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Identification of hydrogen species in alunite-type minerals by multi-nuclear solid-state NMR spectroscopy

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Abstract

The various hydrogen species present in a series of synthetic hydroniumjarosite \(((\text{H}_3\text{O})\text{Fe}_3\text{(SO}_4\text{)}_2(\text{OH})_6)\), and ammonioalunite \(((\text{NH}_4)\text{Al}_3\text{(SO}_4\text{)}_2(\text{OH})_6)\) as well synthetic potassium \((\text{Cr}^{3+} \text{and V}^{3+})\) and hydronium \((\text{V}^{3+}, \text{Cr}^{3+}, \text{and Ga}^{3+})\) analogues were identified and quantified by \(^1\text{H}\) and \(^2\text{H}\) MAS NMR spectroscopy. The results confirm the defect mechanism proposed for alunite (Nielsen et al., Am Miner 2007, 92, 587), and allow for identification and quantification of even a few percent structural defects. For the paramagnetic samples, the isotropic shift for \(G_2\)-OH group \((\text{V}^{3+}, \text{Cr}^{3+}, \text{and Fe}^{3+})\) span more than 1100 ppm, which is related to different d-electron configuration \((d^2, d^3, \text{and } d^5)\). Analysis of the \(^1\text{H}\) and \(^{27}\text{Al}\) MAS NMR spectra shows that the synthetic ammonioalunite contains small amounts (5-10\%) of hydronium. Furthermore, the close structural relationship between of hydronium and gallium alunite is reflected by the \(^{27}\text{Al}\) and \(^{71}\text{Ga}\) quadrupole coupling parameters. Thus, the current work demonstrates the applicability of solid state NMR spectroscopy for identification and quantification of hydrogen species in both dia- and paramagnetic minerals.

Keywords: jarosite, alunite, gallium alunite, solid state NMR, paramagnetic NMR, hydronium ion, acid mine drainage
Introduction

The alunite supergroup consists of more than 40 different minerals and synthetic analogues, which have the general formula $DG_3(TO_4)_2(OH)_6$ (Hendricks 1937; Kolitsch and Pring 2001; Smith et al. 1998). The most common $D$, $G$, and $T$ cations are $D = K^+$, $Na^+$, $H_3O^+$, $G = Fe^{3+}$, $Al^{3+}$, and $T = S^{6+}$ (Brophy et al., 1962; Parker, 1962). Additionally, the hydroxyl groups may be replaced by minor amounts of $Cl^−$ and $F^−$ (Gunneriusson et al. 2009). Minerals of the alunite supergroup are of both geological and industrial importance. In the metallurgical industry dissolved iron, zinc, and other impurities are removed from the processing solutions by precipitation of alunite-type minerals (Basciano and Peterson, 2007a; Dutrizac and Jambor, 2000). In 2004 the Mars mission rover Opportunity discovered the presence of several ferric sulfate minerals on Mars, including jarosite. Jarosite is a hydrous iron-sulfur mineral formed under aqueous conditions implying the existence of water on this planet at some time in its history (Klingerhöfer et al., 2004; Madden et al., 2004; Squyres et al., 2004). Moreover, the magnetic properties of especially the jarosite-type minerals ($G = Fe^{3+}$ and $T = SO_4$) as well as the synthetic chromium and vanadium analogues have received attention from the Physics community due to the presence of a so-called Kagomé lattice in the structure (Matan et al. 2011).

The alunite supergroup of minerals is divided into subgroups based on which ions occupy the $G$ and $T$ sites. The jarosite group is characterized by $G = Fe^{3+}$ and $T = S^{6+}$, whereas the alunite group has $G = Al^{3+}$ and $T = S^{6+}$ (Brophy et al., 1962; Hendricks, 1937). Members of the alunite supergroup are isostructural and belong to the trigonal crystal system with space group $R3m$, $Z = 3$ with similar unit cell parameters, $a \sim 7$ Å and $c \sim 17$ Å, (Hendricks, 1937; Wang et al., 1965). The crystal structures of alunite and jarosite were first solved by Hendricks (1937). It consists of corner sharing $FeO_2(OH)_3$ octahedral sheets with tetrahedral sulfate groups positioned alternately above and below the sheets thereby connecting the
layers. The $K^+$ ($D$) ions are positioned in the cavities formed, as illustrated in Figure 1. The planar octahedral sheets in $a,b$-plane are stacked in a ABCA sequence along the along the $c$-axis with a distance of 5.6 Å between the Fe-Fe sheets in jarosite (Bisson and Wills, 2008; Greedan, 2001; Wills and Harrison, 1996). The Fe$^{3+}$ ions are located on a triangular, so-called Kagomé lattice with Fe-Fe distances of 3.67 Å (Bisson and Wills 2008). The octahedral environment around the Fe ion itself is somewhat distorted with two axial O(S) bonds (2.07 Å) and the four slightly shorter equatorial OH bonds (1.99 Å), where O(S) indicates an oxygen atom from the sulfate group. The Fe octahedra are tilted 18° with respect to the crystallographic $c$-direction towards the center of a triangle (Bartlett and Nocera, 2005; Goreaud and Reveau, 1980). The SO$_4$ tetrahedra are built from three oxygen atoms shared with three different Fe$^{3+}$ ions and an apical oxygen atom. This latter oxygen atom has hydrogen bonds to three OH groups from three different Fe$^{3+}$ ions in the next layer with an oxygen-oxygen distance, O(S)$\cdots$OH, of about 2.778-2.915Å (Basciano and Peterson, 2007a; Frost et al., 2005a; Nielsen et al., 2008). The $K^+$ ($D$ site) ions are located between the tetrahedral-octahedral-tetrahedral layers and are coordinated by six OH groups from the Fe octahedron and six oxygen atoms from the SO$_4$ ions, thereby linking the layers (Hendricks, 1937; Wang et al., 1965).

Both synthetic and natural species in the alunite group minerals are known to contain high concentrations of structural defects, as up to one third $G$ site irons has been reported to be missing especially for synthetic jarosite and alunite samples (Greedan 2001). Protocols for preparation of stoichiometric samples with $G = V^{3+}$, $Cr^{3+}$, and $Ga^{3+}$ (Grohol and Nocera 2002; Nocera et al. 2004) as well as $Al^{3+}$ (Rudolph et al. 2003) have been reported, which has been confirmed by solid state NMR spectroscopy for $G = Fe^{3+}$ (Nielsen et al. 2007) and $Al^{3+}$ (Grube 2011) Similarly, the $D$ site rarely has full occupancy. The following mechanism for
structural defects has been confirmed for alunite and jarosite (Nielsen et al. 2008; Nielsen et al. 2007).

\[
\text{G(OH)₄O₂ + 3H}^+ + \text{H}_3\text{O}^+ \rightarrow \square\text{(OH}_2\text{)}₄\text{O}_2 + \text{H}_2\text{O} + \text{Fe}^{3+}
\]

These vacancies results in the creation of new local environments especially hydrogen species, in addition to the hydroxyl groups (\(G_2\)-OH) as well as possibly hydronium (\(H_3O^+\)) and ammonium (\(NH_4^+\)) on the \(D\) site. A \(G\) site vacancy results in four water molecules each coordinated to a single metal ion (\(G\)-OH\(_2\)) and that the \(G\) site ion is (formally) replaced by a water molecule on the \(D\) site, as illustrated in Figure 1b. However, there has been much ambiguity in literature on the presence of hydronium species in alunite-type minerals (Bohmhammel et al. 1986; Gillard and Wilkinson 1964; Ripmeester et al. 1986; Schukow et al. 1999; Wilkins et al. 1974) as they are very difficult to detect. Conventional X-ray diffraction does not provide information about the local hydrogen environment and large quantities of deuterated samples is needed for neutron studies. Vibrational spectroscopy (Raman and infra-red, FT-IR) have often been used to examine hydrous materials, but the vibrational bands of the hydrogen species often overlap in alunite supergroup minerals, which prevent reliable assignment of the vibrations difficult (Murphy et al., 2009; Breitinger et al., 1997). In contrast, \(^{1,2}H\), \(^{23}Na\), \(^{27}Al\), and \(^{39}K\) NMR solid state spectroscopy (SSNMR) has provided detailed insight into the local structure of the diamagnetic alunite sample (\(D\text{Al}_3\text{(SO}_4\text{)}_2\text{(OH)}_6\) with \(D = \text{Na, K, H}_3\text{O and D}_3\text{O}\)), which allowed for identification and quantification of the different hydrogen species as well as the defect mechanism in equation 1(Grube and Nielsen 2015; Nielsen et al. 2008; Ripmeester et al. 1986). SSNMR of the transition metal alunite group minerals (\(G = V, \text{Cr, and Fe}\)) are challenging due to magnetic properties. However, \(^2H\) MAS NMR spectroscopy allowed for identification and quantification of the different hydrogen species using a combination of paramagnetic shifts.
Here we present results from a detailed solid state $^{1,2}$H, $^{27}$Al, and $^{71}$Ga NMR study of a series of related alunite-type species with $G = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Ga}^{3+}, \text{Cr}^{3+}$, and $\text{V}^{3+}$ with emphasis on structural characterization of the different hydrogen species such as $G_2\text{-OH}, \text{H}_2\text{O}, \text{H}_3\text{O}^+$, and $\text{NH}_4^+$ and the different degree of structural defects with the objective to determine and ideally quantify the relative concentration of the different hydrogen species in these materials. The diamagnetic samples were studied at ultra-high magnetic field (21.5 T) to ensure resolution of the different hydrogen species, whereas the paramagnetic samples were studied at a moderate field (11.7 T).

**Experimental**

Synthesis: The samples were prepared by a hydrothermal synthesis following previously reported procedures, as outlined below and summarized in Table 1, which also summarizes the reagents, reaction time and temperature for the individual syntheses. The following reagents were used: water - $\text{H}_2\text{O}$, deuterium oxide - $\text{D}_2\text{O}$ (99.8% isotopic, Alfa-Aesar), iron(II) sulfate hydrate - $\text{Fe}_2(\text{SO}_4)_3\cdot5\text{H}_2\text{O}$ (reagent grade, Alfa-Aesar), aluminum sulfate hydrate - $\text{Al}_2(\text{SO}_4)_3\cdot15\text{H}_2\text{O}$ (reagent grade, Alfa Aesar), gallium sulfate hydrate - $\text{Ga}_2(\text{SO}_4)_3\cdot5\text{H}_2\text{O}$ ($\geq99.99\%$, Sigma-Aldrich), chromium sulfate hydrate - $\text{Cr}_2(\text{SO}_4)_3\cdot\text{xH}_2\text{O}$ ($\geq99.99\%$, Sigma-Aldrich), lithium sulfate hydrate $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ ($\geq99.99\%$, Sigma-Aldrich), ammonium sulfate - $(\text{NH}_4)_2\text{SO}_4$ ($\geq99.99\%$, Sigma-Aldrich), vanadium chloride - $\text{VCl}_3$ (97%, Sigma-Aldrich), metallic vanadium (Sigma-Aldrich), sulfuric acid - $\text{H}_2\text{SO}_4$ (conc, Sigma-Aldrich) and deuterated sulfuric acid - $\text{D}_2\text{SO}_4$ (98 wt.% in $\text{D}_2\text{O}$, Sigma-Aldrich).
All solid reagents were completely dissolved in H$_2$O/D$_2$O before hydrothermal treatment in a sealed Teflon-lined Parr vessels ($V_{\text{internal}} = 15$ mL), which was partially filled (Table 1). Subsequently, the vessels were allowed to cool to room temperature (RT) and then cooled on ice. The product was scraped from the walls of the Teflon vessels, separated from the solution by filtration, washed with a small amount of water (D$_2$O for deuterated samples) then dried at $T = 40$ °C and gently ground prior to analysis. Partially deuterated samples were prepared by mixing D$_2$O with fully hydrated starting chemicals. However, the presence of a small amount of $^1$H in the samples does not interfere with the $^2$H NMR experiments. The ammonioalunite sample was reheated in 1.0 M H$_2$SO$_4$ - 0.5 N NH$_4$SO$_4$ solutions at $T = 200$ °C. After 72 h the sample was cooled, rinsed, filtered, and dried as ascribed above. It is noted that the hydronium chromium and vanadium jarosite syntheses had a very small yield (< 5 %) despite several synthesis optimizations.

Powder X-ray diffraction: Each sample was characterized by powder X-ray diffraction (PXD) using a Siemens D 5000 powder X-ray diffractometer. Diffraction patterns were collected in the 2θ range of 5-90° using Cu $K\alpha$ radiation, operating at 35 kV and 35 mA at 20 °C. All diffraction patterns were matched by the software EVA and the unit cell dimensions were calculated using the program LAPODS (Dong and Langford 2000). No crystalline impurities were detected by PXD (Figure S1).

Solid-state NMR: $^1$H and $^{27}$Al spectra were recorded at 21.1 T (900 MHz for $^1$H) using an Agilent 1.6 mm HXY MAS probe with 35 kHz spinning and single pulse. The $^{71}$Ga NMR spectra were recorded at 11.7 T (500 MHz for $^1$H) in an Agilent 4mm HXY MAS probe under static conditions using a quadrupole echo. The 11.7 (500/89) and 21.1 (900/63) T magnets are both connected to Agilent VNMRS (Direct Drive) NMR spectrometers. Data processing and analysis was performed using WinSolids developed by Klaus Eichele (2010).
and STARS. SpinWorks (Marat 2010) and the Varian software were used for integration. $^2$H MAS NMR was performed on an INOVA 500 MHz NMR spectrometer using a Chemagnetics 3.2 mm HX MAS NMR probe. The magic-angle was carefully set using the $^{23}$Na or $^2$H resonance in NaNO$_3$ and CD$_3$COONa, respectively.

Thermogravimetric analysis: TGA was performed on aluminum(III) and iron(III) sulfate hydrate in order to determine the exact water content of the hydrates using a TG 92-12 Setaram thermal analysis system. Samples of about 30 mg were heated from RT to 700-900 °C at 10 °C/min in a nitrogen atmosphere.

Results

NMR spectroscopy of alunite is naturally divided in two groups due to magnetic properties of the sample around room temperature. For the diamagnetic alunite the $\delta_{\text{iso}}$(1H) provides direct information about the nature of the different hydrogen species from high-resolution $^1$H MAS NMR spectra using established chemical shift correlations. Paramagnetic samples ($G = V^{3+}$, $\text{Cr}^{3+}$, and $\text{Fe}^{3+}$) are best studied by $^2$H MAS NMR of deuterated samples due to the strong interaction of the nuclear spin with the unpaired electrons (Nielsen et al. 2008). Furthermore, the dynamics of the hydrogen species is probed by $^2$H MAS NMR spectroscopy for selected samples. Finally, $^{27}$Al and $^{71}$Ga NMR spectroscopy of alunite and gallium alunite provided insight into the local environment of the $D$ sites.

Diamagnetic samples:

Table 2 summarizes the results from the analysis of the $^{1,2}$H MAS NMR spectra of the diamagnetic alunite samples $(H_3O)Ga_3(SO_4)_2(OH)_6$, $(D_3O)Ga_3(SO_4)_2(OH)_6$, $(NH_4)Al_3(SO_4)_2(OH)_6$, and $(ND_4)Al_3(SO_4)_2(OH)_6$. The $^1$H MAS NMR spectra were recorded at 900 MHz (21.1 T) with 35 kHz spinning speeds. This provides a significantly increased
spectral resolution as compared to our earlier data reported at 9.4 and 11.7 T using moderate spinning speeds (15-20 kHz) (Grube and Nielsen 2015; Nielsen et al. 2007).

The $^1$H MAS NMR spectra of $(H_3O)Ga_3(SO_4)_2(OH)_6$ (Figure 2a) consists of two strong signals at $\delta_{iso}(^1H) = 4.2(5)$ and $10.6(1)$ ppm with a relative intensity of 2:0.92 in good agreement with the expected 2:1 ratio. In addition, there are two small signals at $\delta_{iso}(^1H) = 6.3(5)$ and $9.0(1)$ ppm each representing less than 2% of the total intensity, c.f., Table 2.

Based on our previous studies of the isostructural schlossmacherite, $(H_3O)Al_3(SO_4)_2(OH)_6$ (Nielsen et al. 2007) we assign the resonances at $\delta_{iso}(^1H) = 4.2(5)$, 6.3(5), and 10.6(1) ppm to Ga$_2$-OH, Ga-OH$_2$, and H$_3$O$^+$, respectively. The 9.0(1) ppm resonance (1% of the total intensity c.f., Table 2) is assigned to an unknown impurity and will not be discussed further.

Thus, $^1$H MAS NMR shows that the concentration of Ga-OH$_2$ sites is small, i.e., our $(H_3O)Ga_3(SO_4)_2(OH)_6$ is almost stoichiometric. Based on the intensity of the peaks in the SSNMR spectra the concentration of Ga$^{3+}$ vacancies, denoted $x$, can be determined using the following equation (Nielsen et al. 2008):

$$4x = 6 \frac{1/2I(Ga-OH_2)}{I(Ga_2-OH)+1/2I(Ga-OH_2)}$$

The intensities of Ga-OH$_2$ and Ga$_2$-OH, listed in Table 2, gives a value of $x = 0.01$, suggesting an almost stoichiometric sample. The occupancy of H$_3$O$^+$ was determined from the intensity of the Ga$_2$-OH and H$_3$O$^+$ peaks (67:31), giving a sample composition of $(H_3O)_{0.93}Ga_{2.99}(SO_4)_2(OH)_6$. Similar results are obtained from analysis of the $^1$H MAS NMR spectrum of the deuterated analogue, $(D_3O)Ga_3(SO_4)_2(OD)_6$, which contain some residual protons due to the use of non-deuterated reagents (not shown). The $^1$H MAS NMR spectrum of ammonioalunite $(NH_4)Al_3(SO_4)_2(OH)_6$ (Figure 2a) show three well-resolved resonances assigned to Al$_2$-OH ($\delta_{iso}(^1H) = 3.4(1)$ ppm), NH$_4^+$ ($\delta_{iso}(^1H) = 6.7(1)$ ppm), and H$_3$O$^+$ ($\delta_{iso}(^1H)$
The sample does not contain the Al-OH$_2$ resonance and the observation of a small, but detectable amount of H$_3$O$^+$ ($\approx 1\%$) implies that the sample the concentration of Al (G site) vacancies is below the detection limit for $^1$H MAS NMR ($<1\%$). This is in excellent agreement with the proposed defect mechanism (Nielsen et al. 2007). Furthermore, the presence of both NH$_4^+$ and H$_3$O$^+$ suggest that sample is not a pure ammonium alunite, but contains small amounts of schlossmacherite, as $^{27}$Al SSNMR confirms (vide infra).

The $^2$H MAS NMR spectrum of (D$_3$O)Ga$_3$(SO$_4$)$_2$(OD)$_6$ (Figure 3) is similar to the spectrum of the isostructural deuterated schlossmacherite, (D$_3$O)Al$_3$(SO$_4$)$_2$(OD) (Nielsen et al. 2007), showing the characteristic line shape, Pake doublet, from rigid OD groups. This verifies that hydronium-gallium-jarosite has the same structure as the alunite supergroup minerals as suggested by Johansson (1963). In total three resonances are apparent in the $^2$H MAS NMR spectrum of (D$_3$O)Ga$_3$(SO$_4$)$_2$(OD)$_6$ in Figure 3. These are assigned to Ga$_2$-OD ($\delta_{iso}(^2\text{H}) = 4.9(1) \text{ ppm}$), D$_3$O ($\delta_{iso}(^2\text{H}) = 10.8(1) \text{ ppm}$) and a minor amount ($\approx 1\%$) of Ga-OD$_2$ ($\delta_{iso}(^2\text{H}) = 6.5(1) \text{ ppm}$). The intensities of the $^2$H resonances, the I(D$_3$O$^+$):I(Ga$_2$-OD) ratio, is $\approx 33:67$, which is in excellent agreement with the 1:2 ratio expected based on the formula (D$_3$O)Ga$_3$(SO$_4$)$_2$(OD)$_6$. This intensity ratio and the absence of the Ga-OD$_2$ resonance confirm that this sample is stoichiometric. From a fit of the integrated intensities of the ssbs a $C_Q$ of 222.8(5) kHz and an $\eta_Q$ of 0.04(2) are obtained for the resonance at $\delta_{iso}(^2\text{H}) = 4.9(1) \text{ ppm}$ (Table 2). The obtained $C_Q$ is in excellent agreement with those previously obtained for deuterated schlossmacherite (235 and 227 kHz) (Nielsen et al., 2007; Ripmeester et al., 1986). The size of $C_Q$ indicates that the OD groups are immobile in the structure (Ripmeester et al., 1986; Soda and Chiba, 1969). $\eta_Q \approx 0$, indicates an almost axial symmetry around the O-D···O(S) hydrogen bond. $C_Q$ for the resonance at $\delta_{iso}(^2\text{H}) = 10.8(1) \text{ ppm}$ is 14.6 kHz similar to the value obtained for deuterated schlossmacherite (17(5) kHz) (Nielsen et al., 2007).
narrower ssb pattern and the smaller $C_Q$ indicate rapid molecular motion of the deuterons in this site (Ripmeester et al., 1986; Soda and Chiba, 1969). The estimated $C_Q$ for Ga$_2$-OD 222.8(5) kHz gives an O(S)···OD distance of 2.810(2) when using correlation established by Poplett and Smith (1978). This result corresponds very well with the single crystal XRD data obtained by Johansson (1963) (2.88 Å) and with the distance determined from the FT-IR data (2.814(3) Å, (Grube 2011)) using the Libowitzky (1999) correlation between $\nu$(OH) and O(S)···OH.

Thus, the different hydrogen species in diamagnetic alunite samples can be identified and quantified by analysis of $^1$H MAS NMR spectra recorded at a high field with fast MAS (35 kHz). Furthermore, it also allows for identification of solid-solutions formed such as the small amount of hydronium identified in the stoichiometric ammonioalunite. Information that is very difficult to obtain and especially quantify by diffraction-based techniques and vibrational spectroscopy.

**Paramagnetic alunite minerals and compounds:**

The results from analysis of the $^2$H MAS NMR spectra of the paramagnetic samples KCr$_3$(SO$_4$)$_2$(OD)$_6$, hydronium-chromium-jarosite (D$_3$O)Cr$_3$(SO$_4$)$_2$(OD)$_6$, and vanadium-jarosite KV$_3$(SO$_4$)$_2$(OD)$_6$ in Table 3.

Vanadium- and chromium jarosite, KV$_3$(SO$_4$)$_2$(OD)$_6$ and KCr$_3$(SO$_4$)$_2$(OD)$_6$ are expected to contain a single $G_2$-OD ($G = V^{3+}$ and Cr$^{3+}$) resonance in a $^2$H MAS NMR spectrum with a significant paramagnetic shift, as observed for jarosite, where $\delta_{\text{iso}}(^2\text{H}) \approx 240$ ppm for the Fe$_2$-OD group, c.f., Table 3 (Nielsen et al. 2008). In agreement with this, the $^2$H MAS NMR of KCr$_3$(SO$_4$)$_2$(OD)$_6$ the $^2$H resonance from the Cr$_2$-OD has $\delta_{\text{iso}} = 855.4(8)$ (Figure 4a) and is characteristic asymmetric ssb patterns typical of paramagnetic compounds (Nielsen et al. 2008). A small resonance with at $\delta_{\text{iso}}(^2\text{H}) = 7.6(9)$ ppm (Table 3) is ascribed to an
unknown hydrogen species such as water or hydronium in the vicinity, but not directly
coordinated to Cr. It will not be discussed further. Furthermore, no Cr-OD$_2$ resonances
caused by Cr vacancies are observed in the spectrum implying a stoichiometric sample.

The position of the isotropic resonance contains two contributions, an isotropic chemical shift
and a hyperfine (Fermi-contact) shift. The isotropic chemical shift component is 3-5 ppm, as
estimated from the diamagnetic samples in Table 2, and therefore negligible as compared to
the hyperfine contribution. The asymmetric manifold contains two contributions, the
quadrupole interaction and paramagnetic dipole interaction, which reflects the dynamics and
concentration of unpaired electron spin density, respectively. From simulation of the
experimental spectra, $C_Q$ of 225(15) kHz, $\eta_Q \approx 0$, and a dipolar coupling of 600(100) ppm
were obtained for the Cr$_2$-OD resonance in KCr$_3$(SO$_4$)$_2$(OD)$_6$. The $C_Q$ corresponds well with
the values observed for, e.g., jarosite and hydroniumjarosite (Nielsen et al 2008).

Similarly, $^2$H MAS NMR spectrum of KV$_3$(SO$_4$)$_2$(OD)$_6$ (Figure 4b) shows two resonances,
$\delta_{iso}(^2\text{H}) = 1185(9)$ and $7.1(9)$ ppm, corresponding to V$_2$-OD and an a small amount of
physisorbed D$_2$O respectively. The spectrum was analyzed by a series of trial-and-error
simulations, as iterative fitting failed to give consistent results, and estimates of the
quadrupole tensor components and the paramagnetic shift anisotropy was obtained, as
summarized in Table 3. The much higher $\delta_{iso}(^2\text{H})$ observed for KV$_3$(SO$_4$)$_2$(OD)$_6$ as
compared to the jarosites (containing Fe) and chromium jarosite is due to the decrease in
number of unpaired $d$ electrons on the $G$ ion (Nielsen et al., 2010), as will be discussed later.

Substitution of potassium (K$^+$) with hydronium (D$_3$O$^+$) results in an additional resonance at
$\delta_{iso}(^2\text{H}) = 36.0(1)$ ppm in the $^2$H MAS NMR spectra of (D$_3$O)Cr$_3$(SO$_4$)$_2$(OD)$_6$, which
dominates the spectrum, in addition to the Cr$_2$-OD resonance, c.f., Figure S2a and Table 3.

This is the hydronium ion, which is rotates rapidly in the cavity, as also observed in the Al,
Ga, and Fe analogues (*vide supra* and Gale et al. 2010; Nielsen et al. 2011; Ripmeester et al. 1986). The Cr$_2$-OD ($\delta_{iso}(^2\text{H}) = 827.0$ ppm) has a $\delta_{iso}$ close to that of the resonance observed for Cr$_2$-OD in KCr$_3$(SO$_4$)$_2$(OD)$_6$ ($\delta_{iso}(^2\text{H}) = 855.4(8)$ ppm). The spectrum is of lower quality, as only 11 mg of sample was obtained due to a low synthesis yield (Table 1). This is only about one third of the amount needed to fill the NMR rotor resulting in a poor signal-to-noise ratio. The relative intensities of the resonances obtained from integration of all spinning sidebands and subsequent normalization gives $\approx36:64$ for D$_3$O$^+:$Cr$_2$-OD. This corresponds to a ratio of approximately 1:1.8 which is reasonably close to the 1:2 ratio expected of I(D$_3$O$^+)$:I(Cr$_2$-OD) based on the formula (D$_3$O)Cr$_3$(SO$_4$)$_2$(OD)$_6$ and considering the experimental uncertainties. Furthermore, no Cr-OD$_2$ defects were observed in the $^2$H MAS NMR spectrum. Thus, within the experimental uncertainties, the absence of a Cr-OD$_2$ resonance and the quality of the spectrum, the sample is stoichiometric.

The $^2$H MAS NMR spectrum of (D$_3$O)V$_3$(SO$_4$)$_2$(OD)$_6$ (Figure S2b) contains three fairly narrow resonances at $\delta_{iso}(^2\text{H}) = 36.9(1)$ and 7.5(3) ppm from the hydronium ion and a small amount (7% of the total intensity) of an unknown water species in the vicinity, but not coordinated to V. The V$_2$-OD group is observed at $\delta_{iso}(^2\text{H}) \approx 1380(20)$ ppm, which is 200 ppm higher than for the K analogue, c.f. Table 1. This is quite a large change, as only small variation between the potassium and hydronium analogues are observed for the Fe and Cr analogues, c.f., Table 3. Detailed analysis of the spinning sideband manifold for the V$_2$-OD is not possible, but the overall width and shape resembles that for KV$_3$(SO$_4$)$_2$(OD)$_6$.

*Interpretation of $^{1,2}$H paramagnetic shifts*

The paramagnetic jarosites with $G = V^{3+}(d^2)$, Cr$^{3+}(d^3)$, and Fe$^{3+}(d^5)$ are isostructural and mainly differ in the $d$-electron configuration, which is $d^2$, $d^3$ and $d^5$ (Figure 5a) respectively, resulting in a ferromagnet, an anti-ferromagnet, and a frustrated anti-ferromagnet,
respectively (Nocera et al. 2004). Thus, comparison of the paramagnetic shifts for $^2$H can provide insight into the relative contribution from the different orbitals to the paramagnetic $^2$H NMR shifts. The largest shifts ($\approx 1150$–$1400$ ppm) are observed for V$^{3+}$ on the $G$ site, which is in a nearly ideal tetragonal symmetry, and the hydrogen in the hydroxyl group is located slightly above the $G$-O-$G$ plane (Nocera et al. 2004). This may be explained by a large delocalization of the unpaired electron spin density on the $^2$H by transfer via the p-orbital on oxygen ($d_{xz,xy}$- P(O)-H(S)) as illustrated in Figure 5c creating a large positive paramagnetic shift (Goodenough 1963; Grey and Dupre 2004). The $d_{xy}$ and especially the $d_{x^2-y^2}$ pathways (Figures 5d and e) are anti-ferromagnetic providing a negative contribution to the overall shift (Nocera et al. 2004). In agreement with jarosite ($G = Fe^{3+}$) having the smallest paramagnetic shift (ca 240 ppm), c.f., Table 3.

The $G$ site cation: Solid state $^{27}$Al and $^{71}$Ga NMR spectroscopy of diamagnetic alunite

Further structural insight can be obtained for the diamagnetic alunite minerals by studies of the $G$ site cation ($G = Al^{3+}$ and Ga$^{3+}$), which are NMR nuclei of high abundance although $^{27}$Al is experimentally less demanding. A stoichiometric sample will contain a single $G$ site cation in a distorted octahedral coordination with a significant second order quadrupole line shape even at high magnetic fields. The presence of defects results in creates an additional site, Al$_D$, which is next to a defect(Nielsen et al. 2007), c.f., Figure 1.

The $^{27}$Al MAS NMR spectra of ammonioalunite show a resonance with well-defined 2$^{nd}$ order quadrupolar line shape (Figure 6a), which is assigned to the Al site in ammonioalunite. Closer inspection shows the right hand singularity of a second site, which has nearly similar $^{27}$Al NMR parameters except for a slightly smaller $C_Q$ c.f., Figure 6b. This is not unexpected,
as the $^1$H MAS NMR of this samples show a small amount of hydronium alunite, c.f., Figure 2a). Analysis of spectrum using QuadFit (Kemp and Smith, 2009), gives the same $\delta_{iso}$ ($\delta_{iso}(^{27}\text{Al}) = 3.1$ ppm) and identical $\eta_Q$ ($\eta_Q = 0.1$) within the error-limits. However, a $C_Q$ of 9.90 and 9.10 MHz are obtained for ammonioalunite and hydronium alunite, respectively. The reported values for ammonioalunite for $C_Q$ and $\eta_Q$ are identical within error-limits to those of the isostructural alunite ($D = K$) and natroalunite ($D = Na$) studied earlier (Grube and Nielsen 2015; Nielsen et al. 2007) reflecting the almost identical geometry for Al in these three minerals. $C_Q$ is higher for Al near $\text{NH}_4^+$ ions as compared to $\text{H}_3\text{O}^+$ ions (Table 4) implying a larger distortion of the Al octahedron in the latter, in agreement with the XRD data obtained by Basciano and Peterson (2007a, 2007b). The relative sizes of the quadrupole interaction, which reflect the elongation of the Al octahedron are: $C_Q(\text{Al}_2\text{-OH})$: $(\text{H}_3\text{O})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6 < (\text{NH}_4)\text{Al}_3(\text{SO}_4)_2(\text{OH})_6 < \text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 \approx \text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$, c.f., Table 4 and (Nielsen et al. 2007). However, this does not correlate with the relative size of the $D$ site ion in dodecahedral coordination is: $\text{Na}^+(1.39$ Å) $< \text{H}_3\text{O}^+(1.52$ Å) $< \text{K}^+(1.64$ Å) $< \text{NH}_4^+(1.72$ Å) for a coordination number of 12 (Shannon 1976). For jarosite ($D = \text{Fe}$), which has been subject to the most detailed studies of the magnetic properties, all of the isostructural compounds exhibit magnetic ordering except for hydronium jarosite (Grohol et al. 2003). The $^{27}\text{Al}$ quadrupole coupling constant clearly reflects subtle changes in the $G$ octahedron caused by the different anions. In some respect, ammonia ($\text{NH}_4^+$) is closely related to hydronium ($\text{H}_3\text{O}^+$) as both are acidic and can form hydrogen bonds albeit with lower acidity (higher pKa).

$^{71}\text{Ga}$, the preferred isotope for Ga NMR, has stronger quadruple interaction, which in combination with a nuclear spin, $I$, of three half ($I(^{27}\text{Al}) = 5/2$) (Massiot et al. 1999) cannot be studied by magic-angle spinning (MAS). The scaling factor between $^{71}\text{Ga}$ and $^{27}\text{Al}$ is given by the relative ratio of their quadrupole moment ($C_Q(^{71}\text{Ga})/C_Q(^{27}\text{Al}) = 3.11(13)$)
(Massiot et al. 1999). A $C_Q(^{71}\text{Ga}) \approx 26 \text{ MHz}$ is predicted using the reported value for schlossemanite (8.5 MHz) c.f., Table 4. In agreement with this, the static $^{71}\text{Ga}$ SSNMR spectrum of $(\text{H}_2\text{O})\text{Ga}_3(\text{SO}_4)_2(\text{OH})_6$ (Figure 6c) shows an almost 250 kHz wide quadrupolar line shape from which $C_Q = 19.7(3)$, $\eta_Q = 0.16(3)$ and $\delta_{iso}(^{71}\text{Ga}) = -12(5) \text{ ppm}$ are determined from analysis of spectra at two different fields (21.1 and 11.7 T) (Table 4, Nielsen et al. 2007)). Only the high frequency singularity is sharp, whereas the low frequency “horn”/singularity is smeared out showing a distribution for the $^{71}\text{Ga}$ quadrupole coupling due to small variation in the local environment. However, the very strong quadrupole interaction makes it very sensitive to even small variations and the effect of a structural defect propagates. Inclusion of the chemical shifts anisotropy in the simulations did not improve the fit of the experimental data. No other $^{71}\text{Ga}$ NMR resonances were detected confirming that the sample contains very few defects, in agreement with $^1\text{H}$ MAS NMR data for this sample (Table 2).

**Conclusions**

Hydrogen species and their mobility were identified and quantified by a combination of $^1\text{H}$ and $^2\text{H}$ MAS NMR spectroscopy for a series of synthetic analogues of jarosite and alunite as well as five other alunite type minerals ($G = \text{V}^{3+}$, $\text{Cr}^{3+}$, and $\text{Ga}^{3+}$). The results confirm the defect mechanism proposed earlier for alunite (Nielsen et al. 2007). For the diamagnetic samples, the hydrogen species was identified and quantified by $^1\text{H}$ MAS NMR using 35 kHz magic angle spinning and an ultra-high magnetic field 900 MHz, which allowed for identification of even small amounts of hydronium (1-3 %). For the paramagnetic samples ($G = \text{V}^{3+}$, $\text{Cr}^{3+}$, and $\text{Fe}^{3+}$) large hyperfine shifts due to the presence of unpaired $d$-electrons on the transition metal ion were observed. This decreased with the number of $d$-electrons of the transition metal. The hydronium and ammonium ions were found to be highly mobile in all samples investigated,
as evident from $^2$H MAS NMR spectra of deuterated samples. Thus, the current work demonstrates the applicability of solid state NMR spectroscopy for identification and quantification of hydrogen species in both dia- and paramagnetic minerals.

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Nielsen UG, Heimmaa I, Samoson A, Majzlan J, Grey CP (2011) Insight into the local magnetic environments and deuteron mobility in jarosite (AFe3(SO4)2(OD,OD2)6, A = K, Na, D3O) and hydronium alunite ((D3O)Al3(SO4)2(OD)6), from variable-temperature 2H MAS NMR spectroscopy Chemistry of Materials 23:3176-3187


Shannon R (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides Acta Crystallographica Section A 32:751-767


Table 1. Sample name, chemical formula, chemical composition of the initial solution, synthesis conditions, yield as well as lattice parameters determined from powder X-ray diffraction.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Chemical formula</th>
<th>Reactants</th>
<th>Temp. &amp; time</th>
<th>Yield</th>
<th>Unit cell (Å)</th>
<th>Synthesis method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydronium gallium alunite</td>
<td>(H$_3$O)Ga$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>12.7 mL H$_2$O, 1.043 g Ga$_3$(SO$_4$)$_2$·5H$_2$O, 0.255 g conc. H$_2$SO$_4$</td>
<td>180 °C, 72 h</td>
<td>0.208 g</td>
<td>a = 7.184(1), c = 17.186(4)</td>
<td>(Kydon et al 1968)</td>
</tr>
<tr>
<td>Deuterated hydronium gallium alunite</td>
<td>(D$_2$O)Ga$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>12.7 mL D$_2$O, 1.043 g Ga$_3$(SO$_4$)$_2$·5H$_2$O, 0.255 g conc. H$_2$SO$_4$</td>
<td>180 °C, 72 h</td>
<td>0.229 g</td>
<td>a = 7.184(1), c = 17.172(4)</td>
<td>(Kydon et al 1968)</td>
</tr>
<tr>
<td>Ammonioalunite</td>
<td>(NH$_4$)Al$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>12.7 mL H$_2$O, 1.339 g Al$_3$(SO$_4$)$_2$·15H$_2$O, 0.216 g (NH$_4$)$_2$SO$_4$ Reheated in H$_2$SO$_4$ + (NH$_4$)$_2$SO$_4$</td>
<td>140 °C, 48 h</td>
<td>0.238 g</td>
<td>a = 7.004(1), c = 17.86(1)</td>
<td>(Basciano and Peterson 2000)</td>
</tr>
<tr>
<td>Deuterated chromium alunite</td>
<td>KCr$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>10 mL D$_2$O, 0.872 g K$_2$SO$_4$, 0.108 g metallic Cr, 0.35 mL conc. H$_2$SO$_4$</td>
<td>210 °C, 120 h</td>
<td>0.293 g</td>
<td>a = 7.229(1), c = 17.232(9)</td>
<td>(Grohol and Nocera 2002)</td>
</tr>
<tr>
<td>Deuterated hydronium chromium alunite</td>
<td>(D$_2$O)Cr$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>2.642 g Cr$_3$(SO$_4$)$_2$·xH$_2$O, 10 mL D$_2$O</td>
<td>205 °C, 168 h</td>
<td>0.011 g</td>
<td>a = 7.246(1), c = 17.02(4)</td>
<td>(Murphy et al 2009)</td>
</tr>
<tr>
<td>Deuterated vanadium alunite</td>
<td>KV$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>10 mL D$_2$O, 0.872 g K$_2$SO$_4$, 0.136 g metallic V, 0.35 mL conc. H$_2$SO$_4$</td>
<td>210 °C, 120 h</td>
<td>0.99 g</td>
<td>a = 7.263(1), c = 17.467(2)</td>
<td>(Grohol and Nocera 2002)</td>
</tr>
<tr>
<td>Deuterated hydronium vanadium alunite</td>
<td>(D$_2$O)V$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>0.631 g VC$_3$, 0.443 g Li$_3$SO$_4$·H$_2$O</td>
<td>145 °C, 24 h</td>
<td>0.062 g</td>
<td>a = 7.327(1), c = 17.00(2)</td>
<td>(Murphy et al 2009)</td>
</tr>
</tbody>
</table>
Table 2. $^1$H and $^2$H MAS NMR data for diamagnetic samples showing chemical shift ($\delta_{\text{iso}}(1^H/2^H)$) and the relative concentration of the species as well as for the deuterated samples also the $^2$H quadrupole coupling parameters ($C_Q$ and $\eta_Q$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Resonance</th>
<th>$\delta_{\text{iso}}(1^H/2^H)$ (ppm)</th>
<th>$C_Q$ (kHz)</th>
<th>$\eta_Q$</th>
<th>Relative conc. (%)$^1$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{H}_3\text{O})\text{Ga}_3(\text{SO}_4)_2(\text{OH})_6$</td>
<td>Ga$_2$-OH</td>
<td>4.2(5)</td>
<td>-</td>
<td>-</td>
<td>85(1)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Ga-OH$_2$</td>
<td>6.3(5)</td>
<td>-</td>
<td>-</td>
<td>&lt; 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Other (“H$_2$O”)</td>
<td>9.0(1)</td>
<td>-</td>
<td>-</td>
<td>$\approx$ 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_3$O$^+$</td>
<td>10.6(1)</td>
<td>-</td>
<td>-</td>
<td>13(1)</td>
<td></td>
</tr>
<tr>
<td>$(\text{D}_3\text{O})\text{Ga}_3(\text{SO}_4)_2(\text{OD})_6$</td>
<td>Ga$_2$-OD</td>
<td>4.9(1)</td>
<td>222.8(5)</td>
<td>0.04(2)</td>
<td>86(3)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>D$_3$O</td>
<td>10.8(1)</td>
<td>14.6(2)</td>
<td>0.1(1)</td>
<td>14(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D$_2$O</td>
<td>6.5(1)</td>
<td>-</td>
<td>-</td>
<td>$&lt; 1(3)$</td>
<td></td>
</tr>
<tr>
<td>$(\text{NH}_4)\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$</td>
<td>Al$_2$-OH</td>
<td>3.4(1)</td>
<td>-</td>
<td>-</td>
<td>85(1)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>NH$_4$</td>
<td>6.7(1)</td>
<td>-</td>
<td>-</td>
<td>14(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_3$O$^+$</td>
<td>10.5(1)</td>
<td>-</td>
<td>-</td>
<td>$\approx$ 1</td>
<td></td>
</tr>
<tr>
<td>$(\text{H}_3\text{O})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$</td>
<td>Al$_2$-OH</td>
<td>4.0(3)</td>
<td>-</td>
<td>-</td>
<td>73(4)</td>
<td>Nielsen et al.</td>
</tr>
<tr>
<td></td>
<td>Al-OH$_2$</td>
<td>6.2(5)</td>
<td>-</td>
<td>-</td>
<td>$\sim 5^2$</td>
<td>2007</td>
</tr>
<tr>
<td></td>
<td>Other (“H$_3$O”)</td>
<td>9.5(5)</td>
<td>-</td>
<td>-</td>
<td>18(4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H$_3$O$^+$</td>
<td>10.6(5)</td>
<td>-</td>
<td>-</td>
<td>15(4)</td>
<td></td>
</tr>
<tr>
<td>$(\text{D}_3\text{O})\text{Al}_3(\text{SO}_4)_2(\text{OD})_6$</td>
<td>Al$_2$-OD</td>
<td>4.0(5)</td>
<td>235(9)</td>
<td>0.02(5)</td>
<td>85(5)</td>
<td>Nielsen et al.</td>
</tr>
<tr>
<td></td>
<td>D$_3$O</td>
<td>10.1(5)</td>
<td>17(5)</td>
<td>$\sim 0.45$</td>
<td>15(5)</td>
<td>2007</td>
</tr>
</tbody>
</table>

$^1$ The integrated intensity have been corrected for spin multiplicity and renormalized.

$^2$ The total intensity of two overlapping resonances.
Table 3. $^2$H MAS NMR data for paramagnetic samples showing chemical shift, relative concentration and $^2$H quadrupole coupling parameters, ($C_Q$, $\eta_Q$) and dipolar coupling.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Group</th>
<th>$\delta_{iso}(^2H)$ (ppm)</th>
<th>$C_Q$ (kHz)</th>
<th>$\eta_Q$</th>
<th>$d$ (ppm)</th>
<th>Relative conc. (%)$^1$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D$_2$O)Fe$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>Fe$_2$-OD</td>
<td>240(60)</td>
<td>233(15)</td>
<td>$\approx$0</td>
<td>1173(500)</td>
<td>77(3)</td>
<td>Nielsen et al. 2008</td>
</tr>
<tr>
<td></td>
<td>Fe-OD$_2$</td>
<td>70(30)</td>
<td>114(15)</td>
<td>$\approx$1</td>
<td>293(500)</td>
<td>10(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D$_2$O</td>
<td>0(10)</td>
<td>98(15)</td>
<td>-</td>
<td>0(500)</td>
<td>13(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>KCr$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>Cr$_2$-OD</td>
<td>855.4(8)</td>
<td>225(15)</td>
<td>$\approx$0</td>
<td>600(100)</td>
<td>98(3)</td>
</tr>
<tr>
<td></td>
<td>D$_2$O</td>
<td>7.6(9)</td>
<td>$\approx$0</td>
<td>-</td>
<td>-</td>
<td>2(3)</td>
<td></td>
</tr>
<tr>
<td>(D$_2$O)Cr$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>Cr$_2$-OD</td>
<td>827.0(50)</td>
<td>185(20)</td>
<td>$\approx$0</td>
<td>1000(200)</td>
<td>80(3)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>D$_2$O</td>
<td>36.0(1)</td>
<td>55(10)</td>
<td>0.4(4)</td>
<td>100(400)</td>
<td>19(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D$_2$O</td>
<td>7.4(1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$&lt;1(3)$</td>
<td></td>
</tr>
<tr>
<td>KV$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>V$_2$-OD</td>
<td>1185.2(9)</td>
<td>220(20)</td>
<td>$\approx$0</td>
<td>730(200)</td>
<td>94(3)</td>
<td>$\chi \approx^\circ 90$</td>
</tr>
<tr>
<td></td>
<td>D$_2$O</td>
<td>7.1(9)</td>
<td>220(20)</td>
<td>$\approx$0</td>
<td>730(200)</td>
<td>6(3)</td>
<td>This work</td>
</tr>
<tr>
<td>(D$_2$O)V$_3$(SO$_4$)$_2$(OD)$_6$</td>
<td>V$_2$-OD$^2$</td>
<td>1380(20)</td>
<td>?</td>
<td>?</td>
<td>=</td>
<td>%</td>
<td>This work</td>
</tr>
<tr>
<td>Unknown</td>
<td>93.5(9)</td>
<td>$\approx$100</td>
<td>$\approx$1</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D$_2$O</td>
<td>36.9(9)</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D$_2$O</td>
<td>7.5(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>

$^1$ The integrated intensity corrected for spin multiplicity and subsequently renormalized.

$^2$ Parameters determined from KV$_3$(SO$_4$)$_2$(OD)$_6$ reproduces this site except for the change in isotropic shift.
Table 4. Solid-state NMR for the diamagnetic alunite type minerals with $G = \text{Ga}$ and Al showing $^{27}\text{Al}$ and $^{71}\text{Ga}$ NMR quadrupole coupling parameters and isotropic chemical shifts.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Site</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>Conc. (%)$^1$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H$_2$O)Ga$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>Ga$^+$</td>
<td>19.7(3)</td>
<td>0.16(3)</td>
<td>-12(5)</td>
<td>$\approx$100</td>
<td>This work</td>
</tr>
<tr>
<td>(NH$_4$)Al$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>Al-NH$_4$</td>
<td>9.85(30)</td>
<td>0.1(1)</td>
<td>3.1(5)</td>
<td>92(2)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Al-H$_3$O &amp;</td>
<td>9.10(30)</td>
<td>0.1(1)</td>
<td>3.1(5)</td>
<td>8(2)</td>
<td></td>
</tr>
<tr>
<td>KAl$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>Al1</td>
<td>10.45(10)</td>
<td>0.05(2)</td>
<td>3.0(5)</td>
<td>$\approx$100$^4$</td>
<td>(Grube and Nielsen 2015)</td>
</tr>
<tr>
<td>(H$_2$O)Al$_3$(SO$_4$)$_2$(OH)$_6$</td>
<td>Al1</td>
<td>8.45(10)</td>
<td>0.10(10)</td>
<td>3.4(4)</td>
<td>$\approx$100</td>
<td>(Nielsen et al. 2007)</td>
</tr>
</tbody>
</table>

1 The integrated intensity corrected for spin multiplicity and renormalized.
2 A small chemical shift anisotropy was determined ($\delta_\sigma = -65(5)$ ppm, $\eta_\sigma \approx 0$). The quadrupole and chemical shift tensors have the same orientation.
3 The sample contains two different Al sites, which are assigned to Al in ammonium alunite (NH$_4$-Al) and a small amount of hydronium alunite H$_3$O-Al based on earlier reported values (Nielsen et al. 2007).
4 The alunite was stoichiometric, but small amounts of unknown impurities are seen.
Figure 1. The crystal structure of the mineral jarosite. a) Polyhedral representation of the structure of alunite viewed along the b axis. The octahedra and tetrahedra represent AlO_6 and SO_4, respectively whereas the potassium ions are grey. b) The local structure in the aluminium-layer near an aluminium vacancy. Al(1) refers to a stoichiometric site, and Al_o referrers to the next nearest neighbour to an aluminium vacancy site.
Figure 2. a) $^1H$ SSNMR spectra of the diamagnetic ammonioalunite, $(NH_4)Al_3(SO_4)2(OH)_6$ and b) $^1H$ SSNMR spectra of the diamagnetic hydronium gallium alunite, $(D_2O)Ga_3(SO_4)2(OH)_6$ with the different hydrogen species assigned. Spectra recorded at 900 MHz. The asterisk indicate negligible amount of an unknown impurity.
Figure 3. $^2$H MAS NMR spectrum of a deuterated hydronium gallium alunite, (D$_3$O)Ga$_5$(SO$_4$)$_2$(OH)$_6$, measured at 11.7 T. The inset shows the two local proton environments and a small amount of physisorbed water.
Figure 4. $^2$H SSNMR of a) KCr$_3$(SO$_4$)$_2$(OD)$_6$ and b) KV$_3$(SO$_4$)$_2$(OD)$_6$ recorded using 13 and 14 kHz spinning speed, respectively. The isotropic resonances are indicated.
Figure 5. a) The d-orbital energy level diagrams for the paramagnetic jarosite samples as well as illustration of the relative orientation of the different d-orbitals, which may contribute to the paramagnetic shifts. The \( d_{z^2} \) orbital is nearly perpendicular to the \( G^{3+}-O-H \) plane as illustrated in a, and not involved (Nocera et al. 2004).
Figure 6. a) Experimental and b) simulated $^{27}$Al MAS NMR spectrum of (NH$_4$)Al$_3$(SO$_4$)$_2$(OH)$_6$. c) Experimental and d) simulated $^{71}$Ga MAS NMR spectrum of (H$_3$O)Ga$_3$(SO$_4$)$_2$(OH)$_6$. The parameters used for the simulations are given in Table 4.
Identification of hydrogen species in alunite-type minerals by multi-nuclear solid-state NMR spectroscopy

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**Figure S1**: Powder X-ray diffractograms of the samples investigated by solid state NMR spectroscopy.
Figure S2. $^2$H MAS NMR spectra of the paramagnetic compounds deuterated a) hydronium chromium alunite (D$_3$O)Cr$_3$(SO$_4$)$_2$(OD)$_6$ and b) hydronium vanadium alunite (D$_3$O)V$_3$(SO$_4$)$_2$(OD)$_6$. The spectra were acquired at 11.7 T using 17 and 18 kHz spinning speeds, respectively. The data obtained from analyses of these spectra are reported in Table 4.
Figure S3: $^{27}$Al 3QMAS NMR spectrum of (NH$_4$)$_3$Al$_3$(SO$_4$)$_2$(OH)$_6$. 