Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.27463

An XAS study on the effect of ionizing radiation on the redox state of the structural iron in hydrated clay minerals

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The Swedish KBS-3 concept, among other nuclear waste disposal projects, involves a Bentonite clay buffer surrounding copper canisters containing nuclear waste. Smectite-rich Bentonites, like Wyoming Bentonite MX80, have elaborate chemical, hydraulic, and mechanical properties due to the surface chemistry and layer charge of their main component, Montmorillonite. This research examines the effects of ionizing radiation on Fe(II)/Fe(III) cycling, mineral transformations, and redox interactions with interlayer Cu(II) in smectite-rich Bentonite clays, crucial for nuclear waste repository safety.

Previous studies using γ-radiation have demonstrated a substantial reduction of structural Fe(III) to Fe(II) in dilute montmorillonite suspensions[1] or hydrated smectite-rich Bentonite[2][3]. However, most findings relied on wet chemistry techniques post-irradiation, highlighting the need for *in-situ* irradiation combined with simultaneous X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD).It is well known that ionizing radiation at high doses can induce defects in clay minerals and adjacent geochemical environments[4]. While prior studies found no interlayer changes upon radiation exposure[5], a varying Fe(II)/Fe(III) ratio may cause lattice strain and structural charge defects over time, as elevated Fe(II) in the octahedral sheet is unstable.

This study examines Fe(III) to Fe(II) cycling due to interactions with primary radicals from radiolysis of clay pore water (Figure 1). Using the synchrotron beamline Balder at MAX IV, a multi-modal XRD and XAS approach to analyze crystal and unit cell changes (XRD), interatomic distances and local symmetry (EXAFS), and oxidation state and coordination environment (XANES, Figure 2).

In addition to Wyoming Bentonite MX80, Fe-rich (Nau-1, Nau-2) and Fe-free (Syn-1) clays were investigated to explore 1) effects of physical conditions relevant to nuclear waste repositories (anoxic, varying water content), 2) structure in highly reduced clays (radical scavengers, Na-dithionite), and 3) redox states of Cu/Fe in Cu-exchanged smectite.

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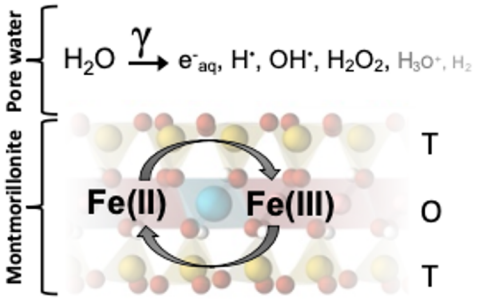

Figure 1: *Schematic process of Fe(II)/Fe(III) cycling (flip-flopping) due to reactions with reactive species formed by water radiolysis.*

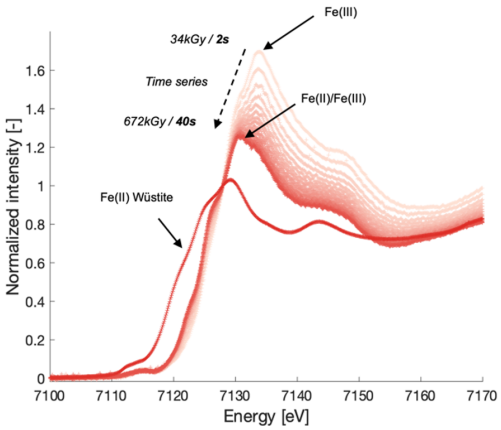

Figure 2: XANES time series – MX80 29 wt%, 10% 2-PrOH in anoxic conditions
Timestep: 2 s, number of steps: 20. Wüstite spectrum was added to illustrate the energy shift as a guide for MCR-ALS. 34kGy to 672kGy are the total doses in the local volume, with a beam size surface of about 100 μm^2.