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Analysis of uranyl-bearing phases by EXAFS spectroscopy: Interferences, multiple scattering, accuracy of structural parameters, and spectral differences

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ABSTRACT

As part of a larger study of uranium speciation in complex environmental samples, we have collected and analyzed the U L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectra of nineteen minerals and compounds containing uranium as the uranyl moiety, UO_2^{2+}. Analysis of seventeen of these spectra yielded structural parameters for uranyl local environments that agree with their published crystal structures; the clarkeite EXAFS spectrum and published crystal structure do not agree, and zellerite lacks a published structure. EXAFS fitting results for clarkeite show significant variability in the local environment of uranium, indicating that this phase is not truly hexagonal. Although zellerite lacks a published structure, its EXAFS spectrum is quite similar to that of rutherfordine, suggesting a similar uranyl local environment, and possibly a related structure. Our analysis of the uranium EXAFS spectra of the nineteen phases indicates that multiple scattering (MS) contributes significant spectral amplitude, especially MS associated with the uranyl moiety and carbonate and phosphate ligands. The signal from MS associated with bidentate carbonate is strong and ubiquitous, even in aqueous $UO_2(CO_3)_3^{4-}$, suggesting that this signal may serve as an indicator of bidentate carbonate binding to uranyl in adsorption complexes. Multiple atomic shells at similar distances, or split atomic shells—both common features in the structure of uranyl-containing phases—produce interferences in the EXAFS spectrum that reduce the accuracy of the analysis. EXAFS-derived interatomic distances do not differ significantly from those derived from XRD, except when spectral interferences cause systematic errors in the analysis. Spectral differences and similarities have been analyzed using statistical methods. Quantitative analysis of the EXAFS spectra of samples containing multiple uranium phases may be complicated by the similarity of spectra from the same or related uranium-containing mineral groups, and by the possibility that two phases may mask the presence of a third. As EXAFS spectroscopy cannot always unambiguously determine the speciation of uranium in environmental samples, other complementary analytical techniques should be employed as well.