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MAS NMR study of pentacoordinated magnesium in grandidierite

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ABSTRACT

The 11.7 T ^{25}Mg, ^{27}Al, ^{29}Si, and ^{11}B MAS NMR spectra are reported for well-characterized grandidierite, $(Mg,Fe)Al_3SiBO_9$, which contains both Al and Mg in fivefold coordination with oxygen. The ^{25}Mg spectrum is the first to be reported for ^{5}Mg, and exhibits a quadrupolar lineshape from which the nuclear quadrupolar coupling constant (3.8 ± 0.1 MHz), the asymmetry parameter (0.6 ± 0.05), and the isotropic chemical shift (55 ± 2 ppm) were derived by spectral simulation. These spectroscopic parameters are discussed in terms of the crystallographic geometry of the fivefold-coordinated site.

INTRODUCTION

Grandidierite, $(Mg,Fe)Al_3SiBO_9$, is an unusual magnesium aluminum borosilicate that holds considerable interest for crystallographers and spectroscopists because it contains both Mg and Al in fivefold coordination. Its structure consists of edge-sharing AlO_6 chains running parallel to the *c* axis, joined along the *a* axis by BO_3 and AlO_5 units and along the *b* axis by MgO_5 and SiO_4 units (Stephenson and Moore 1968).

MAS NMR has been used by Smith and Steuernagel (1992) to investigate the fivefold-coordinated Al site in grandidierite. The ^{29}Si and ^{11}B spectra have also been reported by these authors, but the ^{25}Mg spectrum arising from the highly unusual fivefold-coordinated Mg site has not been reported.

In a survey study of the ^{25}Mg spectra of several minerals and related inorganic materials containing mostly octahedral Mg in sites of varying distortion, MacKenzie and Meinhold (1994a) recorded isotropic chemical shifts ranging from −4–80 ppm; the shifts of the spectra that could be most reliably simulated ranged from about 5–14 ppm, with the sharp resonance from the highly symmetrical octahedral site in periclase appearing at 26.5 ppm. Fewer examples of the ^{25}Mg spectra arising from tetrahedral Mg sites are known; a single resonance reported by Dupree and Smith (1988) at 52 ppm in the ^{25}Mg spectrum of $MgAl_2O_4$ has been attributed to fourfold-coordinated Mg, and on this basis, resonances at 45–79 ppm in the ^{25}Mg spectra of $MgSiN_2$ and $MgAlSiN_3$ have likewise been attributed to fourfold-coordinated Mg (MacKenzie and Meinhold 1994b). Fiske and Stebbins (1994) reported isotropic ^{25}Mg chemical shifts of 8 and 49 ppm, corresponding to sixfold and fourfold coordination in diopside ($CaMgSi_2O_6$), and akermanite ($Ca_2MgSi_2O_7$), respectively, from which they deduced that ^{25}Mg shifts of 29 to 34 ppm observed in molten sodium magnesium silicate at 1110–1370 °C might represent an average coordination of about five.

The present work reports the first solid-state ^{25}Mg MAS NMR natural abundance spectrum of a crystallographically well defined fivefold-coordinated Mg site in the mineral grandidierite.

EXPERIMENTAL METHODS

The grandidierite, from the mineral collection of Kiel University, originated from southern Madagascar; this is the type locality and was also the origin of the samples used in previous studies (McKie 1965; Stephenson and Moore 1968; Smith and Steuernagel 1992). The X-ray powder diffraction pattern of the very pale bluish sample contains all the lines recorded by McKie (1965), which also agree with a more complete powder pattern calculated from the crystal structure of Stephenson and Moore (1968) using the computer program POWDER CELL version 1.8 (Kraus and Nolze 1996). No additional phases were detectable by X-ray powder diffraction.

The room-temperature MAS NMR spectra were obtained at 11.7 T using a Varian Unity 500 spectrometer and a high-speed 5 mm Doty probe operating at a computer-controlled rotor speed of 10 kHz. The ^{25}Mg spectra were acquired using both Hahn spin echo and Bloch decay pulse sequences. The Hahn spin echo sequence utilized 16-step phase cycling (Kunwar et al. 1986) with a refocusing interval of 100 μs to coincide with the 10 kHz sample-spinning speed. The Bloch decay sequence involved 3 μs pulse, recycle delay of 0.1 s, and a 90 μs ringdown delay before acquisition; spectra were processed by shifting the free-induction decay (FID) two points to the left. Shifts were referenced to 1 M aqueous $MgSO_4$, shown in separate experiments to be comparable within 0.2 ppm to the saturated $MgSO_4$ solution (MacKenzie and Meinhold 1994a) and to other aqueous references [1 M $Mg(NO_3)_2$ and 1 M $MgCl_2$].

For comparison with the previous NMR study of Smith and Steuernagel (1992), ^{27}Al, ^{29}Si, and ^{11}B MAS NMR

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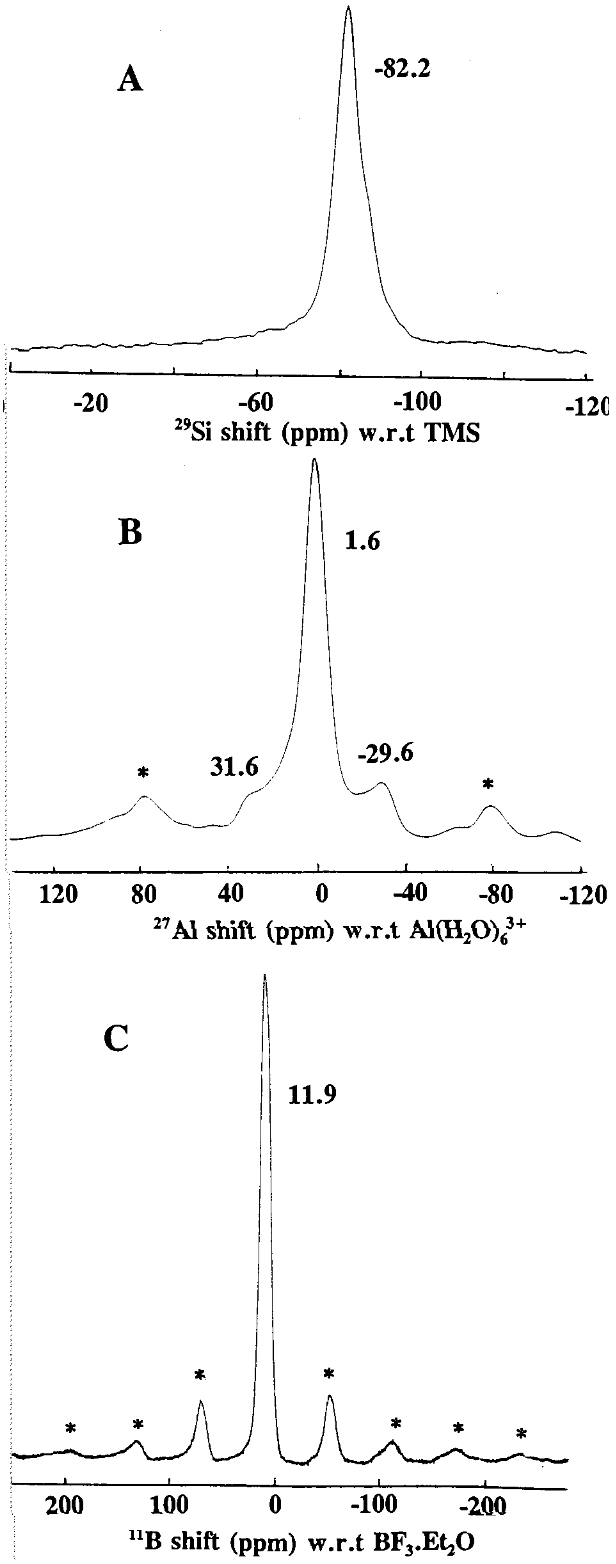

Figure 1. The 11.7 T MAS NMR spectra of grandidierite: (**A**) ^{29}Si, (**B**) ^{27}Al, (**C**) ^{11}B. Asterisks denote spinning side bands.

spectra were also acquired as follows. For ^{27}Al spectra 1 μs $\pi/10$ pulse for solution with recycle delay of 5 s was used; shifts were referenced to 1 M aqueous Al(NO$_3$)$_3$ solution. For ^{29}Si a 6 μs $\pi/2$ pulse was used with a recycle delay of 30 s; shifts were referenced to tetramethylsilane (TMS). For ^{11}B a 1 μs $\pi/8$ pulse for solution was used with a recycle delay of 1 s; shifts were referenced to BF$_3$·Et$_2$O.

Results and discussion

The 11.7 T ^{29}Si, ^{27}Al, and ^{11}B spectra of the present grandidierite are shown in Figures 1A, 1B, and 1C, respectively. These spectra all agree well with those reported by Smith and Steuernagel (1992). The present ^{29}Si shift (-82.2 ppm) is sufficiently close to the reported value of -79.6 ppm to suggest that these resonances arise from the same Si site. The shape of the present ^{27}Al spectrum (Fig. 1B) is similar to the 11.7 T spectrum that was simulated by Smith and Steuernagel (1992) in terms of the two octahedral and one fivefold-coordinated Al resonances expected from the crystal structure. The fivefold-coordinated Al site was simulated by Smith and Steuernagel (1992) with a nuclear quadrupole coupling constant (χ) of 8.7 MHz and asymmetry parameter (η) of 0.95, resulting in an isotropic chemical shift (δ_0) of 41 ppm.

The present ^{11}B spectrum is also similar to that of Smith and Steuernagel (1992), but the center band quadrupolar fine structure is less well resolved. However, these spectra and the X-ray powder diffractograms indicate that the present sample is essentially identical to that studied by Smith and Steuernagel (1992). Figure 2 shows ^{25}Mg MAS NMR spectra obtained using two completely different pulse sequences. Striking similarities are apparent between the spectrum obtained using the Hahn spin-echo sequence with 2.3×10^6 transients (Fig. 2A) and a Bloch decay sequence with 0.5×10^6 transients (Fig. 2B). These spectra show a typical quadrupolar lineshape for a single site and can be simulated by setting the nuclear quadrupole coupling constant $\chi = 3.8 \pm 0.1$ MHz, the asymmetry parameter $\eta = 0.6 \pm 0.05$ with a Gaussian line broadening of 900 Hz (Fig. 2C). The resulting isotropic chemical shift δ_0 for this site is 55 ± 2 ppm. The crystallography of grandidierite (Stephenson and Moore 1968) indicates that the Mg occurs in a single distorted trigonal bipyramidal site, which must therefore correspond to this spectrum.

The position of the center of gravity (δ_{cog}) of the present resonance (-43.5 ppm) falls between the values for fourfold-coordinated and sixfold-coordinated Mg, estimated as -30.8 ppm and -47.2 ppm, respectively, from the published Hahn-echo spectra of akermanite and diopside (Fiske and Stebbins 1994). It should be noted that δ_{cog} depends strongly on the quadrupolar parameters. The bias toward the sixfold-coordinated position is also qualitatively consistent with the mean Mg-O bond lengths for the three different sites [2.042 Å in grandidierite (Stephenson and Moore 1968), 1.915 Å in akermanite, and 2.077 Å in diopside (Fiske and Stebbins 1994)].

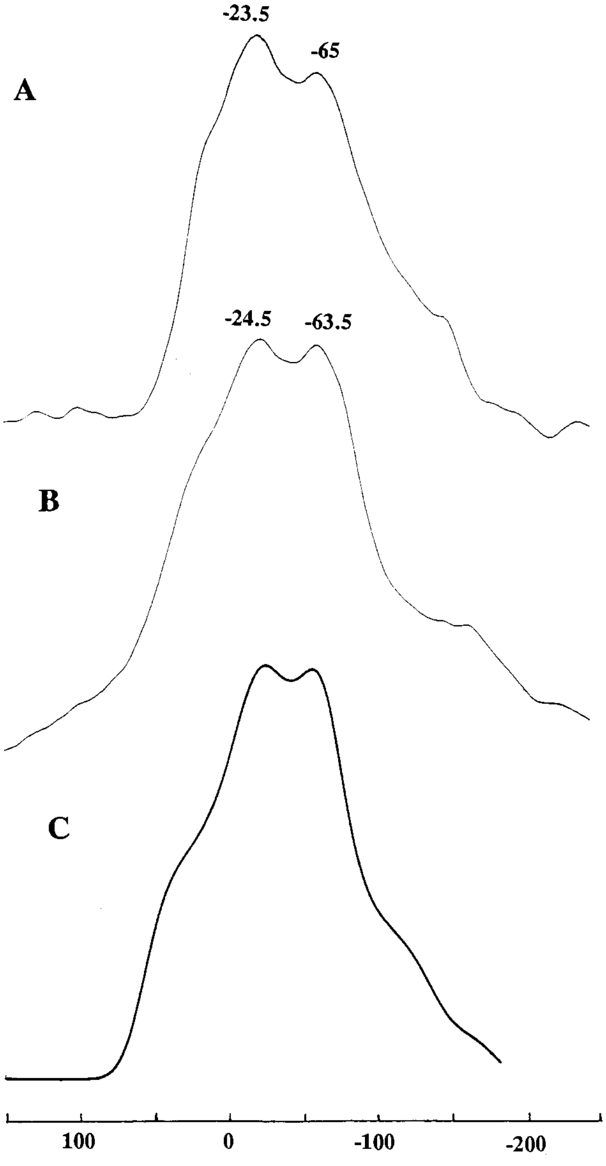

FIGURE 2. The 11.7 T ^{25}Mg MAS NMR spectra of grandidierite: (**A**) using Hahn spin-echo pulse sequence, (**B**) using Bloch decay pulse sequence and (**C**) simulation with χ= 3.8 MHz, η = 0.6, and Gaussian line broadening of 900 Hz.

However, a well known relationship exists between the isotropic shift values (δ_0) and the coordination of ^{27}Al (Müller et al. 1981), and similar trends have also been shown for ^{29}Si (Engelhardt and Michel 1987; Stebbins and McMillan 1993), ^{23}Na (Xue and Stebbins 1993), and ^{6}Li (Xu and Stebbins 1995). If it is assumed that a similar trend is followed by the δ_0 values for ^{25}Mg in fourfold, fivefold, and sixfold coordination, the isotropic shift for the fivefold-coordinated Mg site in grandidierite (55 ppm) is more positive than might be expected from the reported values for fourfold and sixfold-coordinated Mg in other compounds. However, the ^{23}Na chemical shift ranges for each coordination state overlap somewhat, and a similar overlap in the ranges for fourfold and fivefold-coordinated Mg could account for the seemingly large δ_0 value in grandidierite. It should be noted that a similar trend is seen in the ^{27}Al δ_0 value deduced by Smith and Steuernagel (1992) for the fivefold-coordinated Al site in grandidierite (41 ppm); this ^{27}Al shift is closer to the region of tetrahedral shifts than the isotropic shift values reported for well-defined fivefold-coordinated Al sites in other minerals [andalusite (35 to 36 ppm, χ = 5.9 MHz, Alemany and Kirker 1986; Lippmaa et al. 1986; Dec et al. 1991), $Al_2Ge_2O_7$ and $LaAlGe_2O_7$ (36 and 35 ppm, χ = 8.8 and 7.2 MHz, Massiot et al. 1990), pyrophyllite dehydroxylate (29 ppm, χ = 10.5 MHz, Fitzgerald et al. 1989), augelite and senegalite (30.9 and 36.0 ppm, χ = 5.7 and 2.5 to 2.8 MHz respectively, Bleam et al. 1989)]. It is interesting to note that since χ is proportional to the nuclear quadrupole moment, which for ^{25}Mg and ^{27}Al have values of 0.22 and 0.15 $|e| \times 10^{-24}$ cm^2, respectively, the value of χ for an Al in a site identical to the Mg site in grandidierite would be $(0.15/0.22) \times 3.8 = 2.6$ MHz, providing the geometry and the Sternheimer antishielding factors were the same for the identical sites.

To examine possible reasons for the seemingly anomalous behavior of the fivefold-coordinated sites in grandidierite, we considered the geometry of these sites, as reflected in the degree of distortion from the regular trigonal bipyramidal configuration. This is conveniently expressed as an angular distortion index (DI) defined by Baur (1974) and modified for the trigonal bipyramidal case, in which there are six apical-equatorial angles of 90°, three equatorial angles of 120°, and one apical angle of 180°

$$DI = \left(\sum_{i=1}^{10} |\theta_i - \theta_m|\right) \bigg/ \sum \theta_m \qquad (1)$$

where θ_i and θ_m are the observed and true (undistorted) trigonal bipyramidal angles, respectively.

The DI value for the fivefold-coordinated Al site in grandidierite, calculated from the crystal structure of Stephenson and Moore (1968), is 0.07. However, the corresponding Mg site is considerably more distorted from trigonal bipyramidal symmetry, having a DI value of 0.103, which may reflect the substitution of 10 at% Fe^{2+} assumed to be located in this site (Stephenson and Moore 1968). Previous ^{25}Mg observations of octahedral Mg-O (MacKenzie and Meinhold 1994) suggest that as the DI value of these sites increases, the nuclear quadrupole coupling constant χ increases and δ_{cog} becomes more negative. Although it is not yet known whether a similar trend is followed by fivefold-coordinated Mg-O, the large negative value of δ_{cog} for grandidierite could be consistent with the considerable distortion of this site producing large electric-field gradients. The reason that the isotropic δ_0 value for this site is closer to a tetrahedral value than expected is not presently clear, but, in addition to geometrical effects such as bond lengths and angles, δ_0 may be influenced by factors such as the nature of the species in both the first and second coordination sphere, as is the case with ^{29}Si and ^{27}Al chemical shifts. The Mg site in grandidierite is coordinated through O atoms to three Si and nine Al, three of which are fivefold coordinated and the other six are located in the two distinct edge-sharing octahedral chains (Stephenson and Moore 1968). A fuller investigation would be facilitated by the availability of a wider range of compounds containing fivefold-coordinated Mg but this configuration is unfortunately rather rare.

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