LETTER

Observation of five-coordinated Al in pyrophyllite dehydroxylate by solid-state $^{27}$Al NMR spectroscopy at 14 T

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ABSTRACT
The observation and quantification of four-, five-, and six-coordinated Al sites in Al-containing materials such as silica-aluminas, transition aluminas, and clay-derived solids are major problems in solid-state $^{27}$Al NMR spectroscopy. We report herein solid-state $^{27}$Al NMR spectra of the mineral derivative pyrophyllite dehydroxylate; these spectra were obtained at 14 T (the highest available magnetic field), 11.7 T, and 8.4 T under high-speed (> 12 kHz) magic-angle sample-spinning (mass) conditions. The results represent the first observation of the $^{3}$Al site in this mineral derivative. The $^{27}$Al MASS NMR spectrum at 14 T demonstrates the advantage of high-field NMR measurements for observing the signal due to this highly distorted $^{3}$Al site. The NMR spectra and computer simulations were used to determine the isotropic chemical shift (29 ppm), quadrupolar coupling constant (10.5 MHz), and asymmetry parameter ($\eta = 0.6$) for the Al atom in the trigonal-bipyramidal Al-O local environment of this mineral derivative. These high-resolution $^{27}$Al NMR results provide impetus for future solid-state NMR studies of important Al-containing catalysts, ceramic precursors, and other solid oxide materials containing quadrupolar nuclides amenable to solid-state NMR.

INTRODUCTION
$^{27}$Al is the most thoroughly studied quadrupolar nuclide in solid-state NMR spectroscopy. Its applicability to crystalline and amorphous inorganic materials such as zeolites (Klinowski, 1984; Thomas and Klinowski, 1985), oxide catalysts (John et al., 1983), glasses (Kirkpatrick et al., 1986), ceramics (Turner et al., 1987), clays (Kinsey et al., 1985), and clay-derived materials (Fitzgerald et al., 1989; Lambert et al., 1989; MacKenzie et al., 1985a, 1985b; Meinhold et al., 1985; Watanabe et al., 1987) has been extensively explored. A major feature of solid-state $^{27}$Al NMR has been the notable variation of the chemical shift of the central transition ($\frac{3}{2}, -\frac{3}{2}$) resonance with local Al coordination, particularly for 4-coordinated and 6-coordinated Al-O sites (Muller et al., 1986). Since the early work of Mueller et al. (1981), solid-state $^{27}$Al NMR has been widely used qualitatively, and in some cases quantitatively (Fitzgerald et al., 1989), to determine the relative content of octahedral ($^{6}$Al) and tetrahedral ($^{4}$Al) aluminum. $^{4}$Al yields isotropic chemical shifts between 10 and 20 ppm, and those of $^{6}$Al are between 50 and 80 ppm (Muller et al., 1986). Although detection of $^{4}$Al and $^{6}$Al is usually easy at high magnetic fields and magic-angle sample-spinning (mass), quantitation of relative site occupancy is often complicated by second-order quadrupolar line-broadening and the potential loss of signal because of spinning sidebands (Fitzgerald et al., 1989; John et al., 1983; Muller et al., 1986; Thompson et al., 1987; Turner et al., 1987). The spinning sidebands introduce signal intensity between the $^{4}$Al and $^{6}$Al resonances, but this problem has been largely overcome by rapid sample spinning at greater than 12 kHz (Dec et al., 1986; Fitzgerald et al., 1989).

In many cases, the effects of the second-order quadrupolar interaction are more serious. Quadrupolar line-broadening is characterized by the quadrupole coupling constant (qqc), $e^2Q/\hbar$, a measure of the interaction of the nuclear quadrupolar moment ($eQ$) with the electric-field gradient at the nucleus ($eq$). If qqc is large, the $^{27}$Al NMR peak for a given structural site can be broadened, displaced to values more shielded than the true (isotropic)
chemical shift, and split and distorted into complicated line-shapes (Muller et al., 1986; Thompson et al., 1987). For a given qcc, the second-order broadening effects (observed line-widths and line-shapes) decrease as the magnetic-field strength increases, but are still influenced by the asymmetry of the electric-field gradient, described by the asymmetry parameter, $\eta$, which is a measure of the deviation of the electric field of the nucleus from cylindrical symmetry.

For most $^{[4]}$Al and $^{[6]}$Al sites even with large qcc, $^{27}$Al NMR measurements at high magnetic fields (e.g., 11.7 and 14.0 T) minimize second-order line-broadening and permit observation of the true line-shape and position of the resonances (Fitzgerald et al., 1989; Muller et al., 1986; Thompson et al., 1987). Some five-coordinated ($^{[5]}$Al) sites have also been observed (Alemany and Kirker, 1986; Cruickshank et al., 1986).

Quantitative determination of Al-O sites of different coordination and apparently low symmetry in transition aluminas (John et al., 1983), silica-aluminas (Gilson et al., 1987), and Si-Al clay-derived materials (Dec and Maciel, unpublished results, 1989; Fitzgerald et al., 1989; Lambert et al., 1989; MacKenzie et al., 1985a, 1985b; Meinhold et al., 1985; Watanabe et al., 1987) by $^{27}$Al NMR has been difficult. Transition aluminas (John et al., 1983) yield two resonances assigned to $^{[4]}$Al and $^{[6]}$Al, but from a site-symmetry viewpoint, these signals are poorly quantified and understood. Some materials also yield a weak $^{27}$Al NMR signal in the 30 to 45 ppm range that is due to either highly distorted $^{[4]}$Al sites or $^{[5]}$Al sites (Dec and Maciel, unpublished results, 1989). Recent studies of aluminas such as barium-aluminum glycolate (Cruickshank and Dent Glasser, 1985a, 1985b; Cruickshank et al., 1986), dehydrated kaolinite intermediates (Fitzgerald et al., 1989; Gilson et al., 1987; Lambert et al., 1989; MacKenzie et al., 1985b; Meinhold et al., 1985; Watanabe et al., 1987) have also reported the presence of signals for a range of $^{[4]}$Al, $^{[5]}$Al, and $^{[6]}$Al. $^{27}$Al NMR signals in the range of 31 to 37 ppm have been commonly assigned to $^{[5]}$Al on the basis of $^{27}$Al NMR data observed for known $^{[5]}$Al sites contained in andalusite at 35 to 36 ppm (Alemany and Kirker, 1986; Lippmaa et al., 1986) and barium-aluminum glycolate at 36 ppm (Cruickshank et al., 1986). Quantitation of the relative content of the three $^{27}$Al NMR resonances in treated clays, Al$_2$O$_3$-SiO$_2$ gels, and zeolites has been particularly difficult even at 9.4 T and 6-kHz mass speeds because of incomplete averaging of the second-order quadrupolar broadening.

The experimental difficulties in completely or even partially observing 5-coordinated ($^{[5]}$Al) resonances in Al-containing solids is most exemplified by recent $^{27}$Al NMR studies of heated and dehydrated kaolin and pyrophyllite (Fitzgerald et al., 1989; Frost and Barron, 1984; Lambert et al., 1989; MacKenzie et al., 1985a, 1985b; Meinhold et al., 1985; Watanabe et al., 1987). Pyrophyllite is a dioctahedral 2:1 phyllosilicate [Al$_2$Si$_2$O$_5$(OH)$_4$] (Bailey, 1966; Rayner and Brown, 1966; Wardle, 1972; Wardle and Brindley, 1972). On heating, it loses its hydroxyl water from about 550 to 900 °C, forming pyrophyllite dehydroxylate that shows a distinct X-ray pattern characteristic of the presence of $^{[5]}$Al with approximately trigonal-bipyramidal symmetry (Rayner and Brown, 1966; Wardle, 1972). Recent solid-state $^{29}$Si and $^{27}$Al NMR studies (Frost and Barron, 1984; MacKenzie et al., 1985a) of the thermal dehydroxylation of pyrophyllite have shown limited changes in the $^{29}$Si NMR chemical shifts but drastic changes in the $^{27}$Al NMR spectra including a 90% loss of the $^{27}$Al NMR signal intensity. The $^{27}$Al signal of pyrophyllite dehydroxylate has to date been unobservable owing to substantial second-order quadrupolar line-broadening.

We report here solid-state $^{27}$Al NMR spectra of pyrophyllite and pyrophyllite dehydroxylate at 14 T (the highest available magnetic field) under magic-angle sample-spinning (mass) conditions that clearly show the $^{[5]}$Al resonance in the dehydroxylate. The observation of this $^{[5]}$Al resonance indicates the likely success for future studies of other hydroxylated minerals such as kaolin, muscovite, and montmorillonite, which have been proposed to contain $^{[5]}$Al in their dehydroxylated derivatives.

**EXPERIMENTAL DETAILS**

The pyrophyllite was obtained from the D. J. Mineral Kit Company, P.O. Box 761, Butte, Montana, U.S.A. (lot M-260, a natural deposit in Nevada). The mineral specimen was gently crushed, sieved through a 60–80 mesh screen, and hand-picked microscopically. Pyrophyllite dehydroxylate was obtained by heating white, fibrous, powder pyrophyllite in a muffle furnace at 550 °C for 7 d. The fluffy fibrous powder showed X-ray diffraction patterns identical to those reported by Wardle (1972) and Wardle and Brindley (1972), with minor diffraction peaks due to unreacted pyrophyllite.

$^{27}$Al mass NMR spectra were recorded on a modified Nicolet NT-360 NMR spectrometer and on Bruker AM-500 and AM-600 NMR spectrometers, using home-built probes. Mass speeds of 11.0–12.0 kHz were obtained using 6.0-mm (outer diameter) Torlon spinners on the NT-360 spectrometer. Mass speeds of 16–17 kHz were obtained using 4.5-mm (outer diameter) Torlon spinners on the AM-500 and AM-600 spectrometers. The chemical-shift reference (by sample substitution) was an aqueous solution of 1 M AlCl$_3$·6H$_2$O, which was assigned a chemical shift value of 0.0 ppm. Higher chemical shifts correspond to larger resonance frequencies and lower shielding constants. $^{27}$Al 90° pulses for 1 M AlCl$_3$ (aqueous) were 8.5, 6.5, and 6.0 μs at 93.8, 130.3, and 156.4 MHz, respectively. $^{27}$Al pulse lengths of 1.3, 0.5, and 0.5 μs were used at 93.8, 130.3, and 156.4 MHz, respectively, with recorded spectra being obtained using 50-ms relaxation delays. X-ray powder-diffraction analyses of pyrophyllite and its heated derivatives were obtained using a Philips-Norelco diffractometer equipped with a graphite monochrometer, a CuKα X-ray source at 1.5418 Å, and a Dymastar 64A recorder over the 2θ range 1° to 45°.

**RESULTS AND DISCUSSION**

The $^{27}$Al mass nmr spectrum of pyrophyllite at 14 T shows a single sharp resonance at 4.3 ppm (not shown)
were calculated at qcc values of 9.5 to 11.0 MHz and a computer-simulated spectrum (lower) obtained using the Nun program. The best-fit simulated spectrum (Fig. 1) had isotropic chemical shifts of 29 ppm at qcc = 10.5 MHz and qcc values of 0.0 to 1.0 with 200-Hz exponential line-broadening. The simulated spectra were calculated at qcc values of 9.5 to 11.0 MHz and qcc values of 0.0 to 1.0 with 200-Hz exponential line-broadening. The best-fit simulated spectrum (Fig. 1, lower) had isotropic chemical shifts of 29 ppm at qcc = 10.5 MHz and qcc = 0.6. These parameters indicate that the observed Al in the sample is in a 5-coordinated site and has a large electric-field gradient and that the [5]Al site is highly distorted. These [5]Al resonance parameters are comparable to those of the [5]Al sites in andalusite (35-36 ppm, qcc = 5.9 MHz, qcc = 0.69-0.70) and barium-aluminum glycolate (35.3-37 ppm, qcc and qcc undetermined) (Alemany and Kirker, 1986; Cruickshank et al., 1986). Previous solid-state [5]Al NMR studies of pyrophyllite dehydroxylate and other dehydrated pyrophyllite intermediates at lower fields and lower sample-spinning speeds have been unsuccessful primarily owing to the qcc value of the Al site in this material.

Comparisons of the [5]Al NMR spectra of our pyrophyllite dehydroxylate at H0 = 14 T (156.4 MHz), 11.4 T (130.3 MHz), and 8.4 T (93.8 MHz) as shown in Figure 2 illustrate the advantages of higher fields and rapid mass conditions. The 14- and 11.4-T spectra both show the [5]Al signal, although even at 11.4 T, substantial second-order quadrupole effects preclude detailed analysis and determination of the qcc and qcc parameters of this [5]Al site resonance. The spectrum taken at 8.4 T shows the presence of only [5]Al, apparently because of a small amount of undehydroxylated pyrophyllite as confirmed by the xrd analysis. The complete absence of the resonance due to the [5]Al at this field is consistent with previous studies at lower magnetic fields (Frost and Barron, 1984; MacKenzie et al., 1985a).

This study of the [5]Al NMR spectrum of thermally produced pyrophyllite dehydroxylate provides a number of important observations: (1) the isotropic chemical shift and second-order powder pattern of the central (1/2, -1/2) transition of the observed resonance is consistent with its assignment to a [5]Al site similar to that of andalusite and barium-aluminum glycolate (Alemany and Kirker, 1986; Cruickshank et al., 1986; Lippmaa et al., 1986); (2) highly distorted [5]Al sites with large qcc and lower qcc parameters require the highest available magnetic fields to narrow the unsymmetrical powder patterns caused by the large qcc line-broadening effects; (3) rapid (>12 kHz) mass conditions are needed to decrease the intensity of spinning sidebands from the region of spectral interest; and (4) similar solid-state [5]Al NMR studies at H0 = 14 T (156.4 MHz) of other clay-derived materials are likely to be an important approach to obtain quantitative [5]Al, [5]Al, and [5]Al site contents in various Al-containing materials. Experimental solid-state [5]Al NMR studies of various clay-derived and Al-containing solids of importance as inorganic catalysts and advanced materials are in progress.

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