X-ray absorption spectroscopy study of Mn reference compounds for Mn speciation in terrestrial surface environments

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Abstract

X-ray absorption spectroscopy (XAS) offers great potential to identify and quantify Mn species in surface environments by means of linear combination fit (LCF), fingerprint, and shell-fit analyses of bulk Mn XAS spectra. However, these approaches are complicated by the lack of a comprehensive and accessible spectrum library. Additionally, molecular-level information on Mn coordination in some potentially important Mn species occurring in soils and sediments is missing. Therefore, we investigated a suite of 32 natural and synthetic Mn reference compounds, including Mn oxide, oxyhydroxide, carbonate, phosphate, and silicate minerals, as well as organic and adsorbed Mn species, by Mn K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The ability of XAS to infer the average oxidation state (AOS) of Mn was assessed by comparing XANES-derived AOS with the AOS obtained from redox titrations. All reference compounds were studied for their local (<5 Å) Mn coordination environment using EXAFS shell-fit analysis. Statistical analyses were employed to clarify how well and to what extent individual Mn species (groups) can be distinguished by XAS based on spectral uniqueness. Our results show that LCF analysis of normalized XANES spectra can reliably quantify the Mn AOS within ~0.1 v.u. in the range +2 to +4. These spectra are diagnostic for most Mn species investigated, but unsuitable to identify and quantify members of the manganate and Mn(III)-oxyhydroxide groups. First-derivative XANES fingerprinting allows the unique identification of pyrolusite, ramsdellite, and potentially lithiophorite within the manganate group. However, XANES spectra of individual Mn compounds can vary significantly depending on chemical composition and/or crystallinity, which limits the accuracy of XANES-based speciation analyses. In contrast, EXAFS spectra provide a much better discriminatory power to identify and quantify Mn species. Principal component and cluster analyses of k^2-weighted EXAFS spectra of Mn reference compounds implied that EXAFS LCF analysis of environmental samples can identify and quantify at least the following primary Mn species groups: (1) Phyllo- and tectomanganates with large tunnel sizes (2 × 2 and larger; hollandite sensu stricto, romanèchite, todorokite); (2) tectomanganates with small tunnel sizes (2 × 2 and smaller; cryptomelane, pyrolusite, ramsdellite); (3) Mn(III)-dominated species (nesosilicates, oxyhydroxides, organic compounds, spinels); (4) Mn(II) species (carbonate, phosphate, and phyllosilicate minerals, adsorbed and organic species); and (5) manganosite. All Mn compounds, except for members of the manganate group (excluding pyrolusite) and adsorbed Mn(II) species, exhibit unique EXAFS spectra that would allow their identification and quantification in mixtures. Therefore, our results highlight the potential of Mn K-edge EXAFS spectroscopy to assess bulk Mn speciation in soils and sediments. A complete XAS-based speciation analysis of bulk Mn in environmental samples should preferably include the determination of Mn valences following the "Combo" method of Manceau et al. (2012), EXAFS LCF analyses based on principal component and target transformation results, as well as EXAFS shell-fit analyses for the validation of LCF results. For this purpose, all 32 XAS reference spectra are provided in the Online Materials[1] for further use by the scientific community.

Keywords: Manganese, average oxidation state, speciation, X-ray absorption near edge structure (XANES) spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy, linear combination fitting, spectral fingerprinting, soils and sediments