XAFS Characterization of Annabergite and Erythrite

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Introduction

Element-specific local structural information is always of wide interest in the geosciences, especially for fine-grain microcrystalline phases or amorphous species, such as annabergite and erythrite, which occur frequently in weathered minerals or mining operation by-products. These phases may occur as the weathering products of nickel- and cobalt-bearing, minerals such as niccolite (NiAs) and cobaltite [(Co,Fe)AsS], or, more importantly, they may be generated during mining operations as carriers of arsenate released by the milling operation [1].

The structures of annabergite [$Ni_3(AsO_4)_2 \cdot 8H_2O$] and erythrite [$Co_3(AsO_4)_2 \cdot 8H_2O$] are of a vivianite type [2] — that is, symmetry (monoclinic, 2/m), space group (I/m) — and they are featured by alternatively arranged single- and edge-shared bi-octahedron chains (i.e., NiO_6 for annabergite and CoO_6 for erythrite) and by arsenate chains (Fig. 1). Even though the crystallographic data indicate that the arsenate tetrahedrons should be identical for the two minerals, the $Ni^{I,II,III}$ (or $Co^{I,II,III}$) and $Ni^{IV,V}$ (or $Co^{IV,V}$) sites are crystallographically different with regard to the central absorbing arsenic, and the Ni and Co sites for the two minerals are slightly different. This type of structural information can be used to characterize these isostrutural minerals and to offer clues about the structural impact of solid solutions that are important in mineralogy and petrology. Since these structural differences are indicated to be too subtle to be detected by conventional structural techniques, x-ray absorption fine structure (XAFS) was adopted for this study.

Methods and Materials

The fine powder crystalline annabergite sample was synthesized by G. Demopoulos at McGill University [3]. The euhedral single-crystal erythrite was provided by A. Pratt of NRCan in Ottawa; it originally came from Bou-Azer Morocco and had a composition of 25.61 wt% Co; 24.56 wt% As; 0.33 wt% Fe; 0.15 wt% Mn; and 0.78 wt% Ni. XAFS spectra at the As K-edge of annabergite and erythrite (Fig. 2) were collected by using the PNC-CAT bending magnet beamline (20-BM) over the energy range of 11,665-12,837eV with Si<111> monochromator crystals. The energy scale of the recorded XAFS data was calibrated at the Au K-edge energy (11,919.7 eV) by using a gold foil.
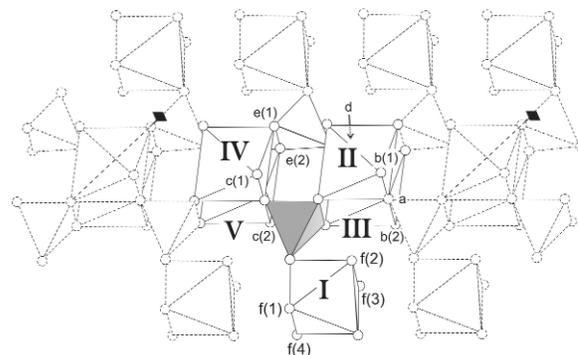
FIG. 1. Crystal structures of annabergite and erythrite. The isostructures of the two minerals are presented by the common single- and bi-octahedron chains bridged by single tetrahedron chains, where the octahedron is centered by either Ni for annabergite or Co for erythrite. The apical ball represents oxygen coordinated to nickel (or cobalt). Note that the local structural environment of central absorbing arsenic is indicated by the polyhedron cluster highlighted by solid-lined octahedron and tetrahedron. The nickel (or cobalt) involved in XAFS modeling is labelled from I to V. The oxygens are assigned from a, b(1) and b(2), c(1) and c(2), d, e(1) and e(2), f(1) to f(4).
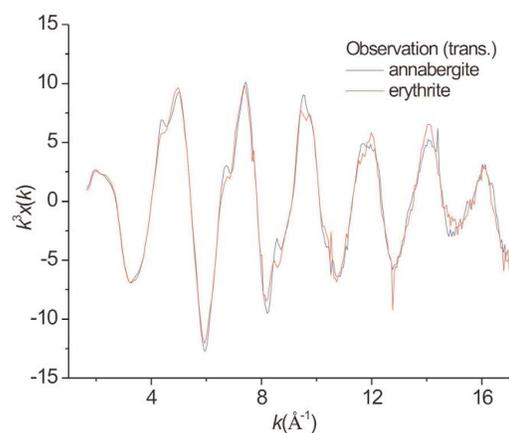
FIG. 2. Annabergite and erythrite As K-edge $k^3\Phi(k)$ data.

Results

The magnitude of the Fourier transform (FT) of the $k^3\Phi(k)$ spectra (Fig. 3.) reveals the following
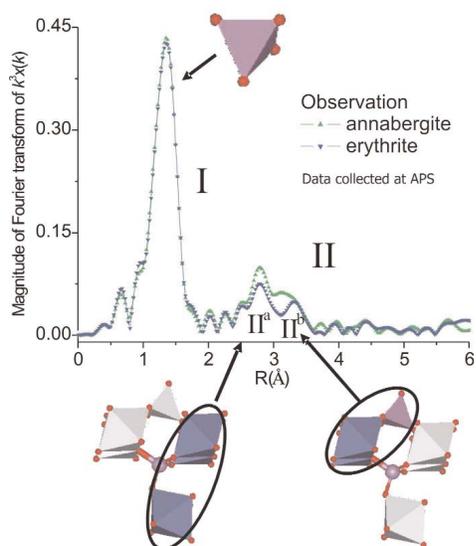
FIG. 3. The assignment of the two sub-shells for the second peak of the magnitude of the Fourier transform for the As K-edge k3c(k) data to the two parts of the As local structure.

information. First, peak I of the FT is attributed to the backscattering within the arsenate tetrahedron and indicates a similarity in morphology between the two minerals. Second, peak II of the FT (Fig. 3) is mainly due to the scattering from the two sub-shells (i.e., II^a from $Ni^{I,II,III}$ sites [or $Co^{I,II,III}$] and II^b from $Ni^{IV,V}$ sites [or $Co^{IV,V}$]) for annaberigte and erythrite. Multiple scattering within the arsenate tetrahedron may contribute to peak II, but it can have only a minor effect on the basis of the previous XAFS study of arsenate in crystalline species (e.g., scorodite) [4]. The major difference between the two samples appears in the peak II region, which indicates that the As local structure discriminates between the two minerals beyond the arsenate tetrahedron. This observation agrees with the previous crystallographic data [2].

The third discovery was made by performing curve fitting on the data sets of the two minerals (Fig. 4). The estimated scattering paths, As-$Ni^{I,II,III,IV,V}$ and As-$Co^{I,II,III,IV,V}$, generally match the crystallographic data [2]. However, some of the scattering paths show significant differences, with crystallographic results indicating a change between the structure data used for FEFF calculation [2] and the samples involved in this study. First, the structural data used by FEFF analysis for annabergite was refined from a sample with a chemistry of $[Ni(1)_{0.99}Mg(1)_{0.01}]$ $[Ni(2)_{1.65}Mg(2)_{0.35}]$ $(AsO_4)_2 \cdot 8H_2O$ [2], which is quite different from the synthesized sample $Ni_3(AsO_4)_2 \cdot 8H_2O$. Second, the structural data used by FEFF for erythrite was determined from a sample with a chemistry of $Co_{2.01}Ni_{0.25}Fe_{0.74}(AsO_4)_2 \cdot 8H_2O$ [2], which is different from the investigated sample of $Co_{2.60}Ni_{0.08}Fe_{0.04}Mn_{0.02}(AsO_4)_2 \cdot 8H_2O$.
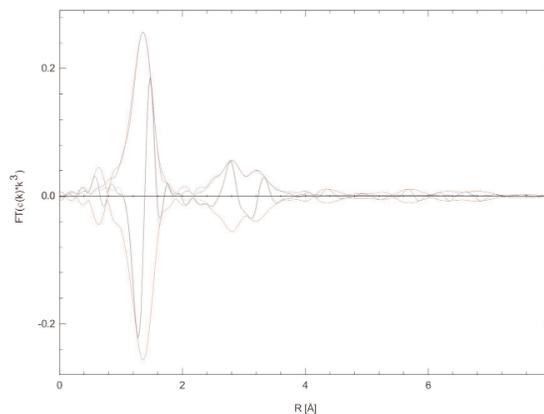
FIG. 4. Nonlinear least-squares curve fitting for the annabergite XAFS by using amplitudes and phases from FEFF 7.

Discussion

XAFS has shown its unique power for characterizing the As local structure of two isostructural minerals. However, the structural effect due to the difference in chemistry (i.e., solid solution effect) is not yet clear, and it has a general impact on mineralogy, petrology, and industry.

Acknowledgments

References

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