

Studying ligands, metals and their complexes in aqueous systems using soft x-ray spectroscopy

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Soft X-ray spectroscopy and spectromicroscopy are emerging techniques that have unique applications in probing the electronic states of metals and their complexes in aqueous solutions. Using the soft X-rays, the $1s$ electrons of light elements (e.g. C) and the $2s$, $2p$, etc. electrons of transition metals and heavy elements (e.g. Se) in aqueous solutions and at mineral-water interfaces can be probed. Element-specificity and high-spectral resolution of soft X-ray methods also permit the examination of small changes in the electronic states of different elements in heterogeneous materials.

The availability of the third generation synchrotron X-ray sources and the development of high resolution zone plates has permitted the examination of wet mineral precipitates at a spatial resolution better than 20 nm recently. Such measurements are also possible for samples in wet state, and in complex heterogeneous matrices. The magnetic structures of nanoparticles and magnetic domains in micron sized minerals can also be studied in wet state using the plane and elliptically polarized soft X-ray beams.

A majority of soft X-ray spectroscopy techniques, and the required facilities to conduct studies on samples of geochemical interest are in the developmental stages. *Ab initio* calculations are also being conducted for different aqueous metal-ligand systems to correlate their spectral variations with the electronic structure.

An introduction to different soft X-ray spectroscopy and spectromicroscopy techniques, available research facilities at the synchrotron light sources, and examples of studies conducted using these methods in model and complex systems will be discussed.

Quantification of Mn valence in minerals at the nanoscale using electron energy-loss spectroscopy

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Introduction

Mn oxides are environmentally significant due to their efficiency in sequestering metals and their REDOX-active nature. These minerals are commonly very fine grained and intermixed so measurements of mineral properties such as valence should be conducted at an appropriate scale. With Electron Energy-Loss Spectroscopy (EELS) in the Scanning Transmission Electron Microscope (STEM), it is possible to measure the Mn valence in oxide minerals at the nanometre scale because the Mn $L_{2,3}$ Energy-Loss Near-Edge Structure (ELNES) varies systematically with valence.

Experimental Methods

In this study, synthetic Mn oxides of known valence were analyzed using EELS, and the $L_{2,3}$ peak intensity ratios and peak separations were determined for the three common valences, MnII, MnIII and MnIV, and for mixed-valence oxides. A ternary calibration relating Mn valence to the $L_{2,3}$ peak intensity ratios and peak separations was developed to quantitatively determine the Mn valence in natural minerals.

Results

With increasing valence from MnII to MnIV, the $L_{2,3}$ peak separations decreased from 11.6 – 10.3 eV and the total peak intensity ratios decreased from 4.0 – 2.1. The valence ratios measured for several natural mineral samples suggest that pyrolusite is dominantly MnIV but contains approximately 25% MnII. Similarly, manganite is dominantly MnIV with approximately 40% MnII. A romanechite sample approached 75% MnIV with 25% MnIII.

Conclusions

A method for quantitative determination of Mn valence in oxide minerals was developed which utilizes the $L_{2,3}$ intensity ratio and peak separation in EELS. The valence of Mn in natural minerals did not conform to the stoichiometry described by the mineral formulae.