

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

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### 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  $^{27}\text{Al}$  MAS NMR. Zunyite contains  $\text{Si}_5\text{O}_{16}$  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  $^{27}\text{Al}$  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  $\text{Si}_5\text{O}_{16}$  pentamer. This assumption is confirmed by the fact that  $\delta_{\text{iso}}$  of Al in the  $\text{AlSi}_4(\text{O},\text{OH})_{16}$  pentamer in harkerite is  $44 \pm 1$  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  $^{27}\text{Al}$  chemical shift (Lippmaa et al., 1986). This correlation holds well for the  $^{27}\text{Al}$  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  $\text{Si}_5\text{O}_{16}$  group, and the second a tridecameric  $\text{Al}_{13}$  group. The  $\text{Si}_5\text{O}_{16}$  group is special because its Si-O-Si intertetrahedral angles are 180°. The  $\text{Si}_5\text{O}_{16}$  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  $\text{Al}_{13}$  group occurs in natural minerals only in zunyite. Similar to it are  $\text{Al}_{13}$  groups in synthetic  $\text{Al}_{13}$  salts (Johansson, 1960). The  $\text{Al}_{13}$  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  $(\text{Si},\text{Al})\text{O}_4$ ,  $\text{AlO}_5$ , or  $\text{AlO}_6$  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  $^{27}\text{Al}$  chemical shift in framework aluminosilicate structures (Lippmaa et al., 1986). Until now, the maximum Al-O-Si angle used in this correlation was  $153.7^\circ$  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  $^{27}\text{Al}$  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  $^{27}\text{Al}$  NMR investigations on zunyite and  $\text{Al}_{13}$  salts established the

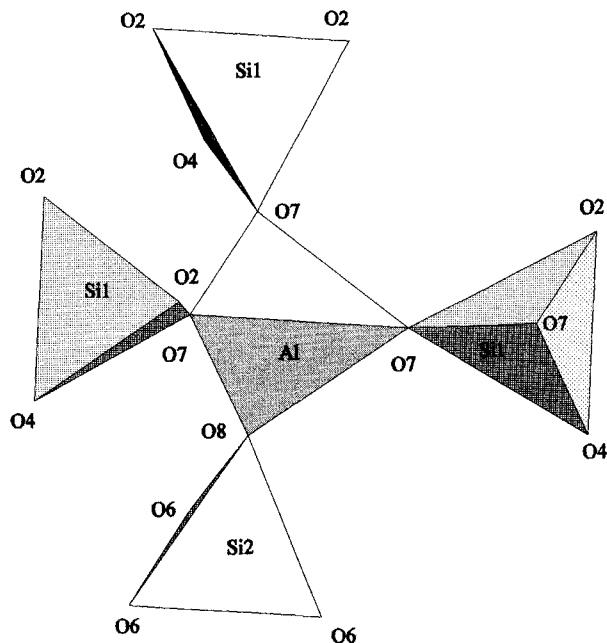


Fig. 1. The  $\text{AlSi}_4\text{O}_{16}$  pentamer in harkerite.

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

We present  $^{27}\text{Al}$  NMR data of the pentamer in harkerite and compare it with  $^{27}\text{Al}$  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  $180^\circ$ , 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 ( $\pm 15$  vol%), viz., rutile, galenite, pyrite, kaolinite and a  $\text{PO}_4$ - and  $\text{SO}_4$ -bearing phase with varying  $\text{PO}_4$ - $\text{SO}_4$  ratios, some of which had a

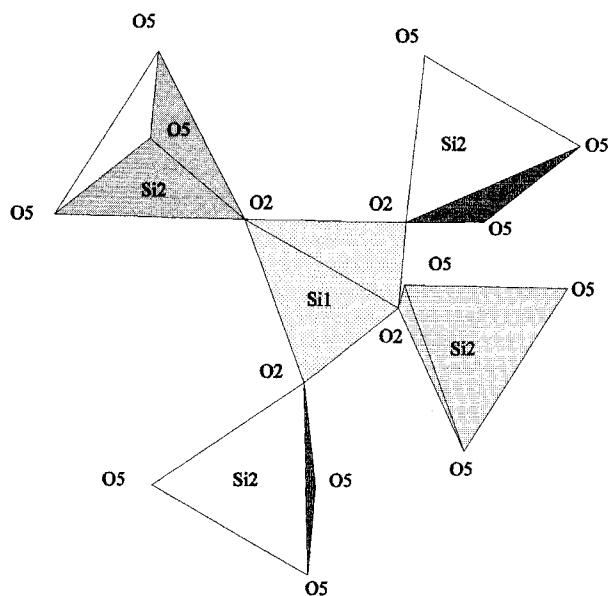


Fig. 2. The  $\text{Si}_5\text{O}_{16}$  pentamer in zunyite.

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 ( $\text{CaMgSiO}_4$ ), calcite ( $\text{CaCO}_3$ ), 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 ( $\text{MgO}$ ), 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  $^{27}\text{Al}$  NMR experiments. Monticellite, kirschsteinite, and serpentine contain 1 wt%  $\text{Al}_2\text{O}_3$ . Diopside contains 0.1 wt%  $\text{Al}_2\text{O}_3$ , 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  $^{27}\text{Al}$  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  $^{27}\text{Al}$  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  $^{27}\text{Al}$  chemical shifts are determined relative to an external standard of aqueous 1-M  $\text{AlCl}_3$  solution. Processing of the FID was carried out without any filtering. The quadrupole interaction and the isotropic chemical shifts ( $\delta_{\text{iso}}$ ) 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  $^{29}\text{Si}$  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- $\mu\text{s}$  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  $\text{Si}_5\text{O}_{16}$  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  $176^\circ$  (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  $\text{Si}_5\text{O}_{16}$  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  $\text{Si}_5\text{O}_{16}$  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  $180^\circ$  (Fig. 2). The  $\text{Si}_5\text{O}_{16}$  pentamer is surrounded by  $\text{AlO}_3(\text{OH})_3$  octahedra from the  $\text{Al}_{13}$  group. Twelve Al atoms are arranged in groups of three  $\text{AlO}_6$  octahedra around a central  $^{(4)}\text{Al}$  atom. The  $\text{Al}_{13}$  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.

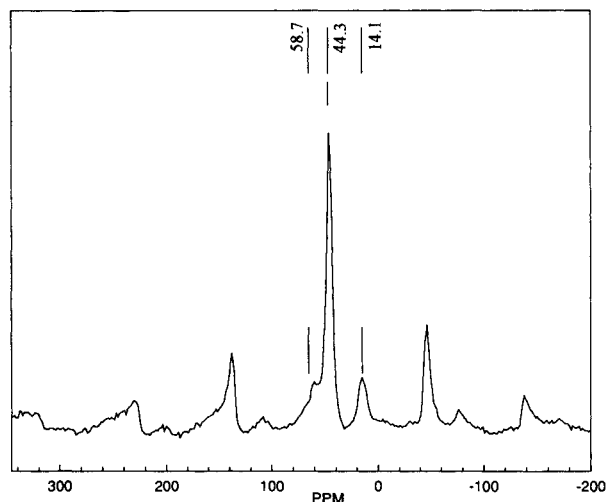


Fig. 3. The  $^{27}\text{Al}$  MAS NMR spectrum of harkerite at a magnetic field of 11.7 T.

## RESULTS AND DISCUSSION

### Harkerite

The  $^{27}\text{Al}$  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  $\text{Fe}^{3+}$  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  $\text{Fe}_2\text{O}_3$  content of 0.85 wt%. The peak position of the  $(-\frac{1}{2} \Rightarrow \frac{1}{2})$  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  $44 \pm 1$  ppm.

The 44-ppm value falls outside the range generally accepted for  $\text{AlO}_4$  (50–80 ppm) and  $\text{AlO}_5$  (30–40 ppm) (Smith, 1993). It fits well the correlation of the  $^{27}\text{Al}$  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  $^{27}\text{Al}$  isotropic chemical shift and  $\theta$  the Al-O-Si intertetrahedral angle. With  $\theta = 176^\circ$  (Guiseppetti et al., 1977),  $\delta_{\text{iso}}$  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  $\text{AlO}_4$  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  $^{27}\text{Al}$  chemical shift of 44 ppm for the Al

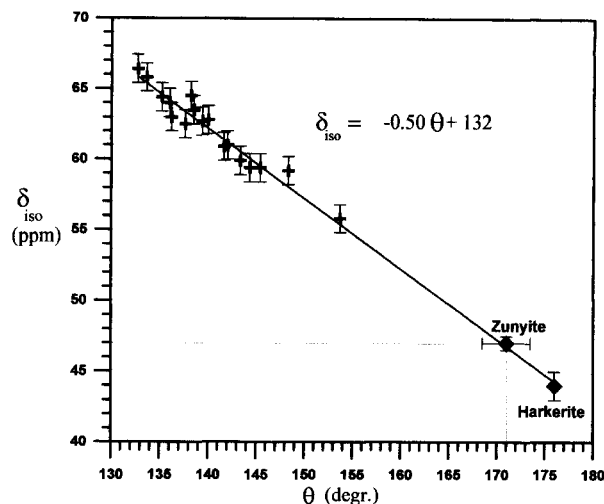


Fig. 4. Correlation between the isotropic chemical shift  $\delta_{iso}$  and the Al-O-Si intertetrahedral angle  $\theta$  for framework silicates. Crosses represent data from Lippmaa et al. (1986).

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.

### Zunyite

Zunyite has been studied previously by means of  $^{27}\text{Al}$  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  $\text{AlO}_4$  tetrahedron; the 7.7-ppm signal with the highest intensity represents Al from the 12  $\text{AlO}_6$  octahedra around the  $\text{AlO}_4$  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 zunyite. 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 zunyite 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  $46.8 \pm 0.5$  ppm and a QCC of 0.5–1.0 MHz. It falls outside the range for  $^{10}\text{Al}$  but is close to the value of 44

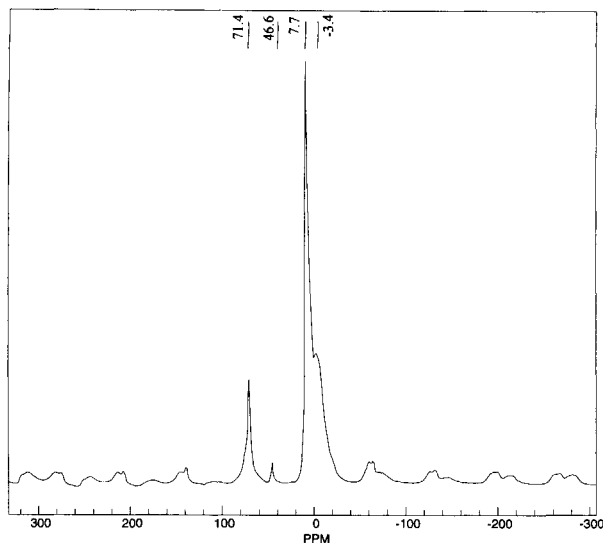


Fig. 5. The  $^{27}\text{Al}$  MAS NMR spectrum of zunyite at a magnetic field of 11.7 T.

ppm for Al in the pentamer of harkerite. As there is no reason to assume the presence of  $^{15}\text{Al}$ , it seems plausible, therefore, that the excess Al known from chemical analyses is incorporated into the  $\text{Si}_5\text{O}_{16}$  pentamer.

Baur and Ohta (1982) concluded from the shortening of the O2-O5 edge in the  $\text{Si}_2\text{O}_4$  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  $^{29}\text{Si}$  NMR study of zunyite. They stated that both the Si1 and Si2 sites are potential recipients for the excess Al. Zagal'skaya and Belov (1964) proposed that the  $\text{Si}_5\text{O}_{16}$  pentamer is in reality a  $\text{AlSi}_4\text{O}_{16}$  pentamer and that Si partly occupies the  $^{14}\text{Al}$  site of the  $\text{Al}_{13}$  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  $\text{Al}^{3+}$  into the central  $\text{Si}^{4+}$  site causes four O2 bonds to be polarized, in contrast to only one O2 for incorporation into the  $\text{Si}^{4+2}$  site. If Al would enter the Si2 site, an Al-O5-Al bond (last Al from an  $\text{Al}_{13}$  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  $^{27}\text{Al}$  MAS NMR spectra of zunyite

| Site                                | $\delta_{\text{iso}}$<br>(ppm) |      | QCC<br>(MHz) |       | $\eta$ | QB*<br>(Hz) |     | FWHH**<br>(Hz) |
|-------------------------------------|--------------------------------|------|--------------|-------|--------|-------------|-----|----------------|
|                                     | 1                              | 2    | 1            | 2     |        | 1           | 2   |                |
| $^{27}\text{Al}$ (Al <sub>3</sub> ) | 72                             | 71.6 | 0.6          | 0.8   | 0      | 20          | 30  | 520            |
| $^{27}\text{Al}$ (Al <sub>3</sub> ) | 8                              | 8.9  | 2.2          | 2.2   | 0      | 280         | 280 | 900            |
| $^{27}\text{Al}$ (penta)            | —                              | 46.8 | —            | 0.5–1 | 0      | —           | 30  | 250            |

Note: 1 = data from Kunwar et al., 1984; 2 = data from this study (error in  $\delta_{\text{iso}}$  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  $^{27}\text{Al}$  chemical shift with the Al-O-Si angle for framework aluminosilicates (vide supra). The  $^{27}\text{Al}$  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  $180^\circ$ , however. The 46.8-ppm value for zunyite must correspond to an angle smaller than  $176^\circ$ , 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  $171.2^\circ$  (Fig. 4). It must be noted that this value is based on an extrapolation of the data of Lippmaa over  $25^\circ$  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  $^{27}\text{Al}$  QCC of  $^{27}\text{Al}$  to the so-called shear strain  $\Psi$  in crystalline aluminosilicates. The shear strain is a measure of the departure of the individual bond angles from the ideal value of  $109.47^\circ$ . It is defined for Al in fourfold coordination as

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

Here  $\theta_i$  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.

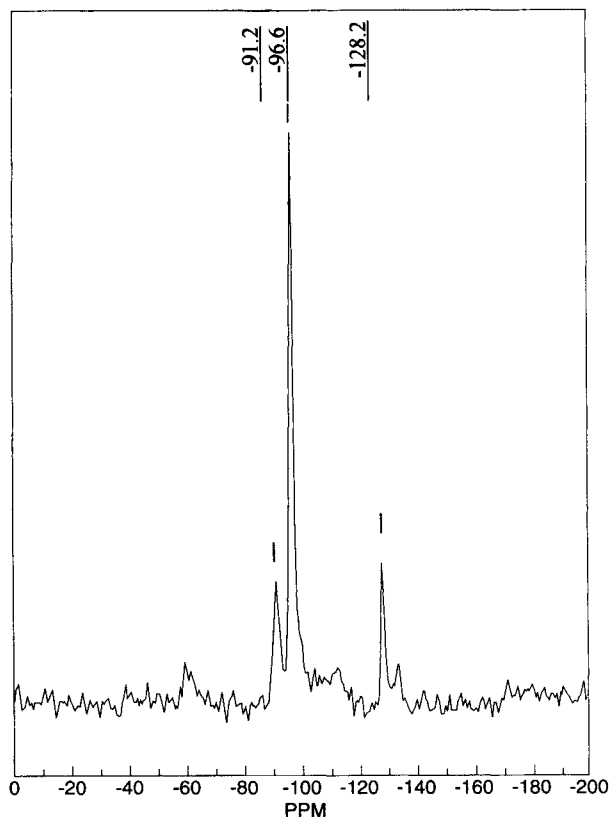


Fig. 6. The  $^{29}\text{Si}$  MAS NMR spectrum of zunyite at a magnetic field of 11.7 T.

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  $180^\circ$ . The  $-128.2$ -ppm peak is from Si in a  $Q^4(4\text{Si})$  configuration, also with Si-O-Si angles of  $180^\circ$ . 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  $180^\circ$ . 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 =  $153.7^\circ$ ) to scolecite ( $\delta_{iso} = 66.4$  ppm; Al-O-Si =  $132.7^\circ$ ). From this study it is apparent that this range can be extended to  $44 \pm 1$  ppm for Al sites in framework aluminosilicate structures with Al-O-Si angles of  $176^\circ$ .

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