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SPECIAL COLLECTION: NANOMINERALS AND MINERAL NANOPARTICLES

The nanocrystalline structure of basaluminite, an aluminum hydroxide sulfate from acid mine drainage

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Abstract

Basaluminite is a poorly crystalline aluminum hydroxysulfate that precipitates in waters affected by acid mine drainage (AMD) and in acid sulfate soils (ASS). Its ability to sequester potentially toxic elements, such as Cu and As, makes it an important component of these systems, with strong environmental implications. Although it was initially described as a mineral, basaluminite is now considered a nanoscale variety of felsöbányaite, a rare mineral. In the present study, chemical analyses of natural and synthetic basaluminites are combined with data from advanced nanoscale characterization techniques such as high-energy X-ray diffraction (HEXD) and their corresponding pair distribution function (PDF) analyses, extended X-ray absorption fine structure (EXAFS), and solid-state nuclear magnetic resonance (ssNMR) spectroscopy. X-ray scattering data are analyzed with reverse Monte Carlo (RMC) modeling to obtain an atomistic representation of the disorder presents in this nanomineral. Sulfur *K*-edge EXAFS results show that sulfate is coordinated to the aluminum-octahedral framework of basaluminite mainly through outer-sphere ligands, though the existence of inner-sphere ligands seems to be significant in synthetic samples. PDF analyses show that both synthetic and natural basaluminites have identical short-range order, with ~1.2 nm coherent domain size, and share structural characteristics with felsöbányaite. Interestingly, ^{27}Al ssNMR reveals the presence of, respectively, ~1 and 5% of tetrahedral and pentahedral coordinations. RMC models of basaluminite highlight the presence of structural point defects. The understanding of this nanocrystalline character has important implications in terms of the reactivity of this nanomineral in AMD and ASS. The lack of correlation between the spatial and temporal occurrence of basaluminite and felsöbányaite suggests that the similarities between both mineral structures could be fortuitous, and highlights the need for a re-evaluation of the status of basaluminite as a nanomineral.

Keywords: Basaluminite, felsöbányaite, structure, PDF, EXAFS, NMR; Nanominerals and Mineral Nanoparticles