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High-Resolution NMR of Inorganic Solids. Influence of Magnetic Centers on Magic-Angle Sample-Spinning Lineshapes in Some Natural Aluminosilicates*

ERIC OLDFIELD,†‡ ROBERT A. KINSEY,‡ KAREN ANN SMITH,‡ JULIE ANN NICHOLS,‡ AND R. JAMES KIRKPATRICK§

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Recently there has been considerable interest in determining the structures of inorganic solids by means of NMR spectroscopy, employing either magic-angle sample-spinning (MASS) techniques (1-11), or variable-angle sample-spinning (VASS) techniques (12-14), the latter being applied to the study of quadrupolar nuclei with nonintegral spins, *I*. We have now begun to apply both MASS and VASS techniques to investigate the structures of naturally occurring silicates and aluminosilicates, and their synthetic glasses. In this communication we report the results of experiments on naturally occurring minerals which contain magnetic centers. The results are of considerable interest since they bear on the question of the use of spinning-sideband patterns to obtain information on chemical structure (15, 16). In particular, our results indicate that great care must be taken to minimize the levels of magnetic impurities in naturally occurring minerals if chemical shift anisotropy (CSA) information is sought (15).

We show in Fig. 1A–C high-field ²⁷Al, ²⁹Si, and ²³Na MASS NMR spectra of the alkali feldspar sanidine [(K, Na)AlSi₃O₈]. Also shown is the ²⁷Al NMR spectrum of whole rock syenite from Larvic, Norway, Fig. 1D. This rock contains alkali feldspar, Fe–Mg silicates, and magnetite (Fe₃O₄).

The results of Fig. 1A–C yield isotropic chemical shifts for ²⁷Al, ²⁹Si, and ²³Na in sanidine of 57.3 \pm 1 from external Al(H₂O)³⁺₆, -97 and -100 \pm 2 ppm from external Me₄Si, and -23.4 \pm 1 ppm from external 1 *M* NaCl, respectively. The ²⁷Al value is consistent with the chemical shift of tetrahedral aluminum in other tectosilicates (*17*, *18*), and that for ²⁹Si is in good agreement with the range -95.7 to -100.9 found by

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FIG. 1. 11.7 Tesla ²⁷Al, ²³Na, and 8.45 Tesla ²⁹Si MASS NMR spectra at 23°C of some natural minerals containing magnetic centers, showing spinning-sideband structure. (A) Sanidine (monoclinic, disordered K, Na-feldspar from Lacher See, Germany), ²⁷Al NMR at 130.3 MHz, 3.5 kHz MASS, 150 scans at 15 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication. (B) Sanidine, ²⁹Si NMR at 71.5 MHz, 2.4 kHz MASS, 36 scans at 500 sec recycle time, 50 kHz spectral width, 20 μ sec 90° pulse excitation, 2048 data points, 100 Hz line broadening due to exponential multiplication. (C) Sanidine, ²³Na NMR at 132.3 MHz, 3.3 kHz MASS, 140 scans at 25 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication. (D) Whole rock syenite (from Larvic, Norway), ²⁷Al NMR at 130.3 MHz, 3.6 kHz MASS, 400 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication. (D) Whole rock syenite (from Larvic, Norway), ²⁷Al NMR at 130.3 MHz, 3.6 kHz MASS, 400 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz linebroadening due to exponential multiplication. (D) Whole rock syenite (from Larvic, Norway), ²⁷Al NMR at 130.3 MHz, 3.6 kHz MASS, 400 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz linebroadening due to exponential multiplication. (D) Whole rock syenite (from Larvic, Norway), ²¹Al NMR at 130.3 MHz, 3.6 kHz MASS, 400 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz linebroadening due to exponential multiplication. Chemical shifts are in ppm with respect to external samples of 1 *M* [²⁷Al(H₂O)₆]Cl₃, Me²₄Si, and 1 *M* ²³NaCl.

Lippmaa *et al.* (1). In the case of the quadrupolar nuclei ²⁷Al $(I = \frac{5}{2})$ and ²³Na $(I = \frac{3}{2})$, only the central $(\frac{1}{2} \leftrightarrow -\frac{1}{2})$ transition is observed and the chemical shifts reported are not corrected for the second-order quadrupole shift of the resonance (9, 10). More importantly, all interactions have an *apparent* CSA of ~60–100 ppm, as deduced from the linear field dependence of the total spectral breadth (data not shown). Accurate CSA values for the quadrupolar systems have not been reported previously, since second-order broadenings will always mask all but the largest shift tensors in such systems at low magnetic field strengths. For ²⁹Si, the apparent CSA seemed at first to us to be consistent with an accurate shift tensor for synthetic diopside (CaMgSi₂O₆) crystals (15) of $\sigma_{11} = -31 \pm 2$ ppm, $\sigma_{22} = -73 \pm 2$ ppm, and $\sigma_{33} = -148 \pm 2$ ppm ($\sigma_{iso} = -84 \pm 2$ ppm, $|\Delta\sigma| = 96 \pm 2$ ppm), or for values of $|\Delta\sigma|$ of about 65, 80 ppm for γ -Ca₂SiO₄ and wollastonite (CaSiO₃) obtained by others using wide-line NMR (19), or for values of ~65, 78 ppm reported by Lippmaa *et al.* (1) for two cyclosilicates.

Results with Larvic syenite, Fig. 1D, cast some doubt about this explanation since the overall linebreadths for the 27 Al and 23 Na spectra (not shown) were ~400 ppm, and more importantly, about 10 wt% of our sample was found to be ferromagnetic, and readily attached itself to a small bar magnet!

These observations thus led us to question the idea of chemical shift anisotropy as being the primary cause of linebroadening in Fig. 1. We thus measured the 9 GHz EPR spectra of several naturally occurring sanidine samples, as well as that of the



FIG. 2. EPR spectra (9 GHz) of natural minerals containing high and low concentrations of magnetic centers. (A) Sanidine, high Fe concentration showing ferromagnetic or superparamagnetic resonance. (B) Whole rock Larvic syenite, as (C). Mexico sanidine, low Fe concentration, showing small paramagnetic Fe³⁺ resonance. (D) Alkali feldspar from Larvic syenite after magnetic separation, showing decreased resonance intensity. All spectra obtained at ~23°C. Spectra all obtained under identical instrumental conditions except that the vertical gain in (B) is only 1/200 that of the other spectra.

Larvic syenite of Fig. 1D, and the alkali feldspar from the same sample after purification in a magnetic separator, Fig. 2A–D.

The EPR spectra of the sanidine and syenite samples of Fig. 1 show intense fer-



FIG. 3. MASS NMR spectra (11.7 Tesla ²⁷Al and ²³Na, and 8.45 Tesla ²⁹Si) at 23°C of some naturally occurring minerals containing low concentrations of magnetic centers, showing decreased spinning-sideband intensities relative to spectra of Fig. 1. (A) Mexico sanidine, ²⁷Al NMR at 130.3 MHz, 3.4 kHz MASS, 150 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication. (B) As (A) but ²⁹Si NMR at 71.5 MHz, 2.6 kHz MASS, 19 scans at 600 sec recycle time, 20 kHz spectral width, 22 μ sec 90° pulse excitation, 2048 data points zero filled to 8192, 100 Hz line broadening due to exponential multiplication (C) As (A) but ²³Na NMR at 132.3 MHz, 3.4 kHz MASS, 150 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, (D) Alkali feldspar from whole rock syenite after magnetic separation, ²⁷Al NMR at 130.3 MHz, 3.1 kHz MASS, 400 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication. (D) Alkali feldspar from whole rock syenite after magnetic separation, ²⁷Al NMR at 130.3 MHz, 3.1 kHz MASS, 400 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication. (D) Alkali feldspar from whole rock syenite after magnetic separation, ²⁷Al NMR at 130.3 MHz, 3.1 kHz MASS, 400 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication. (D) Alkali feldspar from whole rock syenite after magnetic separation, ²⁷Al NMR at 130.3 MHz, 3.1 kHz MASS, 400 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication. Sidebands in each instance may still be due to residual paramagnetic (or ferromagnetic) centers.



FIG. 4. 11.7 Tesla ²⁷Al MASS NMR spectra (corresponding to a resonance frequency of 130.3 MHz) at 23°C of magnetically doped aluminosilicate samples. (A) Mexico sanidine + 5 wt% hematite (Fe₂O₃), 3.5 kHz MASS, 163 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication. (B) Mexico sanidine + 1 wt% magnetite (Fe₃O₄), 3.3 kHz MASS, 100 scans at 5 sec recycle time, 100 kHz spectral width, 4 μ sec 90° pulse excitation, 4096 data points, 50 Hz line broadening due to exponential multiplication.

romagnetic (or superparamagnetic) absorptions (20) (Fig. 2A, B), while other sanidine samples and the separated Larvic feldspar show much weaker ferromagnetic or paramagnetic resonances, characteristic of Fe^{3+} (21, 22) (Fig. 2C, D). When these latter samples were investigated by high-field ²⁷Al, ²⁹Si, and ²³Na MASS NMR, most of the sideband structure observed in Fig. 1 disappeared while the chemical shifts remained the same, as shown in Fig. 3.

These results, taken together, strongly indicate that the spinning sidebands observed in many natural aluminosilicates may be due not to chemical shift anisotropy, but rather to the presence of large magnetic susceptibility broadenings (23), as is observed, for example, in the ¹H MASS NMR spectra of NbH_x powders (24). Line narrowing due to susceptibility matching (25) seems unlikely to be completely successful in the natural minerals due to the heterogeneous nature of the samples (as observed by optical microscopy).

If the above conclusions are correct, it should be possible to reproduce the types of spinning-sideband results shown in Fig. 1 simply by physical admixture of a diamagnetic sample together with a suitable highly magnetic material. The results of Fig. 4 show that this is indeed the case for sanidine. Addition of ~ 5 wt% of the antiferromagnetic oxide Fe₂O₃ (hematite) to Mexico sanidine produces a relatively small increase in the sideband intensity in ²⁷Al MASS NMR spectra (Figs. 3A, 4A), but addition of only 1 wt% of the ferromagnetic oxide Fe₃O₄ (magnetite) causes extensive sideband formation (Fig. 4B), similar to that observed in our first sanidine sample (Fig. 1A), which has a ferromagnetic (or superparamagnetic) EPR signal. These results, in conjunction with the lack of any frequency shift of the centerband upon admixture, strongly suggest the presence of a magnetic susceptibility broadening in these natural minerals.

The results presented above thus indicate that considerable care should be exercised when sideband information from MASS NMR studies of natural minerals is sought.

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As shown elsewhere, chemical shift tensors (e.g., for ²⁹Si in synthetic diopside, $CaMgSi_2O_6$) may be determined with great accuracy from variable-speed MASS experiments (15, 16), but if natural minerals are investigated, it behooves one to carry out EPR and magnetic susceptibility controls to evaluate possible contributions from susceptibility broadening due to magnetic inclusions. In some instances, CSA and "macroscopic" susceptibility broadening may both be present, in which case it may be necessary to employ either magnetic separation methods, synthesis from high-purity reagents.

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