

X-ray absorption spectroscopic study of Fe reference compounds for the analysis of natural sediments

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ABSTRACT

Synchrotron X-ray absorption spectroscopy (XAS) is becoming an increasingly popular tool for the analysis of element speciation in complex natural mixtures such as soils and sediments. Identification of a particular mineral or amorphous solid in a heterogeneous mixture by XAS depends on the spectral uniqueness of the element in the bonding environment associated with a component, and on absorption effects from the components and the matrix. A suite of 27 common, Fe-bearing reference compounds, including sulfides, carbonates, phosphates, oxides, oxyhydroxides, and phyllosilicates, was analyzed to empirically assess the utility of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) for identifying a particular Fe mineral (or class of minerals) in a soil or sediment mixture. We show that XANES spectral features are useful for distinguishing qualitatively among major mineral classes, but not necessarily for identifying minerals within classes. A practical detection limit (based on empirical mixtures) for most mineral classes is on the order of 5% of the total atomic Fe absorption, but detection limits vary depending on the spectral uniqueness of the components, the number of components, and the matrix. Calibration curves for Fe sulfide and non-sulfide (phyllosilicate \pm oxide) component mixtures were made independently from the analyses of XANES and EXAFS fluorescence spectra of binary and ternary mineral mixtures (at 5% total Fe) in a quartz matrix to mimic natural sediments. Because of differences in sample and matrix absorption and fluorescence among sulfide and phyllosilicate minerals, apparent component fractions of pyrite derived from fits deviated significantly from linear binary mixtures. We show that corrections for non-linear fluorescence (as much as 20%) are particularly important for binary mineral mixtures with different densities and absorption characteristics (such as sulfides and phyllosilicates), and for mixtures with similar component abundances (i.e., far from one end-member). An application of the fluorescence calibration for XANES and EXAFS is shown for natural samples. This study points out the importance of a high-quality, experimentally consistent reference compound library, and the need for calibration of fluorescence spectra, in order to quantify accurately the component fractions of complex mixtures using XAS.