Characterization of defects and the local structure in natural and synthetic alunite (K, Na, H₂O)Al₃(SO₄)₂(OH)₆ by multi-nuclear solid-state NMR spectroscopy

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ABSTRACT

The local structural environments in a series of natural and synthetic alunite samples [ideally AAl₃(SO₄)₂(OH)₆, A = H₂O⁺, D₂O⁺, Na⁺, and K⁺] have been probed by solid-state ¹H, ³H, ²³Na, ²⁷Al, and ³⁹K NMR spectroscopy. The natural alunite [KAl₃(SO₄)₂(OH)₆] and synthetic hydronium alunite samples contain few structural defects, whereas the synthetic natroalunite and alunite samples have ca. 10% Al vacancies based on ²⁷Al NMR. A new ²⁷Al local environment (Al₂) was observed and assigned to Al with one Al vacancy in the first cation sphere. Three different proton environments, Al₁-OH, Al-OH₂, and H₂O are detected by ¹H and ³H MAS NMR. The hydronium ion (H₂O⁺) is only observed in hydronium alunite, and is associated with the stoichiometric regions of the sample. It was not detected in ¹H and ³H NMR spectra of alunite and natroalunite despite K (Na) occupancies of significantly less than 100%, as determined from elemental analysis. Thus, our NMR results suggest that the common assumption, namely that an A vacancy and an Al¹⁺ vacancy are compensated by adding an H₂O⁺ and 3 H⁺ (creating 3 Al-OH₂ groups), respectively, is too simplistic. Instead, a significant fraction of the Al¹⁺ vacancies are compensated for by 4 H⁺ ions, resulting in 4 Al-OH₂ groups per vacancy. This substitution is accompanied by the simultaneous deprotonation of a H₂O⁺ ion present on the A site. The resultant H₂O molecule is unnecessary for charge balance, accounting for the A-site deficiency often observed. The presence of Al¹⁺ and A¹⁺ vacancies appears closely correlated based on NMR.

Keywords: Alunite, solid-state NMR, hydronium ion, ²³Na NMR, ²⁷Al NMR, ¹H NMR, ³H NMR, ³⁹K NMR

INTRODUCTION

The alunite [AAI₃(SO₄)₂(OH)₆, A = H₂O⁺, Na⁺, and K⁺] and jarosite [4Fe₃(SO₄)₂(OH)₁₃] series are members of the large alunite group of minerals and related compounds that are relevant in several areas of science, including environmental chemistry (Stoffregen et al. 2000) and materials science (Greedan 2001). These minerals are commonly precipitated from acidic mine waters or acidic hydrothermal solutions (Stoffregen et al. 2000). They are also used in hydrometallurgy, especially in processing of Zn and U ores (Dutrizac and Jambor 2000). Monovalent and divalent metal ions including Pb²⁺, Cd²⁺, and Tl⁺ may be co-precipitated and incorporated in the structure of these minerals, resulting in removal and immobilization of these species from the aqueous environment. Moreover, the magnetic ions in the jarosite structure are located in nodes of a Kagomé lattice and the magnetic properties of these compounds have received much attention (Greedan 2001; Harrison 2004; Nocera et al. 2004). In addition, the identification of jarosite on Mars has been taken as evidence for aqueous processes on the planet (Klingelhöfer et al. 2004; Madden et al. 2004; Squyres et al. 2004).

Minerals of the alunite group crystallize in space group R̅3m. Their general formula is AB₃(SO₄)₂(OH)₆, where B = Fe³⁺, Al³⁺, V³⁺, Cr³⁺... and A = H₂O⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ag⁺, ½ Pb²⁺, NH₄⁺... (Dutrizac and Jambor 2000). Synthetic and natural members of this group generally exhibit considerable non-stoichiometry and contain structural defects on the B site. The presence of these defects may significantly affect the magnetic properties of phases where B = Fe³⁺, V³⁺ and Cr³⁺ as well as the ion exchange capabilities of jarosite (Kurata et al. 1984; Ozeki et al. 1989). Substantial numbers of vacancies are also found at the A¹⁺ site, which usually has an occupancy of 80–95% (Greedan 2001). A further complication is the presence of excess water molecules (~1 H₂O per unit formula) (Ripmeester et al. 1986; Bohnhammel et al. 1986; Drouet and Navrotsky 2003; Drouet et al. 2004). Recently, synthesis procedures for stoichiometric transition metal jarosite have been reported (Grohol and Nocera 2002; Grohol et al. 2003).

The structure of alunite (Fig. 1) consists of sheets of AlO₄(OH) octahedra. The sheets are decorated by sulfate tetrahedra, and the A¹⁺-ions are located between the sheets. The six ligands coordinated to Al³⁺ include four equatorial OH groups shared between the neighboring Al³⁺ ions (denoted as Al₁-OH in this paper) and two axial O atoms of sulfate groups above and