

Characterization of defects and the local structure in natural and synthetic alunite (K, Na, H₃O)Al₃(SO₄)₂(OH)₆ by multi-nuclear solid-state NMR spectroscopy

ULLA GRO NIELSEN,¹ JURAJ MAJZLAN,² BRIAN PHILLIPS,³ MARTINE ZILIOX,⁴ AND CLARE P. GREY^{1,*}

¹Department of Chemistry and Center for Environmental Molecular Science, SUNY Stony Brook, Stony Brook, New York 11794-3400, U.S.A.

²Institute for Mineralogy and Geochemistry, Albert-Ludwigs University of Freiburg, Albertstrasse 23b, Freiburg, D-79104, Germany

³Department of Geosciences and Center for Environmental Molecular Science, SUNY Stony Brook, Stony Brook, New York 11794-2100, U.S.A.

⁴Center for Structural Biology, SUNY Stony Brook, New York 11794-5115, U.S.A.

ABSTRACT

The local structural environments in a series of natural and synthetic alunite samples [ideally $AAl_3(SO_4)_2(OH)_6$, $A = H_3O^+$, D_3O^+ , Na^+ , and K^+] have been probed by solid-state 1H , 2H , ^{23}Na , ^{27}Al , and ^{39}K NMR spectroscopy. The natural alunite [$KAl_3(SO_4)_2(OH)_6$] and synthetic hydronium alunite samples contain few structural defects, whereas the synthetic natroalunite and alunite samples have ca. 10% Al vacancies based on ^{27}Al NMR. A new ^{27}Al local environment (Al_D) was observed and assigned to Al with one Al vacancy in the first cation sphere. Three different proton environments, Al_2-OH , $Al-OH_2$, and H_3O^+ are detected by 1H and 2H MAS NMR. The hydronium ion (H_3O^+) is only observed in hydronium alunite, and is associated with the stoichiometric regions of the sample. It was not detected in 1H and 2H 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 Al^{3+} vacancy are compensated by adding an H_3O^+ and 3 H^+ (creating 3 $Al-OH_2$ groups), respectively, is too simplistic. Instead, a significant fraction of the Al^{3+} vacancies are compensated for by 4 H^+ ions, resulting in 4 $Al-OH_2$ groups per vacancy. This substitution is accompanied by the simultaneous deprotonation of a H_3O^+ ion present on the A site. The resultant H_2O molecule is unnecessary for charge balance, accounting for the A -site deficiency often observed. The presence of Al^{3+} and A^+ vacancies appears closely correlated based on NMR.

Keywords: Alunite, solid-state NMR, hydronium ion, ^{23}Na NMR, ^{27}Al NMR, 1H NMR, 2H NMR, ^{39}K NMR