

Solid-state MAS NMR study of pentameric aluminosilicate groups with 180° intertetrahedral Al-O-Si angles in zunyite and harkerite

PETER J. DIRKEN

Physics Laboratory, University of Kent at Canterbury, CT2 7NR Canterbury, Kent, U.K.

ARNO P. M. KENTGENS, GERDA H. NACHTEGAAL

NSR Center for Molecular Structure, Design, and Synthesis, HF-NMR Facility, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, the Netherlands

AD M. J. VAN DER EERDEN, J. BEN H. JANSEN

Department of Geochemistry, Institute of Earth Sciences, University of Utrecht, Budapestlaan 4, 3508 TA Utrecht, the Netherlands

ABSTRACT

The minerals zunyite, $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$, and harkerite, $\text{Ca}_{24}\text{Mg}_8[\text{AlSi}_4(\text{O},\text{OH})_{16}]_2(\text{CO}_3)_8(\text{BO}_3)_8(\text{H}_2\text{O},\text{Cl})$, have been studied by means of solid-state ^{27}Al MAS NMR. Zunyite contains Si_5O_{16} pentamers and harkerite contains $\text{AlSi}_4(\text{O},\text{OH})_{16}$ pentamers. These pentameric groups are unique because their T-O-Si angles are almost 180°. Chemical analysis of the zunyite sample shows that it has excess Al: the Al-Si ratio is 2.9, compared with the ideal of 2.6.

High-speed spinning ^{27}Al MAS NMR spectra (11–13 kHz) showed two more signals than the spectra obtained by Kunwar et al. (1984). The signal with $\delta_{\text{iso}} = 46.8 \pm 0.5$ ppm represents the excess Al, which enters the central Si1 site of the Si_5O_{16} pentamer. This assumption is confirmed by the fact that δ_{iso} of Al in the $\text{AlSi}_4(\text{O},\text{OH})_{16}$ pentamer in harkerite is 44 ± 1 ppm. Additional proof comes from comparing the electrostatic energy and the quadrupole interaction of Al in either a Si1 or Si2 configuration.

The Al site in the pentamers of zunyite and harkerite can be considered as a $q^+(4\text{Si})$ site. In this case, Al-O-Si angles are correlated with the ^{27}Al chemical shift (Lippmaa et al., 1986). This correlation holds well for the ^{27}Al data for harkerite. The value for zunyite indicates that the structure adapts to the incorporation of Al in the Si1 site by a narrowing of the Al-O-Si angle to $171 \pm 2.5^\circ$. The lower limit of the chemical shift range for Al in framework aluminosilicates is decreased by 12 ppm, from 55.8 ppm for mordenite to 44 ppm for harkerite.

INTRODUCTION

The mineral zunyite, $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$, (Pauling, 1933; Kamb, 1960; Louisnathan and Gibbs, 1973; Baur and Ohta, 1982) contains two rare crystallographic units. The first is a pentameric Si_5O_{16} group, and the second a tridecameric Al_{13} group. The Si_5O_{16} group is special because its Si-O-Si intertetrahedral angles are 180°. The Si_5O_{16} group is very similar to the $\text{AlSi}_4(\text{O},\text{OH})_{16}$ group in the mineral harkerite, $\text{Ca}_{24}\text{Mg}_8[\text{AlSi}_4(\text{O},\text{OH})_{16}]_2(\text{CO}_3)_8(\text{BO}_3)_8(\text{H}_2\text{O},\text{Cl})$ (Tilley, 1951; Guiseppetti et al., 1977). The pentamer in harkerite has Al-O-Si intertetrahedral angles of 176°.

The Al_{13} group occurs in natural minerals only in zunyite. Similar to it are Al_{13} groups in synthetic Al_{13} salts (Johansson, 1960). The Al_{13} complex as it occurs in solution can be used for the pillaring of clay minerals, making them useful catalysts (Plee et al., 1985; Klopogge, 1992).

Magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy is an important technique to deter-

mine the coordination state and local symmetry of structural units such as $(\text{Si},\text{Al})\text{O}_4$, AlO_5 , or AlO_6 polyhedra. Besides determining the coordination state, NMR is also sensitive to polymerization effects, next nearest neighbor effects and bond lengths and angles (Müller et al., 1981; Kirkpatrick, 1988; Stebbins, 1991; Dirken et al., 1992; Smith, 1993).

It is well known that the Al-O-Si angle is correlated with the ^{27}Al chemical shift in framework aluminosilicate structures (Lippmaa et al., 1986). Until now, the maximum Al-O-Si angle used in this correlation was 153.7° for the mineral mordenite. This correlation is important in structural studies of glasses because it can give an estimate of the size of rings building up aluminosilicate glasses (Oestrike et al., 1987; Dirken et al., in preparation). It is also used in ^{27}Al NMR studies of Si-Al ordering in leucite (Phillips et al., 1989) and zeolites (Engelhardt and Michel, 1987) to assign signals in the NMR spectrum to sites in the structure. Previous ^{27}Al NMR investigations on zunyite and Al_{13} salts established the

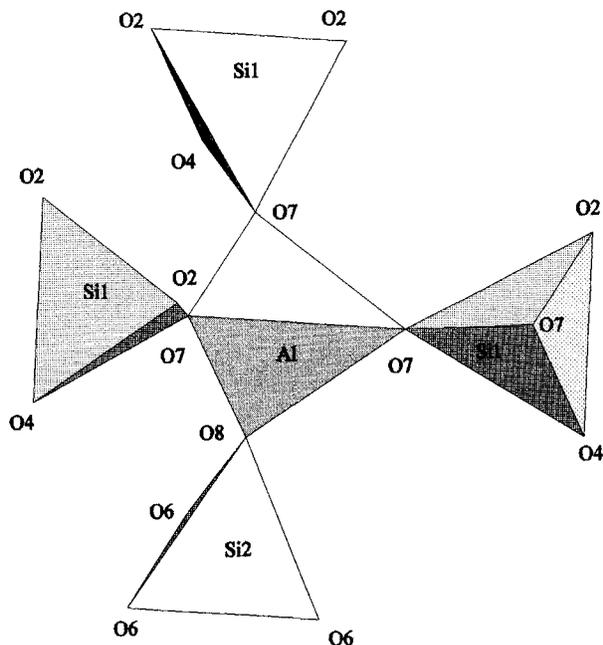


Fig. 1. The $\text{AlSi}_4\text{O}_{16}$ pentamer in harkerite.

existence of a signal from ^{41}Al and ^{61}Al (von Lampe et al., 1982; Kunwar et al., 1984). These NMR data, however, were collected using slow spinning conditions (≈ 3 kHz), with overlapping resonances and spinning sidebands.

We present ^{27}Al NMR data of the pentamer in harkerite and compare it with ^{27}Al NMR data of a zunyite sample with excess Al. The use of fast MAS (11–13 kHz) reveals two extra Al signals for zunyite, one of which is proved to be due to the excess Al that is incorporated into the Si pentamer. The Al chemical shift of this signal is used for assigning Al to the Si1 or Si2 site of zunyite.

Additionally, we try to extend the correlation mentioned above to Al-O-Si angles of 180° , the widest possible angle in aluminosilicates, with the hope of refining models on atomic structure of minerals and glasses.

EXPERIMENTAL METHODS

Samples

Chemical analyses of the samples were determined with a JEOL Jx-8600 Superprobe, using a 15-kV accelerating voltage and a $1\text{-}\mu\text{m}$ spot size. Secondary phases were examined with optical microscopy and with a Philips PW 1050/25 X-ray powder diffractometer using $\text{CuK}\alpha$ radiation.

Zunyite. The zunyite sample is from the type locality, Zuñi mine, San Juan County, Colorado, U.S.A. Microprobe analyses were consistent with previous analyses (Turco, 1962; Baur and Ohta, 1982). The Al-Si ratio is 2.9, compared with 2.6 for the ideal ratio. The sample contained several secondary phases (± 15 vol%), viz., rutile, galenite, pyrite, kaolinite and a PO_4 - and SO_4 -bearing phase with varying PO_4 - SO_4 ratios, some of which had a

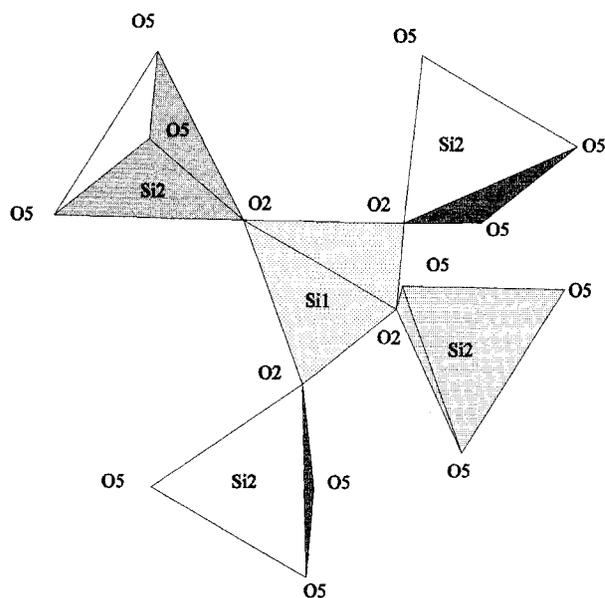


Fig. 2. The Si_5O_{16} pentamer in zunyite.

considerable amount of Ca, Sr, Ce, and Th. This composition could correspond to florencite, which has an alunite-type structure (Burt, 1985). Important for the NMR experiments is the coordination of Al. In kaolinite and the alunite-type phases all Al is present in octahedral coordination.

Harkerite. The harkerite sample is from the type locality at Camas Malag on the Isle of Skye, Scotland. Harkerite was identified by X-ray diffraction and optical microscopy. The mineralogical assemblage of this skarn locality has been described by Tilley (1951). Tilley reported monticellite (CaMgSiO_4), calcite (CaCO_3), and diopside ($\text{CaMgSi}_2\text{O}_6$) as the principal associates of harkerite. Calcite is formed as an alteration product of harkerite.

Our microprobe and X-ray diffraction analyses revealed the existence of additional kirschsteinite ($\text{Ca-Fe}^{2+}\text{SiO}_4$), periclase (MgO), and serpentine [$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$]. Kirschsteinite forms a solid solution series with monticellite.

The Al content of these secondary phases is important for ^{27}Al NMR experiments. Monticellite, kirschsteinite, and serpentine contain 1 wt% Al_2O_3 . Diopside contains 0.1 wt% Al_2O_3 , considerably less than the value of 3.6 wt% given by Tilley (1951). His wet-chemical analyses are believed to be less reliable, however, than our microprobe analyses. Determining the exact stoichiometry of harkerite by means of microprobe analyses is difficult because B is too light to be analyzed. The relative contents of Al, Si, Ca, and Mg, however, are consistent with the analyses of Tilley (1951) and Barbieri (1977).

NMR spectroscopy

The solid-state ^{27}Al NMR experiments were performed on Bruker CXP-300, AM-500, and AMX-600 spectrometers, operating at 78.2 MHz ($B_0 = 7.1$ T), 130.3 MHz

($B_0 = 11.7$ T), and 156.4 MHz ($B_0 = 14.1$ T), respectively. A home-built probe head with a Doty MAS assemblage was used.

As Al is a quadrupole nucleus, care has to be taken to ensure equal excitation of the ^{27}Al resonances (Samoson and Lippmaa, 1983; Dec and Maciel, 1990; Alemany, 1993). Therefore, short pulse excitations ($0.7 \mu\text{s} = \pi/10$) were used, with 0.5-s relaxation delays and 100-kHz spectral widths. For each measurement, 5000–20000 FIDs were collected. The ^{27}Al chemical shifts are determined relative to an external standard of aqueous 1-M AlCl_3 solution. Processing of the FID was carried out without any filtering. The quadrupole interaction and the isotropic chemical shifts (δ_{iso}) are determined by using the field-dependent second-order quadrupole-induced shift of the center of gravity of the peak (Meadows et al., 1982; Engelhardt and Michel, 1987).

The ^{29}Si NMR spectrum of zunyite was collected on a Bruker AM-500 spectrometer using a 5-s relaxation delay, a 50-kHz spectral width, a 5- μs pulse length ($\pi/2$), and a spinning speed of 3.7 kHz. A total of 28000 FIDs were collected, referenced to the -89.2 -ppm resonance (relative TMS at 0 ppm) of a zeolite-A standard. The relaxation delay time was varied, but no changes in the relative intensities of the resonances were observed. Integration of the intensities was carried out on a Sun microcomputer using NMRi software.

CRYSTALLOGRAPHY

Harkerite

Harkerite, $\text{Ca}_{24}\text{Mg}_8[\text{AlSi}_4(\text{O},\text{OH})_{16}]_2(\text{CO}_3)_8(\text{BO}_3)_8(\text{H}_2\text{O}, \text{Cl})$, from a skarn deposit in the Isle of Skye (Scotland) was first described by Tilley (1951). It contains a unique $\text{AlSi}_4(\text{O},\text{OH})_{16}$ pentamer (Davies and Machin, 1970; Machin and Mieke, 1976; Guiseppetti et al., 1977) that is only related to the Si_5O_{16} pentamer in zunyite (Pauling, 1933; Baur and Ohta, 1982). In NMR terminology it can be summarized as four $\text{Q}^1(1\text{Al})$ Si atoms arranged around one $\text{q}^4(4\text{Si})$ Al atom with intertetrahedral angles of 176° (Fig. 1). There are two types of $\text{Q}^1(1\text{Al})$ Si atoms, Si1 and Si2, which are almost identical (Guiseppetti et al., 1977).

Zunyite

The crystal structure of zunyite, $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$, was first described by Pauling (1933) and refined later by Kamb (1960), Turco (1962), and Baur and Ohta (1982). The last authors give an excellent systematic description of this complicated structure. It consists of two crystallographic units, a Si_5O_{16} pentamer and a group of the Keggin molecule type (Furrer et al., 1992) with an $\text{Al}_{13}\text{O}_{16}(\text{OH})_{24}$ stoichiometry. The Si_5O_{16} cluster consists of a central $\text{Q}^4(4\text{Si})$ Si atom and four $\text{Q}^1(1\text{Si})$ Si atoms with Si-O-Si intertetrahedral angles of 180° (Fig. 2). The Si_5O_{16} pentamer is surrounded by $\text{AlO}_3(\text{OH})_3$ octahedra from the Al_{13} group. Twelve Al atoms are arranged in groups of three AlO_6 octahedra around a central $^{(4)}\text{Al}$ atom. The Al_{13} group and the pentamer alternate in a 1:1 ratio, resulting in the $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$ stoichiometry.

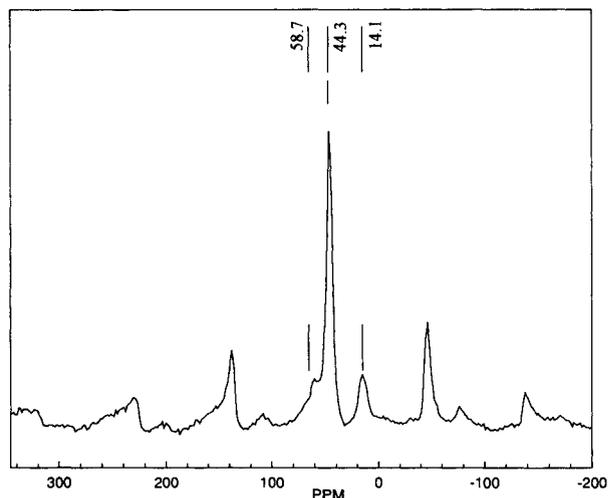


Fig. 3. The ^{27}Al MAS NMR spectrum of harkerite at a magnetic field of 11.7 T.

RESULTS AND DISCUSSION

Harkerite

The ^{27}Al NMR spectrum of harkerite is shown in Figure 3. It is dominated by a set of intense spinning sidebands. These sidebands belong to the peak at 44 ppm, as can be determined by varying the spinning speed. The strong intensities of the spinning sidebands are caused by the presence of Fe^{3+} in the structure. Magnetic coupling of unpaired electrons with Al causes line broadening and the intensity of the center band to be lost into the sidebands (Watanabe et al., 1983; Murdoch et al., 1985). Indeed, Tilley (1951) reported a Fe_2O_3 content of 0.85 wt%. The peak position of the ($-\frac{1}{2} = \frac{1}{2}$) transition is not affected by the presence of Fe (Engelhardt and Michel, 1987).

The peak position is 44.3 ppm at 11.7 T, 43.9 ppm at 7.1 T, and 43 ppm at 14 T. As the error in the peak position is about 1 ppm, the quadrupole interaction is very small ($\ll 1$ MHz), and the isotropic chemical shift is 44 ± 1 ppm.

The 44-ppm value falls outside the range generally accepted for AlO_4 (50–80 ppm) and AlO_5 (30–40 ppm) (Smith, 1993). It fits well the correlation of the ^{27}Al chemical shift with the Al-O-Si angle in framework silicates (Lippmaa et al., 1986), for which $\delta_{\text{iso}}(\text{Al}) = (-0.50\theta + 132)$ ppm, where $\delta_{\text{iso}}(\text{Al})$ represents the ^{27}Al isotropic chemical shift and θ the Al-O-Si intertetrahedral angle. With $\theta = 176^\circ$ (Guiseppetti et al., 1977), δ_{iso} becomes 44 ppm, which is exactly the experimental value (Fig. 4). Of course, the harkerite structure is not a framework structure in the strict sense, since it is essentially a carbonate-borate mineral. However, from the point of view of the central Al atom, it resembles a framework structure because the AlO_4 group is surrounded by 4 $\text{Si}(\text{O},\text{OH})_4$ tetrahedra; i.e., it is a $\text{q}^4(4\text{Si})$ Al atom (Engelhardt and Michel, 1987). The ^{27}Al chemical shift of 44 ppm for the Al

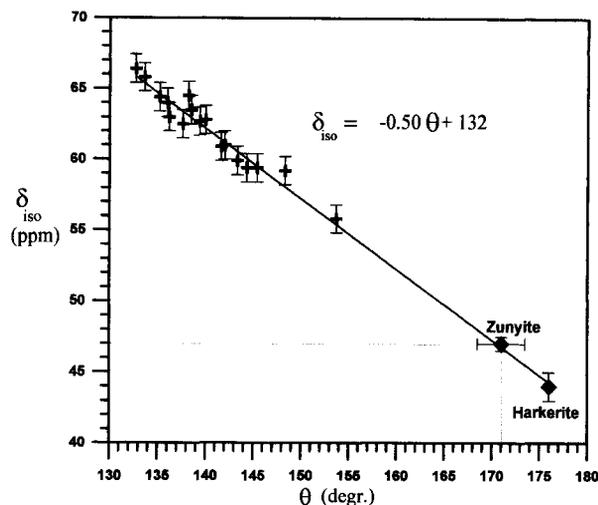


Fig. 4. Correlation between the isotropic chemical shift δ_{iso} and the Al-O-Si intertetrahedral angle θ for framework silicates. Crosses represent data from Lippmaa et al. (1986).

in the harkerite pentamer is close to the 41.1-ppm value observed by Phillips et al. (1987) in Mg-rich vesuvianite. These authors studied the ($\pm\frac{3}{2} \approx \frac{1}{2}$) satellite transitions, which have an improved resolution over the central transition, and attributed the 41.1-ppm signal to Al occupying the fivefold-coordinated B site. In harkerite, however, Al is fourfold-coordinated, and the low chemical shift must be attributed to the influence of the Al-O-Si angle.

The peak at 58.7 ppm and 14 ppm are due to impurities.

Zunyte

Zunyte has been studied previously by means of ^{27}Al NMR by Kunwar et al. (1984). They reported two signals in a 1:12 intensity ratio. These signals are also present in our spectra (Fig. 5). The 71.4-ppm signal represents Al from the central AlO_4 tetrahedron; the 7.7-ppm signal with the highest intensity represents Al from the 12 AlO_6 octahedra around the AlO_4 group. The isotropic chemical shifts and quadrupole data, all determined by means of the field-dependent second-order quadrupole-induced shift, are given in Table 1, together with the data of Kunwar et al. (1984).

In addition to these two signals, there are signals at 46.6 ppm and -3.4 ppm. Both resonances could in principle arise from the secondary phases present in the zunyte. However, the secondary phases all have Al in octahedral coordination, with possible chemical shifts between -15 and +15 ppm. Only the -3.4-ppm resonance is therefore caused by these impurities. The 46.6-ppm resonance is believed to be from the zunyte itself.

The 46.6-ppm peak ($B_0 = 14.1$ T) shifts to 46.1 and 46.3 ppm at magnetic fields of 7.1 and 11.7 T, respectively. This corresponds with an isotropic chemical shift of 46.8 ± 0.5 ppm and a QCC of 0.5–1.0 MHz. It falls outside the range for ^{161}Al but is close to the value of 44

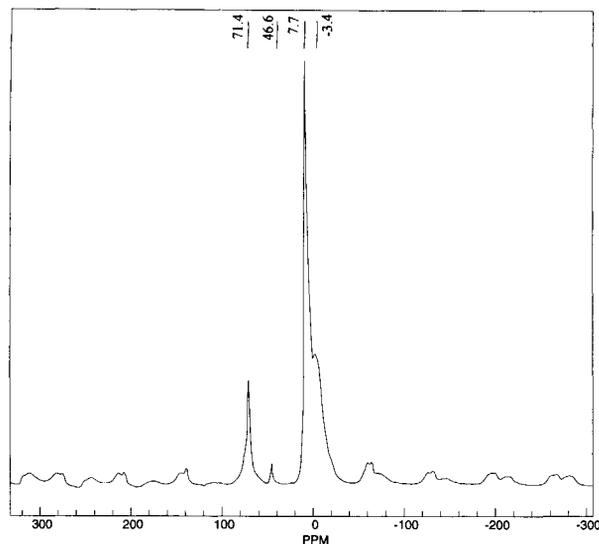


Fig. 5. The ^{27}Al MAS NMR spectrum of zunyte at a magnetic field of 11.7 T.

ppm for Al in the pentamer of harkerite. As there is no reason to assume the presence of ^{151}Al , it seems plausible, therefore, that the excess Al known from chemical analyses is incorporated into the Si_5O_{16} pentamer.

Baur and Ohta (1982) concluded from the shortening of the O2-O5 edge in the Si_2O_4 tetrahedron and the increase in the O5-O5 edge (Fig. 2), that Al occupies the Si1 site. Sherriff et al. (1991) did not give an unambiguous interpretation of their X-ray and ^{29}Si NMR study of zunyte. They stated that both the Si1 and Si2 sites are potential recipients for the excess Al. Zagal'skaya and Belov (1964) proposed that the Si_5O_{16} pentamer is in reality a $\text{AlSi}_4\text{O}_{16}$ pentamer and that Si partly occupies the ^{141}Al site of the Al_{13} group. Louisnathan and Gibbs (1972), however, considered that to be in error, since the Al-O2 bond length (1.73–1.8 Å) is not compatible with the value derived from structure refinements (1.628 Å). This value however, is also not compatible with an occupation by Si alone.

Incorporation of more than one Al atom into the pentamer is unlikely because of Al avoidance (Loewenstein, 1954; Liebau, 1985).

In addition to the arguments proposed by Baur and Ohta (1982) there are a number of arguments that suggest that Al is in a central Si1 site.

First of all, incorporation of Al^{3+} into the central Si^{4+} site causes four O2 bonds to be polarized, in contrast to only one O2 for incorporation into the Si^{4+2} site. If Al would enter the Si2 site, an Al-O5-Al bond (last Al from an Al_{13} group) would be formed and polarization of the O5 would be lost. This polarization leads to an additional bonding energy, which favors an $\text{Al1}(\text{Si}2)_4\text{O}_{16}$ pentamer over an $\text{Al}2\text{Si1}(\text{Si}2)_3\text{O}_{16}$ pentamer. This effect has previously been used to explain the preference of various ions for crystallographic sites in the spinel structure (Blasse, 1964; Hill et al., 1979).

TABLE 1. Data from ^{27}Al MAS NMR spectra of zunyite

Site	δ_{iso} (ppm)		QCC (MHz)		η	QB* (Hz)		FWHH** (Hz)
	1	2	1	2		1	2	
^{27}Al (Al ₃)	72	71.6	0.6	0.8	0	20	30	520
^{27}Al (Al ₃)	8	8.9	2.2	2.2	0	280	280	900
^{27}Al (penta)	—	46.8	—	0.5–1	0	—	30	250

Note: 1 = data from Kunwar et al., 1984; 2 = data from this study (error in δ_{iso} and QCC is 0.5 ppm and 0.5 MHz, respectively).
 * QB = second-order quadrupole broadening at $B_0 = 11.7$ T.
 ** FWHH = full width at half height at $B_0 = 11.7$ T.

A second argument for positioning Al on the Si1 site is the close resemblance in structure and NMR data between harkerite and zunyite. The Al in harkerite, which is in a coordination comparable with Al in a Si1 site in zunyite, fits the correlation between the ^{27}Al chemical shift with the Al-O-Si angle for framework aluminosilicates (vide supra). The ^{27}Al isotropic chemical shift in the pentamer of zunyite differs only by 2.8 ppm from that of harkerite. The value of 46.8 ppm does not fit an Al-O-Si angle of 180° , however. The 46.8-ppm value for zunyite must correspond to an angle smaller than 176° , since this is the value for a known Al-O-Si angle in harkerite. In fact, 46.8 ppm corresponds to an Al-O-Si angle of 171.2° (Fig. 4). It must be noted that this value is based on an extrapolation of the data of Lippmaa over 25° to one data point for harkerite. As a result, the error in the Al-O-Si angle for zunyite might be large ($\pm 2.5^\circ$).

A third argument for Al in the Si1 site comes from the observed quadrupole parameters. The quadrupole interaction (Cohen and Reif, 1957; Müller, 1982) can be used to give an estimate of the distortion of the first coordination sphere of an atom in a particular site (Smith, 1993). The larger the quadrupole coupling constant (QCC), the higher the distortion of the site. Ghose and Tsang (1973) related the ^{27}Al QCC of ^{27}Al to the so-called shear strain Ψ in crystalline aluminosilicates. The shear strain is a measure of the departure of the individual bond angles from the ideal value of 109.47° . It is defined for Al in fourfold coordination as

$$\Psi = \sum_i |\tan(\theta_i - 109.47^\circ)|.$$

Here θ_i are the individual O-Al-O angles of the actual tetrahedron.

Since the crystal structure of zunyite is known, the shear strain of Al in a Si1 site and Al in a Si2 site and the corresponding QCC can be calculated and compared with the experimental value. For Al occupying Si1, with bond distances and angles remaining constant, the predicted QCC is 1 MHz ($\Psi = 0$), close to our experimental value of 0.5–1.0 MHz. This is a very small value for Al in aluminosilicates, only comparable with sodalites [QCC = 590–890 kHz (Freude and Haase, 1993)]. For Al occupying Si2, the predicted QCC is 2 MHz ($\Psi = 0$), considerably higher than our 0.5–1.0-MHz value.

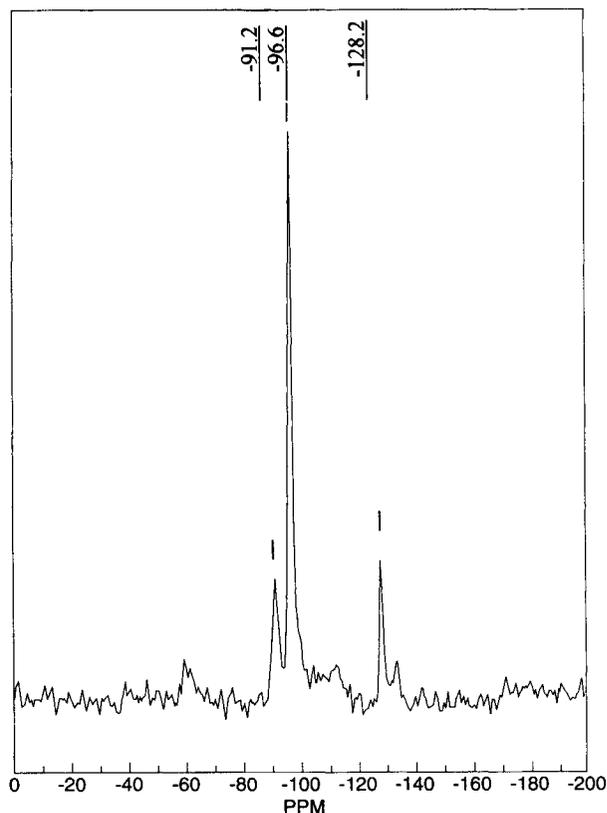


Fig. 6. The ^{29}Si MAS NMR spectrum of zunyite at a magnetic field of 11.7 T.

The error in the correlation is rather large (approximately 1 MHz), but it is apparent that, in the case of Al in a Si2 configuration, the QCC would be larger than the value for Al in a Si1 configuration.

Our Si spectrum (Fig. 6) is comparable with those previously reported (Grimmer et al., 1983; Sherriff et al., 1991). The -96.6 -ppm peak is from Si in a $Q^1(1\text{Si})$ configuration with Si-O-Si angles of 180° . The -128.2 -ppm peak is from Si in a $Q^4(4\text{Si})$ configuration, also with Si-O-Si angles of 180° . The relative intensities of the $Q^1(1\text{Si})$ and $Q^4(4\text{Si})$ have been determined by integration of the peak areas and are 1:4, as expected from the stoichiometry of the pentamer.

The -91.2 -ppm peak is reported in all Si spectra of zunyite. It was assumed by Grimmer et al. (1983) and Sherriff et al. (1991) to arise from nacrite, which is present as a secondary phase. We report kaolinite as a secondary phase, which is closely related to nacrite.

It must be noted, however, that the value of -91.2 ppm is the value that is to be expected for a Si atom in a $Q^1(1\text{Al})$ site with Si-O-Al angles of 180° . This site is formed by incorporating Al into the Si1 site. It is apparent from X-ray diffraction and optical microscopy that kaolinite is responsible for most of the intensity at -91.2 ppm. However, it cannot be ruled out that part of the intensity (up to 50%) is due to the Si in a $Q^1(1\text{Al})$ in the

zunyte sample itself. The samples that have been measured previously by NMR (*vide supra*) all come from the Zuñi mine, and therefore all have excess Al in the structure. The -91 -ppm signal in these studies could, therefore, well be due to Si in a $Q^1(1Al)$ site in the zunyte. A topic of further study might be obtaining ^{27}Al and ^{29}Si NMR spectra of a (synthetic or natural) zunyte that has no excess Al. Baur and Ohta (1982) reported a structure refinement of such a zunyte from Quartzsite, Arizona.

Until now, $q^4(4Si)$ sites and their ^{27}Al NMR chemical shifts were reported from mordenite ($\delta_{iso} = 55.8$ ppm, Al-O-Si = 153.7°) to scolecite ($\delta_{iso} = 66.4$ ppm; Al-O-Si = 132.7°). From this study it is apparent that this range can be extended to 44 ± 1 ppm for Al sites in framework aluminosilicate structures with Al-O-Si angles of 176° .

ACKNOWLEDGMENTS

We gratefully acknowledge the assistance we received from T. Broers and T. Bouten, both from the Institute for Earth Sciences in Utrecht, for the XRD and microprobe analyses, respectively. Geomar B.V., Rijswijk, the Netherlands, is thanked for providing the type locality material of harkerite. We thank J. van Os, J. Joordens, and H. Jansen, all from the HF-NMR facility in Nijmegen, for technical assistance during the NMR experiments. R.D. Schuiling and G. Blasse critically reviewed the paper.

REFERENCES CITED

- Aleman, L.B. (1993) Critical factors in obtaining meaningful fast MAS NMR spectra of non-integral spin quadrupolar nuclei: A review with particular emphasis on ^{27}Al MAS NMR of catalysts and minerals. *Applied Magnetic Resonance*, 4, 179–201.
- Barbieri, M., Cozzupoli, D., Federico, M., Fornaseri, M., Merlino, S., Orlandi, P., and Tolomeo, L. (1977) Harkerite from the Alban Hills, Italy. *Lithos*, 10, 133–141.
- Baur, W.H., and Ohta, T. (1982) The Si_5O_{16} pentamer in zunyte refined and empirical relations for individual silicon oxygen bonds. *Acta Crystallographica*, B38, 390–401.
- Blasse, G. (1964) Crystal chemistry and some magnetic properties of mixed metal oxides with spinel structures. *Philips Research Reports Supplement*, no. 3, 139 p.
- Burt, D.M. (1985) Compositional and phase relations among rare earth element minerals. In *Mineralogical Society of America Reviews in Mineralogy*, 21, 259–308.
- Cohen, M.H., and Reif, F. (1957) Quadrupole effects in nuclear magnetic resonance studies of solids. *Solid State Physics*, 5, 321–438.
- Davies, W.O., and Machin, M.P. (1970) Isomorphous replacements in harkerite and the relation of sakhaite to harkerite. *Canadian Mineralogist*, 10, 689–695.
- Dec, S.F., and Maciel, G.E. (1990) High-speed MAS NMR spectra of quadrupolar nuclides at high magnetic fields. *Journal of Magnetic Resonance*, 87, 153–159.
- Dirken, P.J., Jansen, J.B.H., and Schuiling, R.D. (1992) Influence of octahedral polymerization on ^{23}Na and ^{27}Al MAS NMR in alkali fluoroaluminates. *American Mineralogist*, 77, 718–724.
- Engelhardt, G., and Michel, D. (1987) High resolution solid state NMR of silicates and zeolites, 485 p. Wiley, Chichester, U.K.
- Freude, D., and Haase, J. (1993) Quadrupole effects in solid state nuclear magnetic resonance. In P. Diehl, E. Fluck, H. Günther, R. Kosfeld, and J. Seelig, Eds., *Progress in nuclear magnetic resonance*, 29, 1–90.
- Furrer, G., Ludwig, C., and Schindler, P.W. (1992) On the chemistry of the Keggin Al_{13} polymer: I. Acid-base properties. *Journal of Colloid and Interface Science*, 149(1), 56–67.
- Ghose, S., and Tsang, T. (1973) Structural dependence of quadrupole coupling constant e^2qQ/h for ^{27}Al and crystal field parameter D for Fe^{3+} in aluminosilicates. *American Mineralogist*, 58, 748–755.
- Grimmer, A.-R., von Lampe, F., Tarmak, M., and Lippmaa, E. (1983) Solid-state high resolution ^{29}Si NMR in zunyte. *Chemical Physics Letters*, 97, 185–187.
- Guiseppe, G., Mazzi, F., and Tadini, C. (1977) The crystal structure of harkerite. *American Mineralogist*, 62, 263–272.
- Hill, R.J., Craig, J.R., and Gibbs, G.V. (1979) Systematics of the spinel structure type. *Physics and Chemistry of Minerals*, 4, 317–339.
- Johansson, G. (1960) On the crystal structures of some basic aluminium salts. *Acta Chemica Scandinavica*, 14, 771–773.
- Kamb, W.B. (1960) The crystal structure of zunyte. *Acta Crystallographica*, 13, 15–24.
- Kirkpatrick, R.J. (1988) MAS NMR spectroscopy of minerals and glasses. In *Mineralogical Society of America Reviews in Mineralogy*, 18, 341–403.
- Kloprogge, J.T. (1992) Pillared clays: Preparation and characterization of clay minerals and aluminum-based pillaring agents. *Geologica Ultraetina. Mededelingen van de Faculteit Aardwetenschappen der Universiteit Utrecht*, no. 91, 349 p.
- Kunwar, A.C., Thompson, A.R., Gutowsky, H.S., and Oldfield, E. (1984) Solid state aluminum-27 NMR studies of tridecameric Al-oxo-hydroxy clusters in basic aluminum selenate, sulfate, and the mineral zunyte. *Journal of Magnetic Resonance Communications*, 60, 467–472.
- Liebau, F. (1985) Structural chemistry of silicates: Structure, bonding and classification, 347 p. Springer-Verlag, Berlin.
- Lippmaa, E., Samoson, A., and Mägi, M. (1986) High-resolution ^{27}Al NMR of aluminosilicates. *Journal of the American Chemical Society*, 108, 1730–1735.
- Loewenstein, W. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates. *American Mineralogist*, 39, 92–96.
- Louisnathan, S.J., and Gibbs, G.V. (1972) Aluminum-silicon distribution in zunyte. *American Mineralogist*, 57, 1089–1108.
- (1973) Zunyte: A comparison of neutron- and X-ray-diffraction studies. *American Mineralogist*, 58, 138.
- Machin, M.P., and Miehle, G. (1976) $[Al(SiO_4)]^{13-}$ tetrahedral pentamers in harkerite. *Neues Jahrbuch für Mineralogie Monatshefte*, 228–232.
- Meadows, M.D., Smith, K.A., Kinsey, R.A., Rothgeb, T.M., Skarjune, R.P., and Oldfield, E. (1982) High resolution solid-state NMR of quadrupolar nuclei. *Proceedings of the National Academy of Sciences*, 79, 1351–1355.
- Müller, D. (1982) Zur Bestimmung chemischer Verschiebungen der NMR-Frequenzen bei Quadrupolkernen aus den MAS-NMR-Spektren. *Annalen der Physik*, 39, 451–460.
- Müller, D., Gessner, W., Behrens, H.-J., and Scheler, G. (1981) Determination of the aluminium coordination in aluminium-oxygen compounds by solid-state high-resolution ^{27}Al NMR. *Chemical Physics Letters*, 79(1), 59–62.
- Murdoch, J.B., Stebbins, J.F., and Carmichael, I.S.E. (1985) High-resolution ^{29}Si NMR study of silicate and aluminosilicate glasses: The effect of the network-modifying cations. *American Mineralogist*, 70, 332–343.
- Oestrike, R., Yang, W.-H., Kirkpatrick, R.J., Hervig, R.L., Navrotsky, A., and Montez, B. (1987) High-resolution ^{23}Na , ^{27}Al , and ^{29}Si NMR spectroscopy of framework aluminosilicate glasses. *Geochimica et Cosmochimica Acta*, 51, 2199–2209.
- Pauling, L. (1933) The crystal structure of zunyte $Al_{13}Si_5O_{20}(OH,F)_{18}Cl$. *Zeitschrift für Kristallographie*, 84, 442–452.
- Phillips, B.L., Allen, F.M., and Kirkpatrick, R.J. (1987) High-resolution solid-state ^{27}Al NMR spectroscopy of Mg-rich vesuvianite. *American Mineralogist*, 72, 1190–1194.
- Phillips, B.L., Kirkpatrick, R.J., and Putnis, A. (1989) Si,Al ordering in leucite by high-resolution ^{27}Al MAS NMR spectroscopy. *Physics and Chemistry of Minerals*, 16, 591–598.
- Plee, D., Borg, F., Gatineau, L., and Fripiat, J.J. (1985) High-resolution ^{27}Al and ^{29}Si nuclear magnetic resonance study of pillared clays. *Journal of the American Chemical Society*, 107, 2362–2369.
- Samoson, A., and Lippmaa, E. (1983) Excitation phenomena and line-intensities in high-resolution NMR powder spectra of half-integer quadrupolar nuclei. *Physical Review B*, 28, 6567–6570.
- Sherriff, B.L., Grundy, H.D., and Hartman, J.S. (1991) The relationship between ^{29}Si MAS NMR chemical shift and silicate mineral structure. *European Journal of Mineralogy*, 3, 751–768.

- Smith, M.E. (1993) Application of ^{27}Al NMR techniques to structure determinations in solids. *Applied Magnetic Resonance*, 4, 1–64.
- Stebbins, J.F. (1991) NMR evidence for five-coordinated silicon in a silicate glass at atmospheric pressure. *Nature*, 351, 638–639.
- Tilley, C.E. (1951) The zoned contact-skarns of the Broadford area, Skye: A study of boron-fluorine metasomatism in dolomites. *Mineralogical Magazine*, 214, 621–666.
- Turco, G. (1962) La zunyite: Recherches expérimentales physico-chimiques en liaison avec l'étude du nouveau gisement de Beni-Embark. *Bulletin de la Société française de Minéralogie et de Cristallographie*, 85, 407–458.
- von Lampe, F., Müller, D., Gessner, A.-R., and Scheler, G. (1982) Vergleichende ^{27}Al NMR-Untersuchungen am Mineral zunyite und basischen Aluminium-Salzen mit tridekameren Al-oxo-hydroxo-aquo-Kationen. *Zeitschrift für anorganische und allgemeine chemie*, 489, 16–22.
- Watanabe, T., Shimizu, H., Masuda, A., and Saito, H. (1983) Studies of ^{29}Si spin-lattice relaxation times and paramagnetic impurities in clay minerals by magic-angle spinning ^{29}Si -NMR and EPR. *Chemistry Letters*, 8, 1293–1296.
- Zagal'skaya, Yu.G., and Belov, N.V. (1964) Concerning the crystal structure of zunyite $\text{Al}_{13}(\text{OH})_{18}\text{Si}_5\text{O}_{20}\text{Cl} = [\text{Al}_{12}(\text{OH})_{18}\square\text{SiO}_4] \cdot [\text{Al}(\text{SiO}_4)_4]\text{Cl}$. *Soviet Physics—Crystallography*, 8, 429–432.

MANUSCRIPT RECEIVED FEBRUARY 16, 1994

MANUSCRIPT ACCEPTED SEPTEMBER 14, 1994