

## NUCLEAR MAGNETIC RESONANCE STUDY OF Al:Si AND F:OH ORDER IN ZUNYITE

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### ABSTRACT

Zunyite [Al<sub>13</sub>Si<sub>5</sub>O<sub>20</sub>(OH,F)<sub>18</sub>Cl] possesses an unusual combination of an Al<sub>13</sub>O<sub>16</sub>(OH)<sub>24</sub> Keggin structure and a Si<sub>5</sub>O<sub>16</sub> pentamer unit. We used <sup>19</sup>F, <sup>27</sup>Al, <sup>29</sup>Si MAS and <sup>27</sup>Al MQMAS NMR spectroscopy of a series of samples with varying Al:Si and F:OH ratios to investigate the degree of atomic order in zunyite. The quadrupole coupling constant (C<sub>Q</sub>) and asymmetry parameter (η) obtained from simulations of <sup>27</sup>Al MAS and MQMAS spectra were compared with those derived from the electric field gradients (EFG), which were calculated from an *ab initio* cluster quantum model using the program Gaussian 98W. This comparison led to unequivocal assignments for <sup>29</sup>Si, <sup>27</sup>Al and <sup>19</sup>F MAS NMR peaks and showed that the number of Al substituting for Si(1) in the pentamer increases with Al content. The number of Al octahedra with one F atom increases with F content, whereas the number with two F atoms remains negligible, indicating that F preferentially occupies AlO<sub>4</sub>OHF octahedra.

*Keywords:* zunyite, <sup>27</sup>Al, <sup>29</sup>Si, <sup>19</sup>F, MAS NMR, multiple quantum MAS (MQMAS NMR), Keggin unit, *ab initio* quantum calculation.

### SOMMAIRE

La zunyite [Al<sub>13</sub>Si<sub>5</sub>O<sub>20</sub>(OH,F)<sub>18</sub>Cl] possède une combinaison inhabituelle d'une unité structurale de Keggin, de stoechiométrie Al<sub>13</sub>O<sub>16</sub>(OH)<sub>24</sub>, et une unité pentamérique, Si<sub>5</sub>O<sub>16</sub>. Nous nous sommes servis de la résonance magnétique nucléaire (NMR), en particulier les spectres <sup>19</sup>F, <sup>27</sup>Al, <sup>29</sup>Si MAS et <sup>27</sup>Al MQMAS, d'une série d'échantillons ayant des rapports Al:Si et F:OH variables, afin d'évaluer le degré d'ordre dans la zunyite. La constante de couplage quadripolaire (C<sub>Q</sub>) et le paramètre d'asymétrie (η) obtenus à partir de simulations des spectres <sup>27</sup>Al MAS et MQMAS ont été comparés aux valeurs dérivées des gradients du champ électrique (EFG), calculées à partir d'un modèle quantique *ab initio* d'une agglomération en utilisant le logiciel Gaussian 98W. Cette comparaison a mené à l'attribution non équivoque des pics MAS NMR de <sup>29</sup>Si, <sup>27</sup>Al et <sup>19</sup>F, et montre que le nombre d'atomes de Al substituant au Si(1) dans l'unité pentamérique augmente avec la teneur en Al. Le nombre d'octaèdres Al avec un atome de F augmente avec la teneur en F, tandis que le nombre d'octaèdres ayant deux atomes de F demeure négligeable, indication que le F préfère occuper un octaèdre AlO<sub>4</sub>OHF.

(Traduit par la Rédaction)

*Mots-clés:* zunyite, résonance magnétique nucléaire MAS <sup>27</sup>Al, <sup>29</sup>Si, <sup>19</sup>F, MAS quantique multiple, (MQMAS NMR), unité de Keggin, calcul quantique *ab initio*.

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## INTRODUCTION

The formula of zunyite,  $[\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}]$ , was first proposed by Pauling (1933), who discovered that it contains a  $\text{Si}_5\text{O}_{16}$  pentamer unit and a group of twelve aluminum octahedra. The structure was refined further by Kamb (1960) and Bartl (1970). The issue of Al:Si order has been a topic of controversy for many years. Zagal'skaya & Belov (1964) suggested that Si should be in the center of the Keggin structure, and Al, in the center of the pentamer. The structure refinements of Louisnathan & Gibbs (1972) and Baur & Ohta (1982) disproved this arrangement, but showed that excess Al could be accommodated in the center of the pentamer.

The  $^{29}\text{Si}$  magic angle spinning nuclear magnetic resonance (MAS NMR) spectrum of zunyite contains the lowest frequency peak ( $-128$  ppm) recorded in aluminosilicate minerals. However, despite several  $^{27}\text{Al}$  and  $^{29}\text{Si}$  NMR studies, there remain problems with peak assignment that may be related to Si-for-Al and F-for-OH substitutions. In this study, four samples of zunyite with varying F, Al and Si contents were analyzed, and the degree of atomic order was investigated with multiple-nuclei NMR spectroscopy and theoretical calculations.

## BACKGROUND INFORMATION

The structure is composed of two unusual units: an  $\text{Al}_{13}\text{O}_{16}(\text{OH})_{24}$  Keggin structure (Baker & Figgis 1970) and a  $\text{Si}_5\text{O}_{16}$  pentamer group. The pentamer units consist of four outer  $\text{SiO}_4$  tetrahedra with  $\text{Q}^1(1\text{Si})$  environments linked to a central  $\text{SiO}_4$  tetrahedron with a  $\text{Q}^4(4\text{Si})$  environment, the Si–O–Si bond angles being  $180^\circ$  (Louisnathan & Gibbs 1972). These are linked together by Keggin groups (Fig. 1), which are built of four trimers of hexacoordinated Al atoms connected by their vertices to a central  $\text{AlO}_4$  tetrahedron (Louisnathan & Gibbs 1972) (Fig. 1). This unit has the  $\alpha$ -Keggin conformation, which is only found in zunyite (Baker & Figgis 1970, Allouche *et al.* 2001).

Among the six nearest-neighbor (nn) atoms of the octahedrally coordinated Al(2) (Fig. 2), there are three oxygen atoms that form bridges to tetrahedral sites. Two O(5) atoms are shared with the Si(2) tetrahedron in the pentamer unit and with Al(2) in the Keggin unit, and O(1) is linked to the Al(1) of the central tetrahedron of the Keggin unit. Three other oxygen atoms complete the Al(2) octahedron: one O(3) and two O(4) [O(4)A, O(4)B] that are connected to hydrogen atoms. Bartl (1970) identified the positions for these hydrogen atoms using neutron diffraction. The H(2) linked to O(3) lies in the straight line along the *c* axis of zunyite, with the H(2)–O(3) distance being about  $0.99 \text{ \AA}$  (Bartl 1970). Baur & Ohta (1982) suggested two possible positions for the H(1) atoms, which are bonded to O(4): H(1A) and H(1B) (Fig. 2). The interatomic distance for O(4)–H(1A) is  $0.99 \text{ \AA}$ , and that for O(4)–H(1B) is  $0.94 \text{ \AA}$ .

Thus, distinct environments at the Al(2) octahedron are produced.

Bearing in mind that the OH at the O(3) position cannot be replaced by F, owing to the avoidance of Cl for F (Louisnathan & Gibbs 1972, Baur & Ohta 1982), the substitution of F for OH at the O(4) site produces further possible environments at the Al(2) site. The two H positions, H(1A), H(1B), give four possible environments if one OH is replaced by F. There is also the possibility of both O(4)H(1A) and O(4)H(1B) being replaced by F. As a result, a total of seven possible different local environments are possible around Al(2) (Fig. 2):

I: O(1), O(3), 2[O(5)], 2[O(4)H(1A)]

II: O(1), O(3), 2[O(5)], 2[O(4)H(1B)]

III: O(1), O(3), 2[O(5)], O[(4A)H(1A)], F(4)

IV: O(1), O(3), 2[O(5)], O[(4A)H(1B)], F(4)

V: O(1), O(3), 2[O(5)], O[(4B)H(1A)], F(4)

VI: O(1), O(3), 2[O(5)], O[(4B)H(1B)], F(4)

VII: O(1), O(3), 2[O(5)], 2F(4)

Taking into consideration the symmetry of the different local environments, these seven possible environments produce five non-equivalent clusters by combining III with V, and IV with VI, because O(4A) and O(4B) are equivalent.

The  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra have been previously obtained (Grimmer *et al.* 1983, Sherriff *et al.* 1991, Dirken *et al.* 1995). Although assignments of the major peaks at  $-97$  and  $-128$  ppm for  $^{29}\text{Si}$ , and  $72$  and  $10$  ppm for  $^{27}\text{Al}$ , in the MAS NMR spectra of zunyite have been determined, there is still controversy over a minor  $^{29}\text{Si}$  peak at  $-91$  ppm and the  $^{27}\text{Al}$  peaks at about  $46$  ppm and  $-3$  ppm.

Kunwar *et al.* (1984) and Dirken *et al.* (1995) derived a value of  $2.2 (\pm 0.5)$  MHz for the quadrupole coupling constant ( $C_Q$ ) for the broad resonance between  $10$  and  $-3$  ppm in the  $^{27}\text{Al}$  MAS NMR spectrum using a weighted least-squares analysis and the field-dependent second-order quadrupole-induced shift. This value differs significantly from the  $7.3$  MHz suggested by the longitudinal strain  $\alpha$  value of  $0.12$  (Kunwar *et al.* 1984). The peak at about  $10$  ppm is symmetrical in the spectrum shown by Kunwar *et al.* (1984), who assumed that only one site is represented. However, the spectrum obtained by Dirken *et al.* (1995) shows a second broad  $^{27}\text{Al}$  resonance at  $-3$  ppm, which was interpreted as being caused by impurities containing Al in octahedral coordination.

In this study, the  $^{27}\text{Al}$  NMR parameters were estimated from the electric field gradient (EFG) derived

from theoretical *ab initio* cluster quantum calculations for all the possible Al environments in zunyite. Comparison of these values with the experimental NMR data allowed investigation of the assignment of the  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR peaks. The degree of order of Al and Si, and F and OH, in zunyite was investigated using a series of samples of zunyite from different locations, with various values of the Al:Si and OH:F ratios, with additional information from  $^{19}\text{F}$  MAS NMR, and  $^{27}\text{Al}$  3QMAS NMR.

#### EXPERIMENTAL PROCEDURES

##### Materials

Euhedral tetrahedral crystals of zunyite were hand picked under a binocular microscope. Sample 112911 consists of colorless crystals from Utah. Some crystals in this sample are coated with Fe oxides and have oscillatory zoning, shown in an electron back-scatter image acquired with an electron microprobe (EMP). We detected some rutile inclusions and a trace amount of pyrophyllite in this sample by X-ray diffraction. Sample E1609 from the Zuni mine in Colorado is composed of gray crystals with some solid and fluid inclusions. Trace amounts of quartz, rutile and akdalaita were detected by XRD. Sample Karab from the Kazabas deposit in Kazakhstan consists of clear crystals. Rutile and possibly a trace amount of pyrophyllite were found by XRD. Sample M16225 from South Africa contains pink zoned tetrahedra, with trace amounts of rutile, diaspore and akdalaita, as documented by XRD.

##### X-ray diffraction

Powder X-ray diffraction was used to determine the purity of the four samples of zunyite. The data were collected at room temperature with a computer-controlled Philips PW170 automated powder diffractometer using  $\text{CuK}\alpha$  radiation,  $1^\circ$  divergence and anti-scatter slits, a step width of  $0.02^\circ$  for  $\Delta 2\theta$ , a  $2\theta$  range from  $10$  to  $70^\circ$ , and count times of 5 s per step.

##### Chemical analyses

Single crystals of zunyite were analyzed using a computer-controlled electron microprobe (CAMECA SX-50) operating at 15 kV and 20 nA, with a beam size of  $5\ \mu\text{m}$ , and count times of 20 s, with kyanite as a standard for Al and Si, fluorite for F, and halite for Cl. The amount of OH was calculated to ensure charge balance. Results were calculated using a ZAF correction, and matrix corrections were performed with the PAP procedure. Four to thirteen points were analyzed across each mineral grain, and the average composition and standard deviations were calculated for each sample (Table 1).

##### $^{27}\text{Al}$ MAS NMR

The  $^{27}\text{Al}$  MAS NMR spectra for all samples were obtained on a Bruker Avance-500 spectrometer at Queen's University, operating at 130.3 MHz (11.7 T). The MAS NMR experiments were carried out using a 4-mm MAS probe. Powder samples were packed into zirconium oxide rotors and were rotated at speeds from 10 to 12.5 kHz. The single-pulse  $^{27}\text{Al}$  spectra were recorded with a small pulse-width of  $0.4\ \mu\text{s}$  ( $15^\circ$ ) and a recycle delay of 0.3 s. Typically, a spectral width of 125 kHz was used. Peak positions were referenced to  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  using an aqueous solution of aluminum nitrate. The  $^{27}\text{Al}$  MAS NMR spectra were obtained at four different rates of spin (5, 10, 17 and 30 kHz) for sample E1609 at the Université Louis Pasteur, Strasbourg, France.

##### $^{27}\text{Al}$ Multiple Quantum MAS (3QMAS) NMR

The triple-quantum MAS (3QMAS) spectrum for sample 112911 was collected on a Bruker Avance-500 spectrometer at the Queen's University using the z-filter pulse sequence (Frydman & Harwood 1995, Amoureux *et al.* 1996). The pulse widths for 3Q excitation and 3Q-to-1Q conversion were 4.0 and 1.0  $\mu\text{s}$ , respectively. The pulse width for the selective  $90^\circ$  pulse was 20  $\mu\text{s}$ , and the recycle delay was 0.5 s. A total of 480 transients were collected for each of the 128  $t_1$  increments. The 3QMAS spectrum was plotted in full scale without shearing.

##### $^{29}\text{Si}$ MAS NMR

The  $^{29}\text{Si}$  MAS spectra were obtained using a Doty high-speed MAS probe on a Bruker AMX500 Multinuclear Fourier Transform Spectrometer at the Prairie Regional NMR Facility, Winnipeg, Manitoba. Powdered samples of zunyite were spun at 6–8 kHz in a 5 mm rotor with a Doty MAS probe. Spectra were recorded at the frequency of 99.3 MHz (11.7 T) with 4096 data points,  $30^\circ$  pulse, and delays from 5 to 300 s between pulses. Different delays were tried to ensure that all peaks had equivalent rates of relaxation. Peak positions were measured with reference to tetramethylsilane (TMS).

##### $^{19}\text{F}$ MAS NMR

The  $^{19}\text{F}$  MAS NMR experiments were obtained at Université Louis Pasteur using a Bruker DSX500 Spectrometer with a 2.5 mm MAS probehead at a spin rate of 30 kHz, 200 kHz spectral width, 3  $\mu\text{s}$  pulse, 3 s recycle delay, and 64 accumulated free induction decay (FID). The spectra were referenced to 0 ppm for  $\text{CFCl}_3$ , with NaF at  $-221$  ppm as a secondary solid-state reference.

*Ab initio quantum-calculation model*

For nuclei with spin number  $I > \frac{1}{2}$ , such as  $^{27}\text{Al}$ , the non-spherical symmetry of charge distribution on the nucleus produces a nuclear quadrupole moment ( $eQ$ ), which will interact with the electric field gradient (EFG) at the nucleus (Dehmelt & Hubert 1950, Cohen & Reif 1957, Slichter 1992). As a result, the electrostatic interaction between the  $eQ$  and EFG will give a quadrupolar lineshape.

The quadrupolar coupling constant ( $C_q$ ) and asymmetry parameter ( $\eta$ ) can be derived from the EFG using the following equations (Slichter 1992):

$$C_q = eV_{zz}Q / h \quad (1)$$

$$\eta = |V_{xx} - V_{yy}| / V_{zz} \quad (2)$$

where  $e$  is the electron charge,  $Q$  is nuclear quadrupolar moment,  $V_{zz}$  is the maximum EFG tensor component,  $V_{xx}$  and  $V_{yy}$  are the other two components of EFG tensor in principal axis system (PAS), and  $h$  is Planck's constant.

The EFG tensors for each of the possible Al environments in zunyite were obtained from *ab initio* cluster calculations using a standard, self-consistent-field, molecular-orbital method (SCF-MO) with the 6–

31G(d) basis set and B3LYP exchange functions using Gaussian 98W on a Pentium II computer (Dong *et al.* 2000).

As the more distant atoms are negligible in their contributions to EFG at an Al site, they were not included in the quantum calculations, in a compromise between accuracy and efficiency. Therefore, a total of forty-one atoms in the first four shells, within the radius of 3.23 Å, were included in the cluster around the tetrahedral Al(1)K in the Keggin unit, including twelve H atoms in the third layer. The cluster with Al replacing Si(1) [Al(1)P] in the central tetrahedron of the pentamer unit has twenty-one atoms within the radius of 3.53 Å, including the twelve H atoms in third layer. The cluster with Al replacing the Si(2) [Al(2)P] in the pentamer unit was formed with seven atoms in two shells within the radius of 3.25 Å.

Atoms within the radius of 3.25 Å around Al(2)K were included in the calculation. Thus, fifteen atoms were chosen for clusters without F in the Al(2)K octahedron, with the number of atoms in the cluster being reduced by one for each substitution of F for OH. The coordinates of atoms in the clusters were taken from the single-crystal XRD refinement of the zunyite structure (Baur & Ohta 1982). There are more atoms included in the clusters for tetrahedral Al sites than for octahedral Al sites within a similar radius.

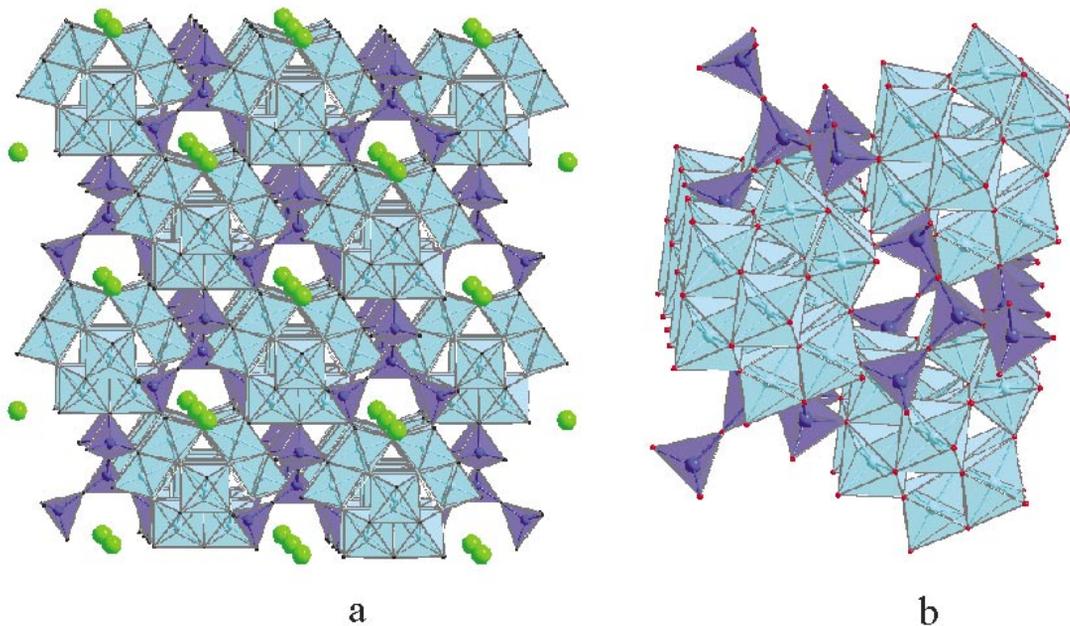


FIG. 1. The zunyite structure, with the Keggin unit connected by the pentamer unit to form the framework. Black: Si or Al tetrahedra, light turquoise: Al octahedron, green spheres: Cl atoms. (a) The Keggin units and pentamers, with compensating chloride ions (b), emphasizing the Keggin and pentamer units.

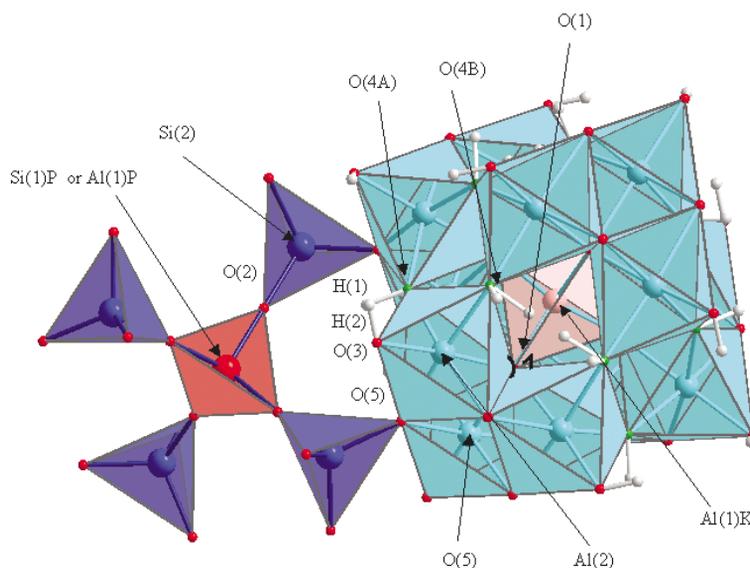


FIG. 2. The pentamer and Keggin structure in zunyite, with labels of atoms. Left: pentamer structure; right: the Keggin structure.

TABLE 1. CHEMICAL COMPOSITION OF SAMPLES OF ZUNYITE

	M16225	E1609	112911	Karab
SiO <sub>2</sub> wt.%	24.67 (0.77)	24.41 (0.63)	23.23 (0.88)	24.51 (1.31)
Al <sub>2</sub> O <sub>3</sub>	55.50 (0.49)	56.06 (0.45)	56.69 (3.2)	55.87 (1.23)
Fe <sub>2</sub> O <sub>3</sub>	0.01 (0.02)	0.01 (0.00)	0.06 (0.06)	0.00
F	4.46 (0.11)	5.07 (0.26)	6.11 (0.42)	6.60 (1.12)
Sum	84.64	85.46	85.99	86.88
Si <i>apfu</i>	4.91	4.86	4.57	4.88
Al	13.03	13.16	13.14	13.12
F	2.81	3.19	3.80	4.16
Ti	0.02	0.00	0.01	0.01
OH	15.18	15.03	14.68	14.2
Cl	1.00	0.92	0.52	0.64
F/OH	0.19	0.21	0.26	0.29
Al/Si	2.65	2.71	2.88	2.69

Zhou & Sherriff (2003) used the extremely well-ordered mineral tugtupite to compare the results of MO calculations using different sizes of cluster with experimental data and theoretical calculations using WIEN2k. They found the maximum uncertainties for  $C_q$ ,  $\eta$  and  $\delta_{iso}$  were  $\pm 0.55$  MHz,  $\pm 0.46$ , and  $\pm 0.7$  ppm, respectively. For a complex disordered material such as glass, MO calculations have been found to give only semi-quantitative estimates of the trends of EFG and so of  $C_q$  and  $\eta$  (Tossell & Lazeretti 1986, Tossell 1993, 1999).

Therefore QI parameters obtained from MO calculations in this study are assumed to be only semiquantitative.

#### Fitting programs for NMR spectra

Simulations of the <sup>29</sup>Si, <sup>19</sup>F and <sup>27</sup>Al MAS NMR spectra were done with the least-squares iterative programs XEDPLOT (Bruker Ltd.), Winfit (Massiot *et al.* 2002) and MASAI (Quoineaud *et al.* 2002). For nuclei with spin number (I) of 1/2, the number, line broadening and initial positions of peaks were input, and the isotropic chemical shifts and relative intensities calculated iteratively. The uncertainty in these values was found to be less than 5% by comparing the results using different input data.

Values of  $C_q$ ,  $\eta$  and  $\delta_{iso}$  for <sup>27</sup>Al were obtained by simulating the central transition lineshape and slices of the 3QMAS spectra using Winfit. The uncertainties for  $\delta_{iso}$ ,  $C_q$ , and  $\eta$  were estimated to be about  $\pm 0.5$  ppm,  $\pm 0.4$  MHz and  $\pm 0.15$ , respectively.

The relative intensities for <sup>27</sup>Al MAS NMR peaks were calculated as Al atoms per formula unit (*apfu*) with the relative intensity of the Al(1)K, Peak A, being scaled to one.

## RESULTS AND DISCUSSION

The F content for the four samples Karab, 112911, E1609 and M16225 varies from 4.46 to 6.60 wt.%, the

Al:Si ratio from 2.65 to 2.88, and the F:OH ratio from 0.19 to 0.29 (Table 1). The trace amount of pyrophyllite found by XRD in the samples 112911 and Karab were not considered sufficient to produce a visible NMR signal.

The  $^{29}\text{Si}$  spectra for all the samples contain three peaks at  $-91$ ,  $-96$  and  $-128$  ppm (Fig. 3). However, the relative intensities of these peaks show some variation among samples (Table 2). The  $^{27}\text{Al}$  MAS NMR spectra for all the samples consist of two narrow, symmetrical peaks at about 72 ppm (Peak A) and 46 ppm (Peak B), as well as a narrow, symmetrical peak at 10 ppm (Peak C) that overlaps a broad peak centered at  $-3$  ppm (Peak D) (Fig. 4). These spectra, for samples of zunyite with different chemical compositions, are very similar to the spectrum of Dirken *et al.* (1995). The intensity of the Peak D increases with F content.

#### Tetrahedral sites

The  $^{29}\text{Si}$  peak at  $-96$  ppm is assigned to Si(1)P in the outer tetrahedra of the pentamer group with  $Q^1(1\text{Si})$  configuration (Grimmer *et al.* 1983, Sherriff *et al.* 1991, Dirken *et al.* 1995). The peak at  $-128$  ppm is assigned to the Si(2) at the inner tetrahedron with  $Q^4(4\text{Si})$  configuration, which is at a very low frequency owing to four almost straight  $\langle\text{Si}-\text{O}-\text{Si}\rangle$  angles (Grimmer *et al.* 1983, Sherriff *et al.* 1991).

Grimmer *et al.* (1983) assumed that the  $^{29}\text{Si}$  peak at  $-91$  ppm is caused by an impurity of nacrite in their sample of zunyite. From the bond distances in the pentamer, Baur & Ohta (1982) showed that excess Al replaces some Si atoms at the inner tetrahedron of the pentamer unit. Dirken *et al.* (1995) suggested that part of the intensity of the peak at  $-91$  ppm might be due to such a replacement. Sherriff *et al.* (1991) demonstrated that substituting one Al for a neighboring Si could cause a positive shift of around 6 ppm for  $^{29}\text{Si}$ , with an Si-O-T angle of  $180^\circ$ . There is a positive correlation between the Al:Si ratio and the relative intensity of the  $^{29}\text{Si}$  peak at  $-91$  ppm (Table 2). Therefore, in this study, we demonstrate that in zunyite, the replacement of an adjacent

Si by Al(1)P shifts the  $^{29}\text{Si}$  peak from  $-96$  ppm to  $-91$  ppm for the  $Q^1\text{Si}(2)(\text{Al})$  configuration.

To investigate the assignment of the  $^{27}\text{Al}$  Peak B, the quantum cluster method was used to calculate the EFG and hence  $C_Q$  and  $\eta$ . The value of  $\delta_{\text{iso}}$  could then be obtained by simulating the experimental spectra, using the calculated quadrupolar parameters, for Al substituting into either the Si(1) or Si(2) sites in the pentamer (Table 3). The incorporation of Al at the Si(1) site [Al(1)P] produces values of 2.35 MHz for  $C_Q$ , 0.93 for  $\eta$  and 46.5 ppm for  $\delta_{\text{iso}}$ . The values for  $C_Q$  and  $\delta_{\text{iso}}$  are close to the values measured by Kunwar *et al.* (1984) and Dirken *et al.* (1995). However, they estimated  $\eta$  value to be between 0 and 0.2. Aluminum substituting at the Si(2) site gives a large value of 6.41 MHz for  $C_Q$ , which does not agree with the narrow symmetrical peak. Thus, our results confirm the finding of Dirken *et al.* (1995) that the  $^{27}\text{Al}$  MAS NMR Peak B is caused by Al replacement of Si(1) in the central tetrahedron of the pentamer.

The Al content of the central position in the pentamer, calculated from relative intensities of peaks, increases from 0.2 *apfu* for M16225, with 13.03 *apfu* total Al, to 0.4 *apfu* for E1609, 112911 and Karab, which have 13.16, 13.14 and 13.12 *apfu* total Al, respectively. With Al substituting for Si in the pentamer, the charge imbalance may be compensated by excess

TABLE 2. ISOTROPIC CHEMICAL SHIFTS AND RELATIVE INTENSITIES FROM SIMULATIONS OF  $^{29}\text{Si}$  MAS NMR SPECTRA

Sample	Al/Si	Peak 1		Peak 2		Peak 3	
		$\delta_{\text{iso}}$	R.I.	$\delta_{\text{iso}}$	R.I.	$\delta_{\text{iso}}$	R.I.
M16225	2.7	-90.6 ppm	16%	-96.0 ppm	64%	-127.8 ppm	20%
Karab	2.7	-90.8 ppm	16%	-96.0 ppm	66%	-127.6 ppm	18%
E1609	2.7	-90.7 ppm	16%	-95.9 ppm	61%	-127.7 ppm	23%
112911	2.9	-90.5 ppm	27%	-95.9 ppm	55%	-127.6 ppm	18%

$\delta_{\text{iso}}$ : isotropic chemical shift; R.I.: relative intensity.

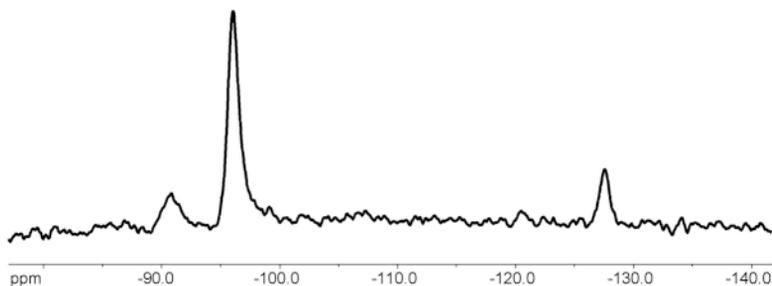


Fig. 3.  $^{29}\text{Si}$  MAS NMR spectrum of zunyite (sample 112911).

H<sup>+</sup> or displacement of H, as no other cation was found in elemental analyses.

All previous investigators agree that the <sup>27</sup>Al Peak A represents the central tetrahedron in the Keggin unit, which is surrounded by twelve Al-centered octahedra (Kunwar *et al.* 1984, Kirkpatrick & Phillips 1993, Dirken *et al.* 1995). The cluster quantum calculation for the central Al tetrahedron in the Keggin unit gave 1.86 MHz and 0.1 for C<sub>Q</sub> and η (Table 3). The C<sub>Q</sub> value is close to that of 2.2 MHz from Kunwar *et al.* (1984), but further from the value of 0.8 MHz proposed by Dirken *et al.* (1995). However, in these studies, a value of zero was assumed for η, and C<sub>Q</sub> was estimated by simulating the field-dependent second-order quadrupolar lineshape. Simulation of the <sup>27</sup>Al spectrum of the Karab specimen in this study gave values of 1.96 MHz for C<sub>Q</sub> and 0.1 for η, close to the results for C<sub>Q</sub> of Kunwar *et al.* (1984). The small values of C<sub>Q</sub> and η are due to the highly symmetrical distribution of atoms around Al(1)K. The shear strain Ψ of Al(1) (Ghose & Tsang 1973) is almost zero because the O–Al–O angles in the tetrahedron are the ideal value of 109.47°. The calculated isotropic chemical shift for Al(1)K is 72.0 ppm, which is in the usual range for Al in tetrahedral configuration. The close agreement between our calculated parameters and the experimental data shows the reliability of the calculated results for the tetrahedron-related peaks in this study.

A 3QMAS experiment was run to obtain better resolution of the octahedral components of the Al spectrum than with MAS NMR. The value of δ<sub>iso</sub> and the second-order quadrupole shift (δ<sup>2Q</sup><sub>iso</sub>) of the two <sup>IV</sup>Al sites can be obtained from the <sup>27</sup>Al 3QMAS spectrum (Fig. 5) using the equations of Baltisberger *et al.* (1996):

$$\delta_{3QMAS} = -(17/31)\delta_{iso} + (10/31)\delta^{2Q}_{iso} \quad (3)$$

$$\delta_{MAS} = \delta_{iso} + \delta^{2Q}_{iso} \quad (4)$$

where δ<sub>3QMAS</sub> is the center of gravity of the peak in the F1 dimension, and δ<sub>MAS</sub>, the center of gravity of the peak measured in the F2 dimension. These conventions are in agreement with the Unified Scaling of MQMAS and STMAS of Amoureux *et al.* (2002). The isotropic chemical shifts were calculated to be 70.6 and 46.2 ppm for these sites using equations (3) and (4). Direct simulation of slices of the 3QMAS spectrum using the MASAI program (Quoineaud *et al.* 2002) gave values for C<sub>Q</sub> and η of 1.96 MHz, 0.1 and 2.25 MHz, 0.7 for the tetrahedron-related peaks A and B (Table 4). There is an excellent agreement between the results from simulations of MQMAS and MAS spectra, and from quantum calculations.

#### Octahedral sites in the Keggin unit

The high percentage of <sup>19</sup>F, a magnetically abundant nucleus with a large magnetogyric ratio (γ), produces strong dipolar interactions, causing very broad <sup>19</sup>F MASNMR peaks for zunyite. In this experiment, no

TABLE 3. CALCULATED EFG TENSORS (ATOMIC UNITS), C<sub>Q</sub> AND η USING THE *ab initio* QUANTUM CLUSTER METHOD FOR ALL POSSIBLE Al SITES IN ZUNYITE

Sites	Peak	EFG tensors			C <sub>Q</sub> (MHz)	η
		V <sub>xx</sub>	V <sub>yy</sub>	V <sub>zz</sub>		
Al(1)K		-0.054	0.024	0.030	1.86	0.1
Al(1)P		-0.067	-0.004	0.068	2.35	0.93
Al(2) (environment I)	3	-0.156	0.049	0.135	3.34	0.55
Al(2) (environment II)	4	-0.071	0.029	0.065	2.44	0.50
Al(2) (environment III & IV)	5	-0.210	-0.009	0.104	7.26	0.45
Al(2) (environment V & VI)	6	-0.131	0.047	0.122	4.50	0.57
Al(2) (environment VII)	7	-0.195	-0.0953	0.201	6.69	0.51

K: Keggin unit, P: pentamer unit.

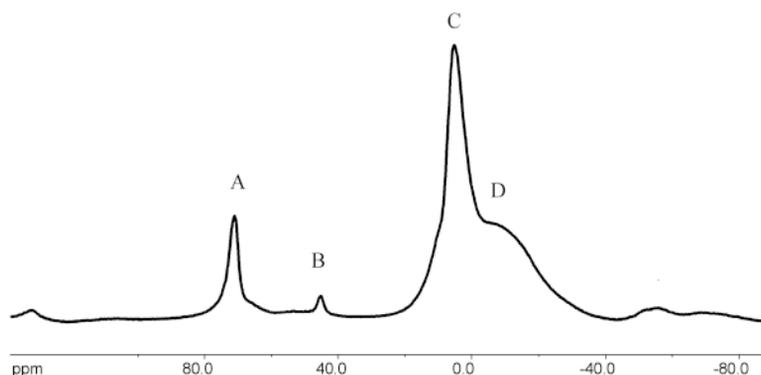


FIG. 4. <sup>27</sup>Al MAS NMR spectrum of zunyite (sample Karab).

efficient homo-decoupling experiment was available to reduce the broadening of lines. However, the high rate of sample rotation, 25 kHz, allowed the observation of multiple sites in the  $^{19}\text{F}$  MAS NMR spectra of zunyite.

The broad  $^{19}\text{F}$  spectrum of samples E1609 can be simulated with two overlapping peaks at  $-133$  and  $-130$  ppm (Fig. 6), which vary in relative intensity with F content (Table 5). Three peaks would be expected for the three Al octahedral environments (III–IV, V–VI and VII), although the differentiation of the aluminum sites would not necessarily apply to fluorine. As the Keggin unit does not have a perfect tetrahedral symmetry, F at the two O(4)H sites would be crystallographically inequivalent, leading to site differentiation. The isotropic chemical shifts of  $-133$  and  $-130$  ppm indicate that F is covalently bonded to Al, in a bridging position (Huve *et al.* 1992, Zeng & Stebbins 2000).

In the  $^{27}\text{Al}$  MAS NMR spectra of zunyite, Peak A narrows and increases in height as the rate of spin increases from 5 to 30 kHz, whereas there is no obvious change in the peaks for octahedral Al (Fig. 7). This increase of the peak with rotation speed, due to the Keggin tetrahedral site, is indicative of a small quadrupolar interaction. Once the central transition is reduced to its second-order lineshape, increasing the rate of spin adds more intensity from the isotropic peaks of the external transitions to the central transition peak. For a low value of quadrupolar interaction, the second-order quadrupolar shifts are small, and these isotropic lines are superimposed. This situation does not occur for the peaks for octahedral Al, with much larger values of  $C_Q$ .

The broad resonance due to octahedrally coordinated  $^{27}\text{Al}$  can be resolved into two components in the isotropic chemical shift dimension (F1) of the  $^{27}\text{Al}$  3QMAS spectrum (Fig. 5). Fluorine coupling, as well as possible disorder caused by H displacement due to  $\text{Al}^{3+}$  charge balance, would cause some broadening of the peaks. The five possible environments of  $^{27}\text{Al}$  described earlier, could have slightly different chemical shifts. The overlap of such peaks could lead to a distribution of chemical shifts and quadrupolar parameters, which could be modeled with the MASAI software of Quoineaud *et al.* (2002). However, only two chemical distributions were found in slices of the 3QMAS  $^{27}\text{Al}$  spectrum, although there may be some distribution of quadrupolar parameters due to the different Al(2) environments. It was

impossible to extract such discrete distributions of  $C_Q$  and  $\eta$  from the experimental spectrum, although multiple environments were indicated by the broad octahedron-related peaks. The MAS  $^{27}\text{Al}$  spectrum was simulated using the quadrupolar parameters measured on slices of the 3QMAS experiments. The intensities of each line in these spectra varies because of the dependence of the triple quantum excitation-conversion efficiency on  $C_Q$  and on the strength of the radio-frequency field. Only four components were therefore used, two for the tetrahedron-related peaks and two for the octahedron-related peaks (Table 4). With this fitting procedure, the lines attributed to the octahedral sites have  $\delta_{\text{iso}}$  values of 7.8 (Peak C) and 14 ppm (Peak D), with  $C_Q$  and  $\eta$  of 2.80 MHz, 0.4, and 7.08 MHz, 0.4 for these two sites (Fig. 8), respectively. These represent 2.5 and 9.5 apfu Al, respectively, for the sample Karab.

Quantum calculations lead to the values of  $C_Q$  and  $\eta$  for the five possible local environments at octahedral Al sites as well as the two tetrahedral sites (Table 3). The EFG tensors for tetrahedral sites Al(1)K, with a site symmetry of  $\bar{4}3m$ , and Al(1)P, with a site symmetry of  $3m$ , are several times smaller than for octahedral Al(2), with a site symmetry of  $m$ . For Al(2), the calculated values of EFG along the X axis ( $V_{xx}$ ) in the principal axis system (PAS) are negative, those along the Z axis ( $V_{zz}$ ) are positive, and those along Y axis ( $V_{yy}$ ) are very small. The maximum EFG components ( $V_{zz}$ ) are negative and along the X crystallographic axis, except in the case of two F substitutions for O(4)H, where the maximum is along the Z axis and positive. These show the general geometrical character for Al(2), where the equatorial ligands overbalance the contributions from the apical ones.

The calculated values of quadrupolar parameters can be grouped into three categories (Table 3). The Al(2) sites with 2 OH (environments I and II) have a  $C_Q$  of 2.4 to 3.3 MHz, those with 1OH and 1 F (environments III, IV, V and VI), a  $C_Q$  of 7.3 and 4.5 MHz, and in those with 2 F (environment VII),  $C_Q$  is 6.9 MHz (Table 3). There is, therefore, a general tendency to increase  $C_Q$  with the progressive replacement of OH by F. The calculated  $\eta$  for all the environments is approximately 0.5, which is close to the experimental value. As the Al–F bond length is shorter than Al–OH (Tossell 1993), higher distortion of the Al(2) octahedron would

TABLE 4.  $^{27}\text{Al}$  PARAMETERS FROM SIMULATIONS OF MAS AND 3QMAS SPECTRA

Site	$\delta_{\text{iso}}$ (ppm)	$C_Q$ (MHz)	$\eta$
Al(1)K	72.2	2.25	1.0
Al(1)P	46.5	1.96	0.7
Al(2) (without F)	7.8	2.80	0.4
Al(2) (with one F)	14.0	7.08	0.4

TABLE 5. RELATIVE INTENSITIES OF THE TWO  $^{19}\text{F}$  MAS NMR PEAKS IN ZUNYITE

	M16225	Karab
Peak 1 (-133 ppm)	40	21
Peak 2 (-130 ppm)	60	79

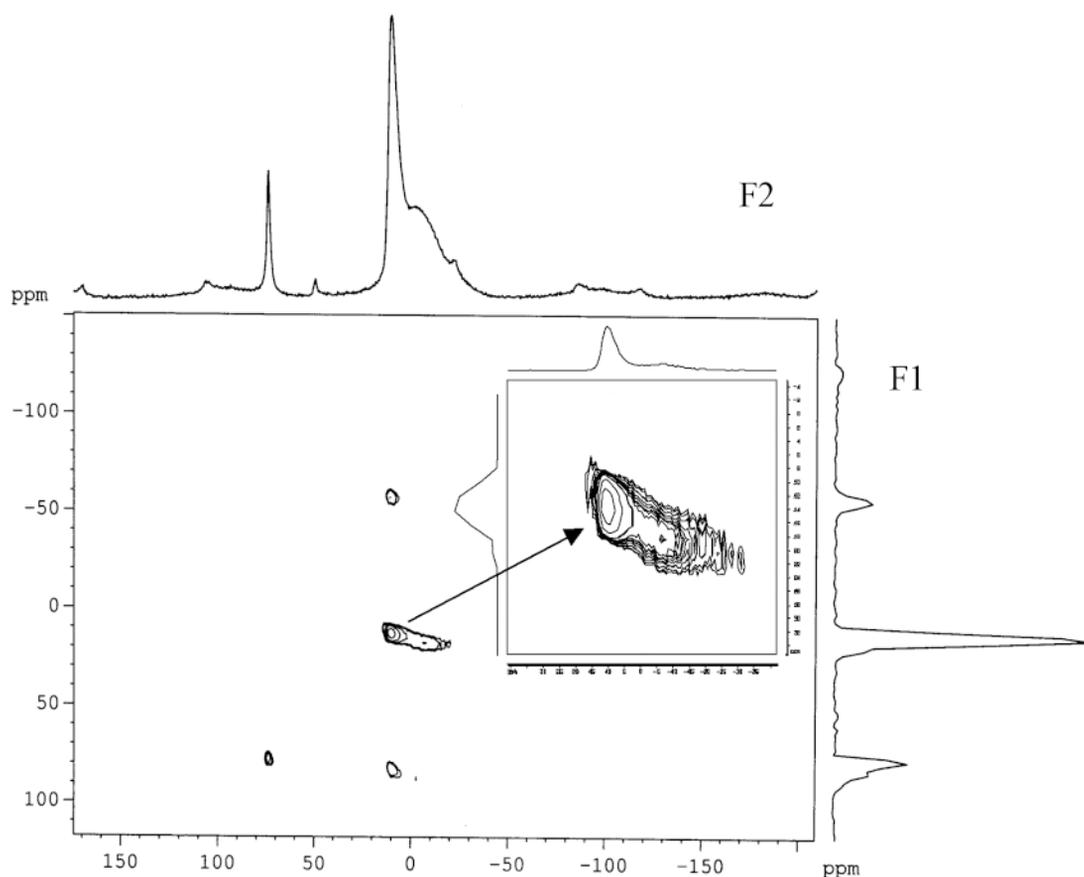


FIG. 5.  $^{27}\text{Al}$  3QMAS spectrum for zunyite (sample 112911), with an inset showing an expanded plot of the sheared spectrum.

be expected with F substitution, and thus a larger EFG and  $C_Q$ .

The experimental values obtained in 3QMAS and MAS experiments for the octahedral sites are in agreement with the trends predicted by the quantum calculations. However, environments I and II cannot be distinguished, nor III to VI. Three environments could therefore possibly be resolved, (I and II), (III to VI) and VII, but one of these three possible components is missing. The atoms associated to each site, 2.5 *apfu* for Peak C and 9.5 *apfu* for Peak D, allowed the assignment. For one fluorine atom in the O(4) site, which bridges two Al(2) atoms, two Al sites are affected. The Karab sample contains 4.16 F *apfu*, leading to 8.32 *apfu* Al(2) affected by one F substitution and 3.68  $^{27}\text{Al}$  without F. For the replacement of two OH by F in one octahedron, the number of Al octahedra affected equals the number of F atoms. For Karab, there would be 7.84 *apfu* Al represented by Peak C, and 4.16 *apfu* by Peak D. The values obtained from the 3QMAS decomposition, 2.5 and 9.5 *apfu* for Peaks C and D, are closer to the values of 3.68

and 8.32 *apfu* for one F substitution than for the values for two atoms substituting. So our data, which do not support the existence of 2F Al(2) environments, are in agreement with those of Baur & Ohta (1982) and with the two  $^{19}\text{F}$  MAS NMR peaks at -133 and -130 ppm. Therefore, the site at 7.8 ppm with a  $C_Q$  of 2.80 MHz,  $\eta$  of 0.4 and 2.5 *apfu*, and the site at 14 ppm with a  $C_Q$  of 7.08 MHz,  $\eta$  of 0.4 and 9.5 *apfu* are Al(2) in octahedral coordination with 2O(4)H and 1F1O(4)H, respectively.

The Mulliken charge distribution, which shows the charge transfer between Al(2) and O, indicates a strong covalent component to the bonds. The covalency of the bond to Al decreases as F replaces OH, indicating that  $^{27}\text{Al}$  would become more shielded, and  $\delta_{\text{iso}}$ , more negative (Dirken *et al.* 1992, Smith 1993, Tossell 1993). Nevertheless, the  $\delta_{\text{iso}}$  of  $^{27}\text{Al}$  at the octahedral sites in the Keggin structure moves from 7.8 to 14.0 ppm with the substitution of F for OH, contradicting the idea that F substitution gives a more negative  $\delta_{\text{iso}}$  (Dirken *et al.* 1992). This anomalous shift must be due to the unusual Keggin conformation in zunyite.

As 3QMAS spectra of several polycations were recently published by Allouche *et al.* (2001), a classification of the quadrupolar interactions of the different types of environment can be undertaken. The  $Al_{30}$  polycation (Allouche *et al.* 2000) has two  $\delta$  Keggin units linked by a ring of four Al octahedra. The  $\delta$  Keggin unit has a trimeric unit connected by vertices, as in the  $\alpha$  Keggin polycation, though the three other trimeric units are of  $\epsilon$

Keggin type (Fig. 9). There are distinct trends in the quadrupolar interactions among the different kinds of Keggin structures. Values of  $C_Q$  for Al(2) of the  $\epsilon$  Keggin units (Johansson 1963) range around  $10 \pm 0.5$  MHz, whereas for the  $\alpha$  Keggin units, they range from 4 to 6 MHz, with  $C_Q$  of the connecting ring sites in  $Al_{30}$  being 5 MHz. The unusual change in  $^{27}Al \delta_{iso}$  with fluorine substitution of the  $\alpha$  Keggin structure in zunyite

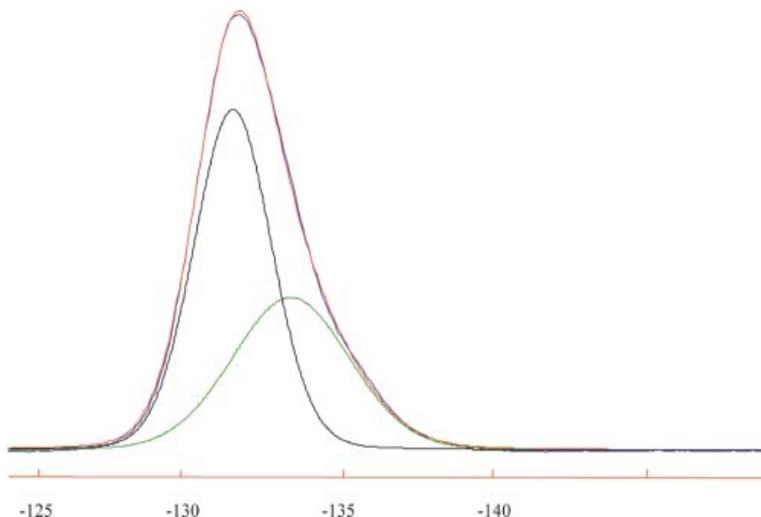


FIG. 6.  $^{19}F$  MAS NMR spectrum of zunyite (sample E1609), simulated with two resonances.

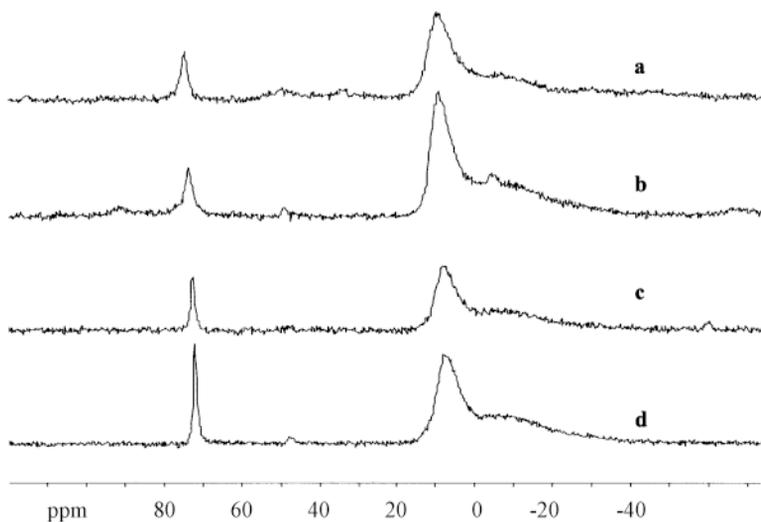


FIG. 7.  $^{27}Al$  NMR MAS spectra of zunyite for sample E1609 with the rotor spinning at (a) 5 kHz, (b) 10kHz, (c) 17 kHz, (d) 30 kHz.

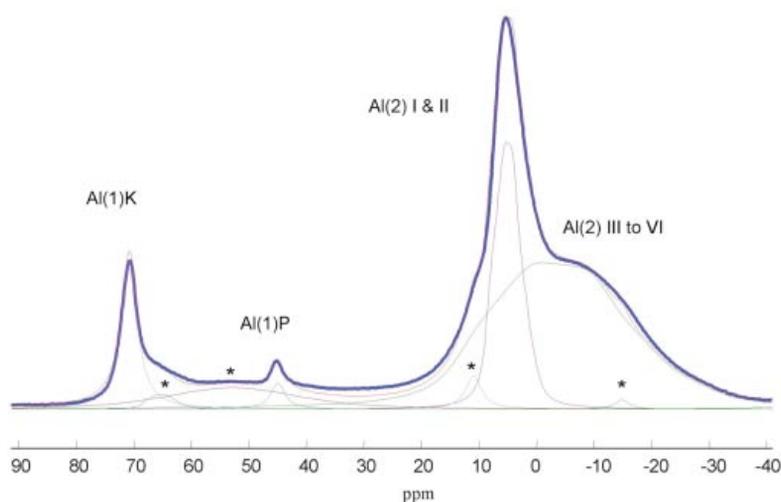


FIG. 8. Simulation of the  $^{27}\text{Al}$  MAS NMR spectrum for sample Karab. (\*) shows spinning side bands.

indicates that a more thorough quantum mechanical investigation is needed to understand these structures.

#### CONCLUSIONS

With the help of *ab initio* quantum mechanical calculations of clusters, a combination of  $^{19}\text{F}$ ,  $^{29}\text{Si}$ ,  $^{27}\text{Al}$  MAS and  $^{27}\text{Al}$  3QMAS NMR spectra has allowed definite assignments for the  $^{27}\text{Al}$ ,  $^{29}\text{Si}$  and  $^{19}\text{F}$  MAS NMR spectral peaks. The  $-91$  ppm peak in the  $^{29}\text{Si}$  spectrum of zunyite corresponds to the 46 ppm peak in  $^{27}\text{Al}$  spectra as Al replaces Si in the central tetrahedron of the pentamer unit. For  $^{27}\text{Al}$ , the peak with  $\delta_{\text{iso}}$  of 7.8 ppm is assigned to Al(2) in the environment with 2 O(4)H, with F-monosubstituted Al(2) being assigned to the peak with  $\delta_{\text{iso}}$  of 14 ppm.

The  $\alpha$  Keggin unit of zunyite is fluorine-substituted, in the intertrimeric O(4) site, leading to the creation of crystallographically inequivalent sites for fluorine, and lowering the symmetry of the central tetrahedral site. Contrary to the usual trend, the  $^{27}\text{Al}$  in the octahedral Al(2) site in zunyite becomes less shielded ( $\delta_{\text{iso}}$  14 ppm) owing to the F substitution for OH than the non-fluorinated sites (7.8 ppm), instead of being more shielded. This is probably due to the special nature of the  $\alpha$  Keggin polycation.

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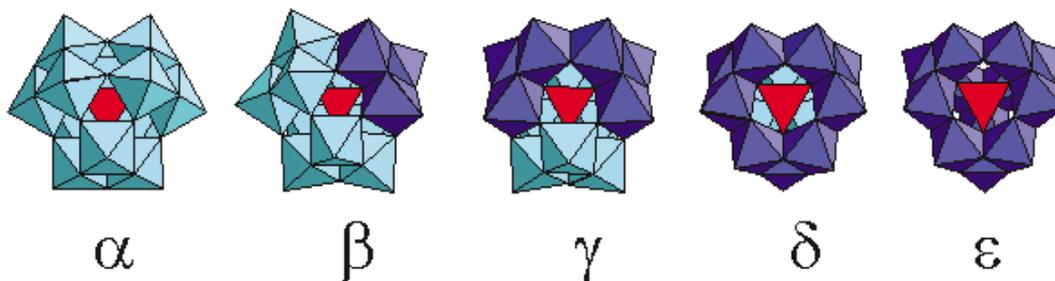


FIG. 9. The five isomers ( $\alpha$  to  $\epsilon$ , from left to right) of Keggin polycations (Baker & Figgis 1970, Allouche *et al.* 2000).  $\text{AlO}_4$  tetrahedra are shown in red, and the different rotations of octahedral isomers through  $60^\circ$  are shown in light and dark blue.

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