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The Cr X-ray absorption *K*-edge structure of poorly crystalline Fe(III)-Cr(III)-oxyhydroxides

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Abstract

Poorly crystalline solids play an important role in many low-temperature geochemical processes, such as trace element speciation and biomineralization. Yet, the structures of many such naturally occurring phases are poorly understood. X-ray absorption spectroscopy is a powerful tool that permits chemically and spatially resolved investigations of poorly crystalline materials. In this study, we compare structural and electronic information derived from different regions of chromium *K*-edge X-ray absorption spectra for a series of poorly ordered iron(III)-chromium(III)-oxyhydroxides. These phases regularly form after the reduction of Cr(VI) by Fe(II) and often dictate the long-term fate of Cr in the environment. The distinct parts of the X-ray absorption spectrum, namely the pre-edge region, the near edge (XANES) region, and the extended (EXAFS) region, provide complementary information about the local chemical environment of Cr. Analysis of the XANES and EXAFS spectra showed that the structure around Cr in the Cr-poor sample is primarily composed of edge-sharing octahedra, whereas the octahedra in the Cr-rich samples are connected by edge-sharing and corner-sharing linkages. The analysis of non-local transitions in the pre-edge spectra indicated the absence of Cr clustering at low Cr substitution. This study demonstrates the advantage of complementary pre-edge, XANES, and EXAFS analysis to deduce information on the medium-range environment around Cr in poorly ordered solids.

Keywords: XANES, EXAFS, pre-edge, chromium, iron, oxyhydroxides, poorly crystalline