

Temperature-resolved synchrotron X-ray diffraction study of dehydration of birnessite-like phases

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Manganese oxide minerals having the birnessite-type layer structure occur in a wide variety of geological settings, including soils, sediments, Mn crusts and nodules, and rock varnish. They readily participate in cation-exchange and oxidation-reduction reactions, and synthetic birnessite-like phases are extensively being studied as possible catalysts and cation-exchange agents. The interlayer region is occupied by H₂O molecules and various cations such as Na⁺, Ca²⁺, K⁺, etc; synthetic birnessite phases have been synthesized having a wide assortment of other interlayer cations. The chemical activity exhibited by birnessite is, at least in part, due to the apparent ease with which the structure adjusts to accommodate a range of interlayer water and cation compositions.

In situ, temperature-resolved synchrotron X-ray diffraction and the Rietveld method were used to investigate the dehydration behaviors of synthetic Na-, Mg-, H-, Ba- and K-birnessites as they were heated from room temperature to ~300 °C. The X-ray diffraction data were collected in air at beam line X7B of the National Synchrotron Light Source, Brookhaven National Laboratory, using a wavelength of 0.9370 Å and a MAR345 full imaging plate detector.

Na- and K-birnessite exhibit complex dehydration behaviors when heated from room temperature to 300 °C, accompanied by three distinct structural changes: at 70-80 °C, 100 °C, and 140-150 °C. The unit-cell volume decreases at each dehydration step but most dramatically above 140 °C. At ~175 °C K-birnessite transforms to an anhydrous layer structure with a layer spacing of 6.69 Å, that persists to at least 300 °C. Upon cooling in air this phase rehydrates. Ba- and Mg- birnessites exhibit only minor volume decreases up to 150 °C. Above this temperature, the Ba-birnessite structure breaks down abruptly, and the unit-cell volume of the Mg phase gradually decreases up to ~350 °C.

Interaction of U(VI) with birnessite: A solution chemistry and EXAFS study

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Radionuclide migration in natural aqueous environment is an ongoing concern in environmental research. Because layer Mn oxides are widespread, have a large surface area and a high density of binding sites, they control the fate of many important metals, including radionuclides. This work investigates the mechanism and kinetic of the uranyl interaction with birnessite, the predominant layer-type MnO₂ mineral at the Earth's surface. The sorption of U(VI) on synthetic birnessite was studied macroscopically with experiments performed under various conditions of pH (ranging from 4 to 6), dissolved U(VI) concentrations ($[U^{VI}] = 3.10^{-7}$ to 7.10^{-4} M), and ionic strength (0.01M to 0.1M, in NaClO₄ or Na₂CO₃ media). Under these conditions, the speciation of U(VI) in solution was contrasted, being dominated either by hydrolyzed species, uranyl-carbonato complexes, or polynuclear species. Sorption kinetic depended on the concentration of dissolved U(VI). The amount of sorbed U(VI) per specific surface area largely exceeded the coverages previously reported on related environmental minerals, such as montmorillonite and ferrihydrite, under similar experimental conditions, thus confirming the strong affinity of U(VI) for the birnessite surface. Sorption isotherms exhibited a complex form, and was indicative of, at least, two types of sorption sites. EXAFS data revealed the presence of two equatorial O shells at ca. 2.31 Å and 2.42- 2.51 Å (in addition to the two axial oxygens at about 1.80 Å), and a Mn shell (except in the Na₂CO₃ media) at 3.4 Å in the pH 4 sorption samples. The average number of Mn atoms decreased and the distance of the second equatorial O shell increased to 2.51 Å with increasing aqueous U(VI) concentration. At pH 6, the equatorial oxygens remained split into two distincts shells, but no nearest Mn was detected. No C shell was detected for any samples, even in the Na₂CO₃ media, nor U-U pair, despite the prevailing presence of polynuclear dissolved species in some of the samples.

From the combination of solution chemistry and EXAFS results, a structural model for the sorption of U(VI) at low pH is proposed, in which the oxygens from the equatorial plane of uranium form two types of surface complexes with edge sites from the birnessite layers. At low aqueous U concentration, adsorption occurred via a bidentate complexation. When the U(VI) concentration increased, the saturation of the previous sites led to the formation of a second type of surface complex, involving monodentate binding to the mineral surface.