was determined by radiochemical analysis. The U(VI) uptake was shown to be very strong as illustrated by distribution ratios (R_d values) ranging between 10^3 L kg^{-1} and 10^5 L kg^{-1}. Sorption isotherms measured on C-S-H phases with different C:S ratios at different pH's all exhibit a non-linear behavior suggesting the presence of multiple U(VI) sorbed species. Increasing the pH from 10.5 to 13.3 by the addition of NaOH or KOH, results in a significant decrease of the U(VI) sorption.

TRLFS data showed the presence of several different U(VI) solid species. Resolution of overlapping luminescence spectra was accomplished by using an iterative target factor analysis approach. Luminescence spectra of the U(VI) sorbed species at low U(VI) loadings were characterized by luminescence emission maxima between 500 nm and 520 nm and four to five vibronic components typical for luminescence emission of the linear $[O=U=O]^{2+}$ structure of the uranyl group. At higher loadings an increasing contribution of species with an emission maximum at 540 nm appeared in the luminescence spectra suggesting the presence of uranate-type species. The vibronic spacings of the emission spectra were found to vary between 660 cm^{-1} and 790 cm^{-1}. From this information it was possible to estimate values of the U-O bond length of the axial oxygens of the sorbed uranyl species. Comparison of the luminescence spectra of the U(VI) sorbed species with spectra obtained from well-known U(VI) reference compounds provided further information on the coordination environment of the sorbed U(VI) species.