Deciphering Ni sequestration in soil ferromanganese nodules by combining X-ray fluorescence, absorption, and diffraction at micrometer scales of resolution

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ABSTRACT

X-ray microprobes are among the most important new analytical techniques to emerge from third generation synchrotron facilities. Here we show how X-ray fluorescence, diffraction, and absorption can be used in parallel to determine the structural form of trace elements in heterogeneous matrices at the micrometer-scale of resolution. Scanning X-ray microfluorescence (μSXRF) and microdiffraction (μSXRD) first are used to identify the host solid phase by mapping the distributions of elements and solid species, respectively. Micro-extended X-ray absorption fine structure (μEXAFS) spectroscopy is then used to determine the mechanism of trace element binding by the host phase at the molecular scale. To illustrate the complementary application of these three techniques, we studied how nickel is sequestered in soil ferromanganese nodules, an overwhelmingly complex natural matrix consisting of submicrometer to nanometer sized particles with varying structures and chemical compositions. We show that nickel substitutes for Mn3+ in the manganese layer of the MnO2-Al(OH)3 mixed-layer oxide lithiophorite. The affinity of Ni for lithiophorite was characteristic of micronodules sampled from soils across the U.S.A. and Europe. Since many natural and synthetic materials are heterogeneous at nanometer to micrometer scales, the synergistic use of μSXRF, μSXRD, and μEXAFS is expected to have broad applications to earth and materials science.

INTRODUCTION

Environmental materials are intrinsically complex, being chemically and structurally heterogeneous at all scales, and their study poses a challenge for investigating metal speciation using conventional techniques. The main difficulties are the partitioning of trace elements into coexisting mineral phases, the identification of the mineral species to which these elements are bound, and the multiplicity of uptake mechanisms. In the absence of robust analytical techniques that could reliably identify and quantify each chemical species, operationally defined chemical extractions have been developed during the last two decades, and several procedures have been certified for quality assurance by the Commission of the European Communities Bureau of Reference (Quevauviller et al. 1994). In these methods, chemical reagents of various strengths are used to break the binding forces and to liberate and subsequently extract the metals from the mineral phases. However, uncertainties remain related to the selectivity of the various extractants and to potential problems due to re-adsorption of the dissolved metal by other phases (Gomez-Ariza et al. 2000; Ho and Evans 2001; Ostergren et al. 1999). Several physical techniques are also used to investigate the crystal chemistry of trace metal impurities in solids, of which electron microscopy (Buseck 1992) and bulk extended X-ray absorption fine structure (EXAFS) (Brown et al. 1999; Manceau et al. 2002) are among the most efficient.

However, as powerful and, as often used as these methods are, none of them separately or together allow one to identify both the nature of the host species and the incorporation mechanism of trace metals at the molecular scale. In the most advanced application of EXAFS spectroscopy to speciation, the number and nature of metal species are rigorously evaluated by principal component analysis (PCA) of a set of experimental spectra. Their proportions subsequently are estimated by least-squares fitting (LSF) of experimental data to the combination of reference spectra previously identified by PCA. Still, PCA is a wholly statistical analytical treatment of a set of mixed spectra, and the quantification procedure requires that all individual species are present in the reference database. As with any desummation technique, there can also be some concerns about the uniqueness of the analysis. In addition, there is no direct link to the actual solid phases (mineral or organic) present in the sample. X-ray micro-diffraction and micro-fluorescence, as an adjunct to EXAFS spectroscopy, ground this multicomponent spectral analysis in reality, obviating the need for any guesswork. Synchrotron-based scanning X-ray microfluorescence (μSXRF) (Sutton and Rivers 1999) and microdiffraction (μSXRD) (Tamura et al. 2002) together allow one to visualize the two-dimensional distribution of metals in minerals, and hence to determine to which particular mineral a given metal is bound, by simultaneous imaging of elemental and mineral distributions within the heterogeneous matrix. The coordination chemistry of the metal, and hence its incorporation mechanism within the mineral host, then is identified by μEXAFS.