High-resolution solid-state ^{27}Al NMR spectroscopy of Mg-rich vesuvianite

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ABSTRACT

High-resolution solid-state ^{27}Al NMR spectroscopic data indicate that the pentahedrally coordinated B site of vesuvianite is at least partially occupied by Al in Fe-poor, Mg-rich vesuvianites. The isotropic ^{27}Al chemical shifts are 41.1 (± 0.5) ppm for the 5-coordinated site and 9.0 and 2.5 (± 1) ppm for the octahedrally coordinated A and AlFe sites, respectively. These results were obtained using a recently developed technique based on observing the $\pm(3/2,1/2)$ satellite transitions of nuclides with spin $I = 5/2$, which provides a substantial increase in resolution relative to traditional MASS NMR examination of the central transition. The ^{29}Si NMR spectra of the same samples contain a broad resonance at -80 ppm.

INTRODUCTION

Vesuvianite is a relatively common but complex silicate mineral that occurs in metamorphic calc-silicate rocks, rodingites associated with serpentinites, and altered alkali syenites. Deer et al. (1982) have given the idealized chemical formula for one-half unit cell as Ca_{19}-$(Al,Fe)_{10}(Mg,Fe)_3(Si_2O_7)_4(SiO_4)_{10}(O,OH,F)_{10}$.

The crystal structure was first solved by Warren and Modell (1931) and subsequently revised by Coda et al. (1970) and Rucklidge et al. (1975). Some aspects of the structure, however, remain enigmatic as witnessed by the amount of recent work on the subject (Giuseppetti and Mazzi, 1983; Allen and Burnham, 1985; Valley et al., 1985; Yoshiasa and Matsumoto, 1986; Fitzgerald et al., 1986).

Many of the problems center on the occupancies of the cation sites lying along the tetrad axis (Fig. 1). Following the nomenclature of Rucklidge et al. (1975), these sites consist of a pentahedrally coordinated square pyramid about the B position, which shares a face with a square antiprism, denoted C. Each has a multiplicity of four. The apical oxygen of the B site, O(10), also lies on the symmetry axis. Because of the proximity of the B and C sites to each other, it is unlikely that neighboring B and C sites are simultaneously occupied (Coda et al., 1970). They are, thus, statistically half-occupied in the average structure. It has been shown that ordering of cations in these half-filled sites reduces the space-group symmetry from the usually observed $P4/nnc$ to subgroups $P4/n$ (Giusep-

petti and Mazzi, 1983; Fitzgerald et al., 1986) and $P\bar{4}$ (Allen and Burnham, 1985).

Assignment of site occupancies is, in general, difficult by X-ray diffraction alone and is particularly hampered in vesuvianite by the large number of different sites, some of which are partially occupied. In vesuvianite, Ca occupies the large 8- and 9-coordinated sites, including the C site mentioned above. There are two different octahedrally coordinated sites, A and AlFe, of multiplicity 8 and 16, respectively. The A site is apparently occupied by Al, and the larger AlFe site is generally occupied by Al, Fe, Mg, Mn, etc. (Rucklidge et al., 1975; Guiseppetti and Mazzi, 1983; Valley et al., 1985; Yoshiasa and Matsumoto, 1986). Most earlier X-ray studies put Fe in the 5-coordinated B site. Mössbauer spectroscopic data (Manning and Tricker, 1975) also indicate that Fe^{2+} may occupy that site. In recent studies of low-Fe Mg-rich vesuvianites, Valley et al. (1985) assigned Mg and Fitzgerald et al. (1986) assigned Al to the B site.

It is well known that the ^{27}Al NMR chemical shift is, to a large degree, dependent on the coordination of the Al (e.g., Müller et al., 1981). In addition, the recently developed technique of observing the spinning sidebands of the $\pm(3/2,1/2)$ satellite transitions (Samoson, 1985) has provided improved resolution and an expeditious way of obtaining accurate isotropic ^{27}Al chemical shifts, corrected for quadrupole shifts (e.g., Lippmaa et al., 1986; Phillips and Kirkpatrick, 1986). As a result, ^{27}Al NMR is now a powerful tool for examining the local environment of Al in many geologically interesting materials. We present here the results of a high-resolution solid-state ^{27}Al NMR study of three Mg-rich vesuvianites with the hope of providing some insight into the site occupancies in vesuvianite.

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NMR SPECTROSCOPY

An introduction to solid-state NMR, including a discussion of nuclear quadrupole effects, is given in Kirkpatrick et al. (1985). Lippmaa et al. (1986) have provided a state-of-the-art review of solid-state ^{27}Al NMR. Briefly, Al in crystallographically different sites gives rise to NMR resonances with slightly different (ppm level) resonance frequencies. These differences are due to differences in electronic structure around the sites related to the number and types of nearest- and next-nearest-neighbor atoms. Because ^{27}Al has nuclear spin number $I = 5/2$, it has a nuclear quadrupole moment. Thus, the resonances are broadened and shifted due to the orientation-dependent interaction of the nuclear electric quadrupole moment with the electric-field gradient at the nucleus. The quadrupole interaction is only partially averaged by rapid sample spinning at the magic angle. For nuclides with $I = 5/2$, improved resolution and a decrease in the magnitude of the correction needed to obtain isotropic chemical shifts are obtained by observing the spinning sidebands of the satellite (3/2,1/2) and $-$(3/2,1/2) transitions in addition to the prominent central transition (Samoson, 1985). Best resolution is obtained at the highest magnetic fields, and for satellite-transition work, the sample must be spun stably at precisely the magic angle. Because the satellite spinning sidebands have low intensity, the spectra must have high signal to noise ratios.

Peak areas of the central transition are quantitative to within $\pm 10\%$ provided sufficiently short radio-frequency pulses are used (Fenzke et al., 1984), but because different sites are likely to have different quadrupole-coupling constants, satellite-sideband intensities are generally not quantitative. Because of severe line broadening induced by paramagnetic centers, only samples with low Fe contents can be successfully studied by high-resolution NMR.

EXPERIMENTAL DETAILS

The ^{27}Al NMR spectra were obtained with a "home-built" pulse and Fourier transform NMR spectrometer that utilizes an 11.70-T superconducting solenoid (Oxford Instruments), corresponding to an ^{27}Al resonance frequency of 130.3 MHz. The samples were spun at 7–7.6 kHz in a probe manufactured by Doty Scientific, fitted with a zirconia rotor and stator. Spinning speeds of over 8 kHz were achieved on a "home-built" probe that uses a small-diameter plastic rotor and "windmill" air bearing. Between 1000 and 3000 free induction decays were collected and added before Fourier transformation into the frequency domain. Short (1-μs) radio-frequency pulses were used, resulting in tip angles of $\leq 15°$. The delay between pulses was typically 1 s. There was no detectable difference between spectra collected with 0.5- to 10-s recycle times. Nominal (50 Hz) exponential multiplication was applied to some spectra to increase signal to noise ratio. The data were collected and processed with a Nicolet 1280 computer. Curve fitting was done interactively using the Nicolet Curve Analysis Program. Isotropic chemical shifts were estimated using the method of Samoson (1985). This method requires knowing the centroid of the $\pm$(3/2,1/2) satellite transitions, measured as the average position of the low-order rotation sidebands, and the position of the central transition. All chemical shifts are re-
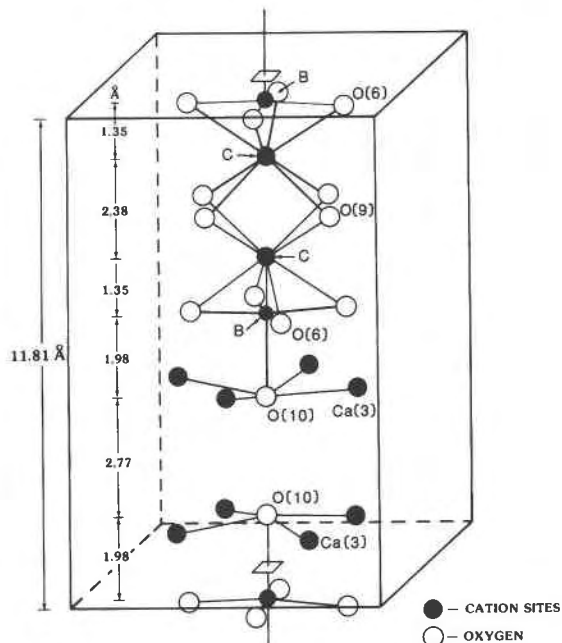

Fig. 1. Schematic representation of atoms along the 4-fold axis of vesuvianite, showing the coordination of the B and C sites.

ported relative to Al(H$_2$O)$_6^{3+}$ in the form of a $1M$ AlCl$_3$ solution. More positive chemical shifts correspond to decreased shielding.

^{29}Si spectra were obtained on a similar instrument using an 8.45-T magnet, a probe manufactured by Doty Scientific, and the methods of Smith et al. (1983). ^{29}Si chemical shifts are reported relative to external tetramethylsilane, which was the standard used.

RESULTS AND DISCUSSION

Fe-poor Mg-rich vesuvianites from Asbestos (Quebec), Luning (Nevada), and Georgetown (California) were examined. The ^{27}Al NMR spectra for these three samples are shown in Figures 2 and 3. A fourth sample from Asbestos, Quebec, was run but contains too much Fe (1.66 wt% as Fe$_2$O$_3$) to yield an informative NMR spectrum. The averages of five microprobe analyses for the three samples described here are given in Table 1, and the resulting number of ions based on 50 cations (one-half unit cell), as suggested by Valley et al. (1985), are presented in Table 2. The sample from Asbestos, Quebec, has the lowest Fe content and, therefore, gives the best resolved NMR spectrum. Thus, much of the following discussion concerns that sample.

Figure 2 shows that it was possible to obtain well-resolved satellite-transition spinning sidebands for the Asbestos sample. The central transition consists of two peaks: an intense peak centered at about -2 ppm and a smaller peak at 40 ppm. The resonance at -2 ppm is in the range of chemical shifts for octahedrally coordinated Al (^{VI}Al).

The satellite sidebands (inset in Fig. 2) indicate that the peak for ^{VI}Al actually consists of two resonances with isotropic chemical shifts of 9.0 and 2.5 (± 1) ppm. On the
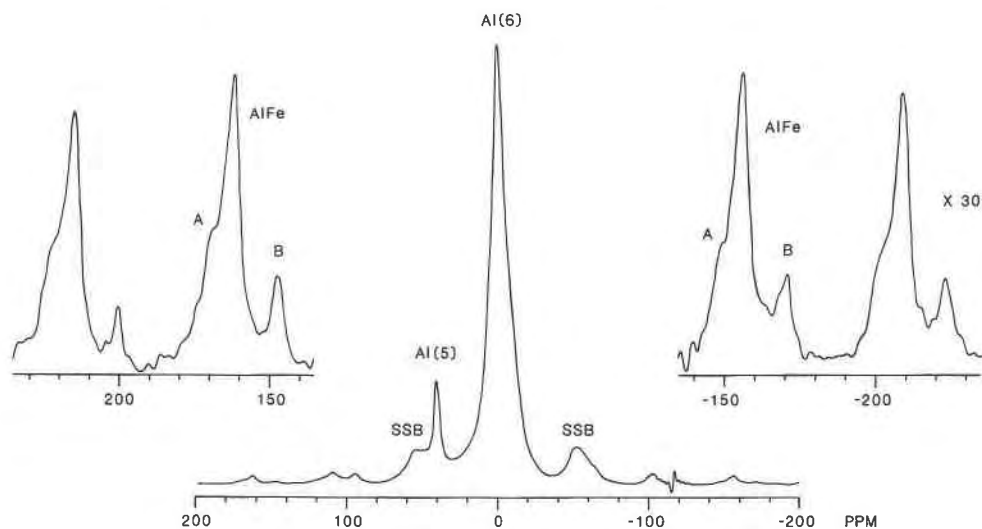
Fig. 2. ^{27}Al NMR spectrum of the Asbestos, Quebec, vesuvianite at 11.7 T and spinning speed of 7.1 kHz. The insets show in expanded scale the spinning sidebands of the satellite $\pm(3/2,1/2)$ transitions. There is signal present in the central transitions from octahedrally coordinated Al (A and AlFe sites) and pentahedrally coordinated Al (B site). The satellite sidebands show decreased line width relative to the central transitions, allowing resolution of signal from the A and AlFe sites. Accurate isotropic chemical shifts can be obtained from the satellite sidebands and are 41.1 (±0.5), 9.0 (±1), and 2.5 (±1) ppm for the peaks assigned to the B, A, and AlFe sites, respectively. SSB are spinning sidebands of the central-transition peaks.

basis of the relative intensities of the satellite peaks and the site multiplicities given above (assuming that the sites do not have vastly different quadrupole-coupling constants), and empirical chemical-shift correlations with octahedrally coordinated Al in other aluminosilicates (Phillips, unpub. data), we tentatively assign these two resonances to the A and AlFe sites of vesuvianite, respectively.

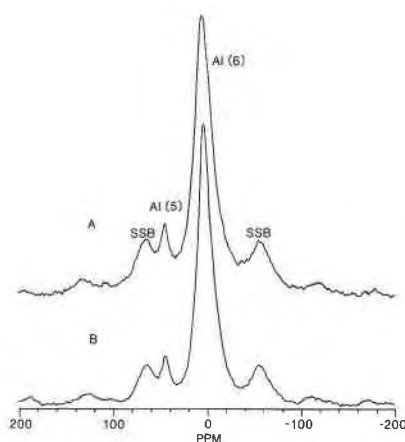The peak with a maximum at about 40 ppm has an isotropic chemical shift of 41.1 (±0.5) ppm, which falls outside the range of known chemical shifts of Al coordinated by four or six oxygens. It is similar, though, to chemical shifts reported for pentahedrally coordinated Al: an isotropic chemical shift of 35 ppm for andalusite (Lippmaa et al., 1986) and a peak with a maximum at 35 ppm for barium aluminate glycolate (Cruickshank et al., 1986). Therefore, we assign this resonance to Al in the unusual 5-coordinated B site of vesuvianite.

Figure 3 shows that similar results were obtained for other vesuvianite samples with slightly higher Fe con-

Fig. 3. ^{27}Al NMR spectra of the (A) Georgetown and (B) Luning vesuvianite samples; 11.7 T and spinning speeds of 8.3 kHz. 50-Hz exponential multiplication was added to increase signal to noise ratio. Note similarity to the spectrum in Fig. 2. As in Fig. 2, there is signal present from 5- and 6-coordinated Al, along with some spinning sidebands. The satellite transition sidebands are not well resolved, presumably owing to paramagnetic line broadening.

TABLE 1. Average of five microprobe analyses for the three vesuvianites studied

	Asbestos, Quebec	Luning, Nevada*	Georgetown, California
SiO$_2$	37.45(51)	36.73(25)	36.92(21)
TiO$_2$	0.01(1)	0.01(1)	0
Al$_2$O$_3$	19.65(34)	18.72(16)	18.90(25)
Cr$_2$O$_3$	0	0.02(1)	0.03(2)
Fe$_2$O$_3$**	0.29(7)	0.98(4)	1.12(19)
MnO	0.04(1)	0.01(0)	0.04(1)
MgO	2.64(21)	3.62(4)	2.58(3)
CaO	36.64(24)	36.47(31)	36.71(33)
Na$_2$O	0	0	0
K$_2$O	0	0	0
F	0.09(6)	0.24(21)	0
	96.81	96.81	96.30
O $\equiv$ F	-0.04	-0.10	0
H$_2$O†	3.23	3.29	3.70
Total	100.00	100.00	100.00

Note: Values in weight percent. Standard deviations in parentheses refer to last figures.
* Includes ZnO 0.01(2), Zn 0.004.
** All Fe is expressed as Fe$_2$O$_3$.
† H$_2$O by difference.

TABLE 2. Number of ions per 50 cations (one-half unit cell) for vesuviante samples studied, based on analyses in Table 1

	Asbestos	Luning	Georgetown
Si	17.993	17.651	17.874
Ti	0.004	0.004	0.000
Al	11.128	10.604	10.785
Cr	0.000	0.008	0.011
Fe	0.105	0.354	0.408
Mn	0.016	0.004	0.016
Mg	1.891	2.593	1.862
Ca	18.863	18.779	19.043
Na	0.000	0.000	0.000
K	0.000	0.000	0.000
F	0.137	0.365	0.000
OH	10.361	10.556	11.960
O	68.364	67.677	67.496

Fig. 4. ^{29}Si NMR spectrum of the Asbestos, Quebec, vesuvianite 8.45 T and spinning at 2.0 kHz. FWHH = full width at half height. Peaks for the three different Si sites cannot be resolved.

tents. Unfortunately, it is not possible to observe well-resolved satellite sideband spectra for these samples owing to the higher Fe contents. Thus, precise chemical-shift measurement is not possible for these.

The higher-Fe Luning and Georgetown samples are deficient in Si, and there may be some Al substitution into the tetrahedral sites. Unfortunately, currently available equipment is not capable of the spinning speeds (>10 kHz) required to put the spinning sidebands of the octahedral signal outside the chemical-shift range of tetrahedrally coordinated Al. Even with these modest Fe contents, the peaks are too broad at slower spinning speeds to detect small amounts of tetrahedrally coordinated Al.

Deconvolution of NMR spectra of quadrupolar nuclides is difficult because the lineshapes of the central transition and its spinning sidebands are complicated (Ganapathy et al., 1982). They can be simulated exactly only if the quadrupole-coupling constant and the asymmetry parameter of the electric-field gradient are known. Unfortunately, no such data exist for vesuvianite. However, it was possible to fit the spectra using curves with mixed Lorentzian and Gaussian shapes. For vesuvianite this requires spinning the samples at the fastest available spinning speeds to adequately distinguish the peak due to Al in the B site from the spinning sidebands of the central transitions due to the octahedrally coordinated Al. In addition to the uncertainty in fitting the spectra with mixed-shape curves, strict quantitation of the central-transition peaks (which must include the spinning sidebands of the central transition) carries an approximately ±10% uncertainty, even with the very short pulses used in this study (Fenzke et al., 1984). Total uncertainty in the proportion of ^{27}Al from these deconvolutions is probably no more than ±20%.

The deconvolutions (Table 3) indicate that between 5 and 7% of the central-transition peak area is attributable to the pentahedral Al signal. The resulting number of Al atoms (based on 50 cations) assigned to the B site is not enough to account for a statistically half-occupied B site (1 per 50 cations) in any of the samples studied. Thus, it appears that some other atom must also be occupying the
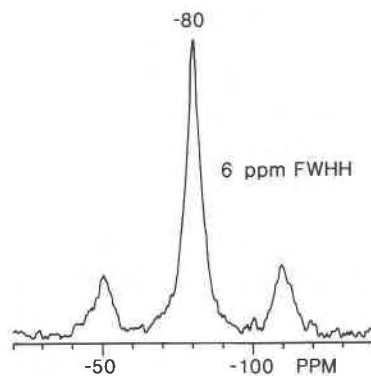
B site. As suggested by X-ray and Mössbauer spectroscopic data, this other atom is mostly likely Fe. As shown in Table 3, the assigned pentahedral Al plus the total Fe content of these samples accounts for the expected total B-site occupancy to within experimental uncertainty.

Because there are three crystallographically different Si sites in vesuvianite, including two polymerization states, Si_2O_7 dimers and isolated SiO_4 tetrahedra, we had hoped that vesuvianite would yield an informative ^{29}Si NMR spectrum. However the spectrum of the sample with lowest Fe content (Fig. 4) consists of a broad featureless peak, 6 ppm wide at half height and centered at −80 ppm from tetramethylsilane. This peak must contain signal from all three sites, but the overlap due to intrinsic line breadths and paramagnetic broadening prevents resolution of separate resonances.

CONCLUSIONS

Although precise quantitation is not possible, the ^{27}Al NMR spectra presented here show unambiguously that some Al occupies the pentahedrally coordinated B site in Mg-rich vesuvianites. This result substantiates the assignment of Al to this site by Fitzgerald et al. (1986). In addition, because the amount of Al found in the B site does not fill a statistically half-occupied site, the assignment of other cations (e.g., Fe in more Fe-rich vesuvianites) is also supported. This result illustrates that cation-oxygen distances computed from an average structure,

TABLE 3. Results of deconvolution of the ^{27}Al NMR central transition peaks

Sample	% of Al signal in Al(5) peak	Corresponding number of ^{V}Al atoms*	Number of Fe atoms*	Total Fe + assigned ^{V}Al*
Asbestos	7.1 (±0.5)	0.8 (±0.2)	0.105	0.9 (±0.2)
Luning	5.7	0.6	0.354	0.95
Georgetown	6.4	0.7	0.408	1.1

Note: Deconvolutions provide the percentage of the Al signal attributable to the signal due to pentahedrally coordinated Al.
* Per 50 cations.

especially in the presence of partially occupied sites, can be misleading when attempting to partition site occupancies among atoms with similar scattering powers. Valley et al. (1985) found the average cation-oxygen distance for the B site for a low-Fe vesuvianite to be 2.023 Å. Because this distance is nearer to that predicted for 5-coordinated Mg, based on effective ionic radii, they preferred to assign Mg to the B site. In this case, high-resolution solid-state NMR proves to be a powerful complement to diffraction studies.

The results also illustrate the increase in resolution for ^{27}Al (and other $I = 5/2$ nuclides) obtainable by observing the spinning sidebands of the $\pm(3/2,1/2)$ satellite transitions. This technique appears to be useful for natural samples with low Fe contents and will be most useful for those phases with multiple Al sites that yield signal that overlaps in the peaks for the central transition.

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