

## Ab Initio Calculations of NMR Parameters of Highly Coordinated Oxygen Sites in Aluminosilicates

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Ab initio calculations have been carried out for the three polymorphs of  $\text{SiAl}_2\text{O}_5$  in order to study the  $^{17}\text{O}$  NMR characteristics of tricoordinated O atoms, O[3], and tetracoordinated O atoms, O[4], that are possibly present in the structure of aluminosilicate glasses. We present  $\delta_{\text{iso}}$ ,  $C_Q$ , and  $\eta$  calculations using the density functional theory-based GIPAW method for all silicon, aluminum, and oxygen sites and in particular for the 14 O[3] atoms, which are bonded to three Al or Si atoms in the andalusite, sillimanite, and kyanite polymorphs of  $\text{SiAl}_2\text{O}_5$ . The O[4] parameters calculated in kyanite are also compared with the corresponding site in  $\alpha\text{-Al}_2\text{O}_3$ . The calculated values for the  $^{29}\text{Si}$  and  $^{27}\text{Al}$  isotropic chemical shift values as well as  $^{27}\text{Al}$  quadrupolar coupling constants ( $C_Q$ ) and asymmetry parameters ( $\eta$ ) are in good agreement with experimental data. Apart from in alumina and in grossite  $\text{CaAl}_4\text{O}_7$ ,  $^{17}\text{O}$  NMR parameters have not been measured experimentally yet but the  $C_Q$  and  $\eta$  values obtained for all sites are consistent with those previously calculated, and the corresponding chemical shift values are reported for the first time. These calculations suggest that it will be difficult to distinguish O( $\text{SiAl}_2$ ) tricoordinated oxygen atoms from O[2] ones in aluminosilicate glasses on the basis of  $^{17}\text{O}$  NMR data alone since positions of the signals overlap either in a two-dimensional ( $\delta$ ,  $C_Q$ ) space or in a 3Q-MAS spectrum. It should be noticed that the tricoordinated O atoms calculated are not surrounded by any cations such as  $\text{Ca}^{2+}$  or  $\text{Na}^+$  while  $^{17}\text{O}$  chemical shift values for  $\text{SiOAl}$  and  $\text{SiOSi}$  show considerable variations with cation type. Nonetheless, the steric hindrance around highly coordinated oxygen sites is important, and we can assume that the first neighbors of the O atoms are usually only Si and Al atoms. Only  $\text{OAl}_4$  sites with hexacoordinated aluminum, exhibiting a smaller  $C_Q$  and relatively high isotropic chemical shift values, can be clearly distinguished from O[2] sites in a 3Q-MAS spectrum.

### Introduction

Although the structures of aluminosilicate glasses and melts have been the subject of many spectroscopic studies of interest because of their applications in the materials sciences and Earth sciences, several controversial issues still remain. More specifically, for example, Toplis et al.<sup>1</sup> and Stebbins et al.<sup>2</sup> have suggested the possible presence of oxygen triclusters O[3] in which the oxygen atoms are linked to three  $\text{SiO}_2$  or  $\text{AlO}_4$  tetrahedra.

Solid state NMR would appear to be a very efficient tool to investigate the local structure of these materials. Recently, Stebbins et al.<sup>3</sup> reported the detection of oxygen triclusters in crystalline  $\text{CaAl}_4\text{O}_7$  (grossite) and in calcium aluminosilicate glasses using  $^{17}\text{O}$  MAS and MQMAS techniques. Interpretation of  $^{17}\text{O}$  spectra can be difficult due to the low natural abundance of the nucleus (0.037%) and the presence of quadrupolar interactions ( $I = 5/2$ ). The resulting second-order quadrupolar line shapes that can only be partially averaged by MAS<sup>4</sup> are usually complex and therefore difficult to simulate. The

development of new high-resolution techniques such as MQ-MAS and the enrichment of them allows these intrinsic difficulties of  $^{17}\text{O}$  solid state NMR to be dealt with. However, the spectra are still very difficult to interpret and no empirical rules have yet been found to enable the assignment of the peaks and to obtain structural information for each site.

In this context, ab initio calculations can be extremely useful in the understanding of the spectra since accurate calculation of the NMR parameters will allow the assignment of all sites present in the structure. Moreover,  $^{17}\text{O}$  enrichment of the samples may in some cases be quite difficult and remain quite expensive. Calculations can obtain the information regarding the NMR characteristics of well-defined sites without having to perform any enrichment.

Ab initio molecular orbital calculations have already been reported for tricluster oxygens O( $\text{SiAl}_2$ ) or O( $\text{Si}_2\text{Al}$ ) in which all of the silicon and aluminum atoms are tetracoordinated<sup>5,6</sup> and suggest that these tricluster oxygens would be difficult to distinguish from Si–O–Al oxygens by  $^{17}\text{O}$  NMR due to very similar electric field gradient (EFG) values. In this study, we investigate highly coordinated O[3] and O[4] oxygen sites present in the three polymorphs of  $\text{SiAl}_2\text{O}_5$  in which at least one of the aluminum atoms is 5- or 6-fold coordinated. The aim is to determine whether these are also difficult to distinguish from Si–O–Al oxygens.

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Recently, Tossel et al.<sup>7</sup> proposed calculations using density functional theory (DFT) and FLAPW method on the O EFG values for eight chemically inequivalent O sites in andalusite and sillimanite polymorphs of  $\text{SiAl}_2\text{O}_5$ , most of which have local geometries closely related to triclusters. At the same time, Iglesias et al.<sup>8</sup> determined the electronic structure of the three polymorphs of  $\text{SiAl}_2\text{O}_5$  by LAPW calculations using the WIEN code.<sup>9</sup> In the present work, we have repeated these EFG calculations using a different code,<sup>10</sup> which has already given very satisfactory results on  $\text{SiO}_2$  polymorphs and zeolites<sup>11</sup> and in sodium silicate crystals and glasses.<sup>12</sup> Moreover, the  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ , and  $^{17}\text{O}$  isotropic chemical shift values of all sites were calculated as well. The main goal of this paper is to determine whether there is a possibility to distinguish clearly tri- and tetracoordinated oxygens in aluminosilicate glasses using their  $^{17}\text{O}$  NMR parameters.

### Computational Methods

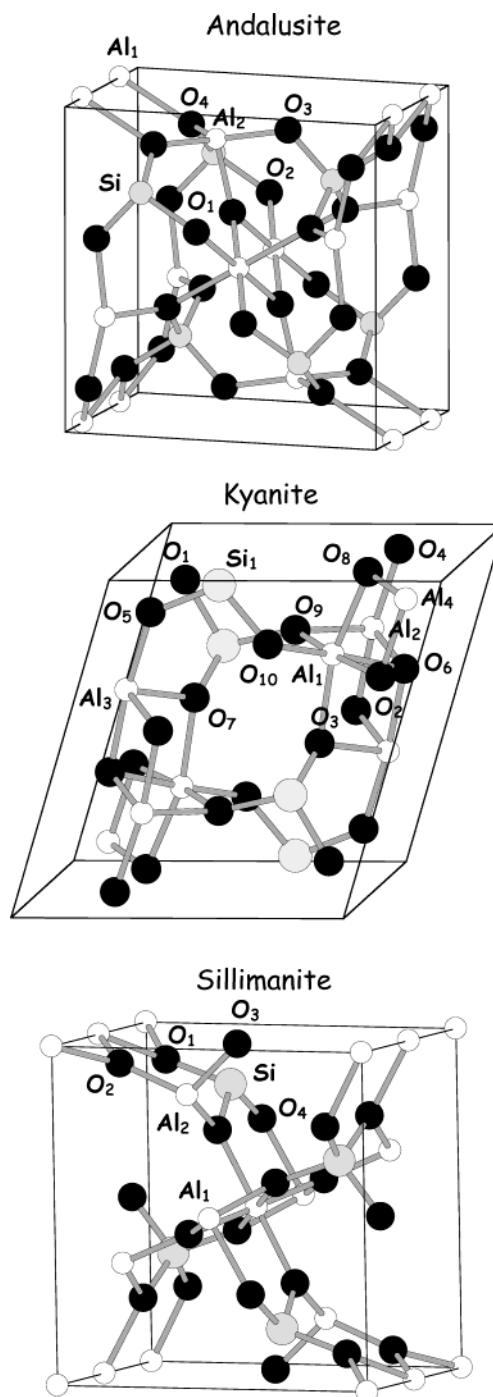
The calculations are performed within Kohn–Sham DFT using the PARATEC code.<sup>10</sup> The PBE generalized gradient approximation<sup>13</sup> is used, and the valence electrons are described by norm-conserving pseudopotentials<sup>14</sup> in the Kleinman–Bylander<sup>15</sup> form. The core of O is  $1s^2$ , and for Si and Al, it is  $1s^2 2s^2 2p^6$ . The core radii are 1.5 au for O, 1.7 au for Si, and 1.8 au for Al. The wave functions are expanded in a plane wave basis set with an energy cutoff of 80 Ry. The crystalline structure is described as infinite periodic systems using periodic boundary conditions. The NMR calculations are performed with the experimental geometries determined by X-ray diffraction.<sup>16–18</sup> The integral over the Brillouin zone is done using a Monkhorst–Pack  $2 \times 2 \times 2$   $k$ -point grid<sup>19</sup> for the charge density and EFG calculation and a  $4 \times 4 \times 4$   $k$ -point grid for the chemical shift tensor calculation.

The calculations have been performed at the IDRIS supercomputer center of the CNRS using a parallel IBM Power4 (1.3 GHz) computer: the calculation of the EFG and the chemical shift tensor requires 4 and 16 h, respectively, on 16 processors.

The shielding tensor is computed using the GIPAW<sup>20</sup> approach, which permits the reproduction of the results of a fully converged all-electron calculation while the EFG tensors are computed using a PAW approach.<sup>11,21</sup> The isotropic chemical shift  $\delta_{\text{iso}}$  is defined as  $\delta_{\text{iso}} = -[\sigma - \sigma^{\text{ref}}]$  where  $\sigma$  is the isotropic shielding (one-third of the trace of the NMR shielding tensor) and  $\sigma^{\text{ref}}$  is the isotropic shielding of the same nucleus in a reference system. In our calculations, absolute shielding tensors are obtained. The chemical shift scales were therefore fixed in such a way that the experimental and theoretical  $\delta$  of reference compounds coincide as follows: polymorphs of  $\text{SiO}_2$  for  $^{17}\text{O}$ <sup>11</sup> and quartz for  $^{29}\text{Si}$ <sup>11</sup>. Crystalline  $\text{AlPO}_4$  berlinite was chosen for  $^{27}\text{Al}$  [ $\delta_{\text{iso}}(^{27}\text{Al}) = 44.8$  ppm as compared to a 1 M solution of  $\text{Al}(\text{NO}_3)_3$  taken as the 0 ppm reference]. The corresponding berlinite calculation was performed with the experimental geometries determined by a crystal structure refinement from Laue photographs taken with synchrotron radiation.<sup>22</sup> The resulting  $\sigma^{\text{ref}}$  for  $^{17}\text{O}$  is 261.5 ppm, 337.3 ppm for  $^{29}\text{Si}$ , and 556.4 ppm for  $^{27}\text{Al}$ .

### Results and Discussion

The unit cells of the three polymorphs containing 32 atoms ( $Z = 4$ ) are presented in Figure 1. The coordination of the aluminum sites varies from four to six, and oxygen atoms have a coordination comprised between two and four with a majority of three-coordinated atoms. Alumina  $\alpha\text{-Al}_2\text{O}_3$  shows a hexa-



**Figure 1.** Units cells of the three polymorphs of  $\text{SiAl}_2\text{O}_5$ .

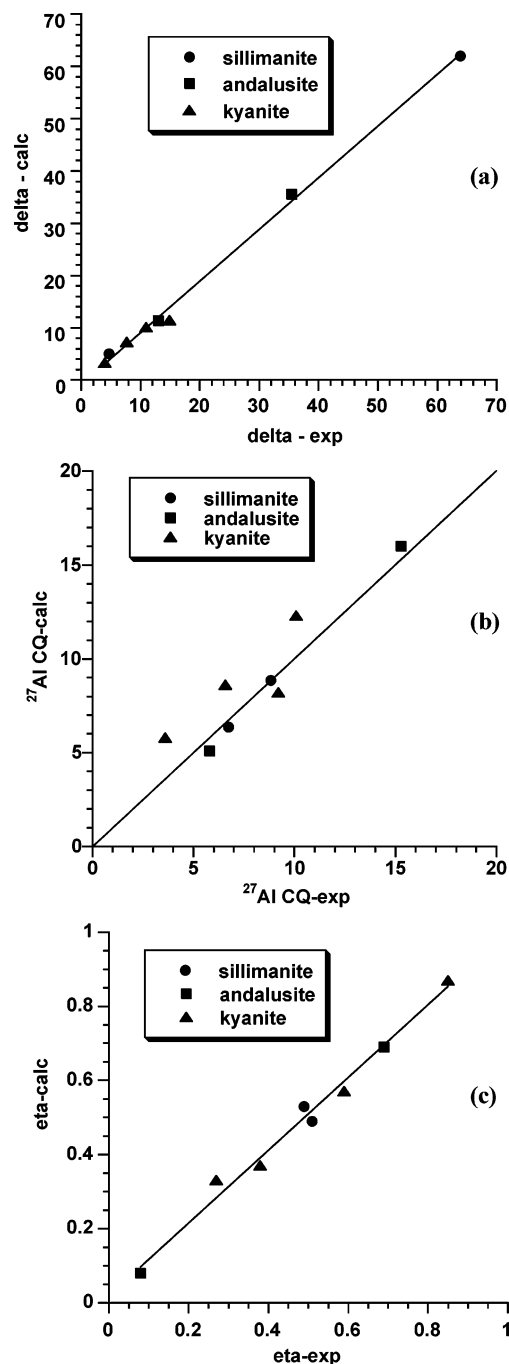
coordinated aluminum and an oxygen atom with a coordination of four that could be compared with the similar sites observed in kyanite. All sites with their respective coordination (indicated between hooks) and first neighbors are summarized in Table 1. To our knowledge, no  $^{17}\text{O}$  experimental data are available for any of the polymorphs, while  $^{29}\text{Si}$  and  $^{27}\text{Al}$  isotropic chemical shift values, as well as quadrupolar coupling constants ( $C_Q$ ) and asymmetry parameters ( $\eta$ ) have been experimentally measured for all three polymorphs.<sup>23–27</sup> These values and the corresponding references are indicated in Table 1 and compared with those obtained from the calculations. There is an excellent agreement between our  $\delta_{\text{iso}}$  calculated values and the experimental data for all aluminum (Figure 2) and silicon sites in the three systems. The aluminum  $\eta$  values are also in good agreement, but

**TABLE 1:**  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ , and  $^{17}\text{O}$  Experimental and Calculated NMR Parameters for the Three Polymorphs of  $\text{SiAl}_2\text{O}_5$  and  $\alpha\text{-Al}_2\text{O}_3$ 

Sillimanite							
site [coordination]	$\delta$ (ppm)		$C_Q$ (MHz)		$\eta$		
	calcd <sup>a</sup>	exp	calcd <sup>a</sup>	exp <sup>23</sup>	calcd <sup>a</sup>	exp <sup>23</sup>	
Al <sub>1</sub> [4]	62.3	63.9 <sup>23</sup>	6.36	6.74	0.63	0.51	
Al <sub>2</sub> [6]	5.3	4.7 <sup>23</sup>	8.85	8.83	0.53	0.49	
Si <sub>1</sub>	-87.6	-86.8 <sup>24</sup>					
	calcd <sup>a</sup>		calcd <sup>a</sup>	calcd <sup>7</sup>	calcd <sup>8</sup>	calcd <sup>a</sup>	calcd <sup>8</sup>
O <sub>1</sub> [3]: 2Al[6], Si[4]	76.0		3.75	3.72	3.63	0.72	0.67
O <sub>2</sub> [3]: 2Al[6], Al[4]	64.5		3.27	3.22	3.19	0.04	0.01
O <sub>3</sub> [2]: Al[4], Si[4]	63.0		4.32	4.23	3.99	0.08	0.08
O <sub>4</sub> [3]: Al[6], Al[4], Si[4]	58.2		4.45	4.41	4.34	0.55	0.52
Andalusite							
site [coordination]	$\delta$ (ppm)		$C_Q$ (MHz)		$\eta$		
	calcd <sup>a</sup>	exp <sup>25</sup>	calcd <sup>a</sup>	exp <sup>25</sup>	calcd <sup>a</sup>	exp <sup>25</sup>	
Al <sub>1</sub> [5]	35.8	35.5	5.1	5.8	0.69	0.69	
Al <sub>2</sub> [6]	11.6	13.0	16.0	15.3	0.18	0.08	
Si <sub>1</sub>	-78.7	-79.6					
	calcd <sup>a</sup>		calcd <sup>a</sup>	calcd <sup>7</sup>	calcd <sup>8</sup>	calcd <sup>a</sup>	calcd <sup>8</sup>
O <sub>1</sub> [3]: 2Al[6], Al[5]	82.5		2.95	2.94	2.87	0.2	0.18
O <sub>2</sub> [3]: 2Al[6], Si[4]	66.6		3.72	3.70	3.65	0.86	0.83
O <sub>3</sub> [3]: 2Al[5], Si[4]	88.3		2.65	2.52	2.48	0.82	0.85
O <sub>4</sub> [3]: Al[6], Al[5], Si[4]	59.1		4.25	4.21	4.18	0.55	0.51
Kyanite							
site [coordination]	$\delta$ (ppm)		$C_Q$ (MHz)		$\eta$		
	calcd <sup>a</sup>	exp	calcd <sup>a</sup>	exp <sup>26</sup>	calcd <sup>a</sup>	exp <sup>26</sup>	
Al <sub>1</sub> [6]	10.4	11.0 <sup>26</sup>	8.2	9.2	0.47	0.38	
Al <sub>2</sub> [6]	3.6	4.0 <sup>26</sup>	5.8	3.6	0.77	0.85	
Al <sub>3</sub> [6]	7.5	7.7 <sup>26</sup>	8.6	6.6	0.47	0.59	
Al <sub>4</sub> [6]	11.7	14.9 <sup>26</sup>	12.3	10.1	0.33	0.27	
Si <sub>1</sub>	-82.3	-82.3 <sup>27</sup>					
Si <sub>2</sub>	-83.3	-83.2 <sup>27</sup>					
	calcd <sup>a</sup>		calcd <sup>a</sup>	calcd <sup>8</sup>	calcd <sup>a</sup>	calcd <sup>8</sup>	
O <sub>1</sub> [3]: 2Al[6], Si[4]	81.0		4.48	4.35	0.74	0.74	
O <sub>2</sub> [4]: 4Al[6]	88		2.38	2.36	0.86	0.81	
O <sub>3</sub> [3]: 2Al[6], Si[4]	76.8		4.30	3.89	0.97	0.89	
O <sub>4</sub> [3]: 2Al[6], Si[4]	78.8		4.39	3.93	0.97	0.96	
O <sub>5</sub> [3]: 2Al[6], Si[4]	81.1		4.17	4.05	0.93	0.93	
O <sub>6</sub> [4]: 4Al[6]	88.8		2.10	1.88	0.77	0.83	
O <sub>7</sub> [3]: 2Al[6], Si[4]	79.9		4.45	4.03	0.84	0.73	
O <sub>8</sub> [3]: 2Al[6], Si[4]	82.5		4.34	3.91	0.82	0.71	
O <sub>9</sub> [3]: 2Al[6], Si[4]	77.3		4.32	4.05	0.80	0.89	
O <sub>10</sub> [3]: 2Al[6], Si[4]	76.9		4.29	4.06	0.78	0.87	
Alumina $\alpha\text{-Al}_2\text{O}_3$							
site [coordination]	$\delta$ (ppm)		$C_Q$ (MHz)		$\eta$		
	calcd <sup>a</sup>	exp	calcd <sup>a</sup>	exp	calcd <sup>a</sup>	exp	
Al[6]	14.4	16.0 <sup>29</sup>	2.27	2.39 <sup>30</sup>	0.0	0.0 <sup>30</sup>	
O[4]: 4Al[6]	81.6	75.0 <sup>28</sup>	2.23	2.17 <sup>28</sup>	0.51	0.55 <sup>28</sup>	

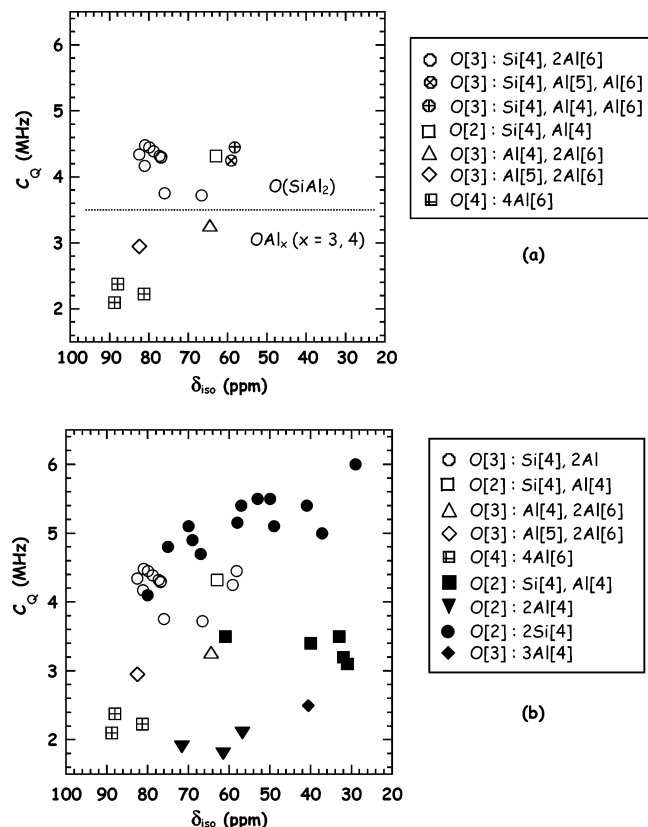
<sup>a</sup> Present work by PARATEC.

regarding the  $C_Q$  values, those obtained for sillimanite and andalusite are much more satisfying than for kyanite (Figure 2). Although there are no  $^{17}\text{O}$  experimental data for these systems, the oxygen EFG values have already been calculated for sillimanite and andalusite by Tossel et al.<sup>7</sup> and for all three polymorphs by Iglesias et al.<sup>8</sup> These previously reported values are in very good agreement with the ones obtained here (Table 1). Moreover, the  $^{27}\text{Al}$  and  $^{17}\text{O}$  NMR parameters of  $\alpha\text{-Al}_2\text{O}_3$  were experimentally determined<sup>28–30</sup> and compare well with our calculations, as well as the  $^{17}\text{O}$  NMR parameters of the tricoordinated OAl<sub>3</sub> site in grossite<sup>31</sup>  $\text{CaAl}_4\text{O}_7$ . The experimental parameters of this OAl<sub>3</sub> environment are indeed  $\delta = 40.6$  ppm,  $C_Q = 2.5$  MHz, and  $\eta = 0.4$  while the calculated values obtained

**Figure 2.** Comparison between the experimental and the calculated values of  $^{27}\text{Al}$   $\delta_{\text{iso}}$  (a),  $C_Q$  (b), and  $\eta$  (c) for the three polymorphs of  $\text{SiAl}_2\text{O}_5$ .

by PARATEC<sup>32</sup> are  $\delta = 43.1$  ppm,  $C_Q = 2.44$  MHz, and  $\eta = 0.23$ . This suggests that the calculated  $^{17}\text{O}$  chemical shifts are reliable enough for direct comparison with experimental data.

Taking advantage of both the  $C_Q$  and the  $\delta$  parameters to discriminate the different sites, the computed NMR parameters for each oxygen environments are presented in Figure 3 in a two-dimensional ( $\delta$ ,  $C_Q$ ) space. At least two different areas seem to arise from this plot: OAl<sub>x</sub> ( $x = 3, 4$ ) is clearly different from O(SiAl<sub>2</sub>) due to smaller  $C_Q$  values. This tendency is in good agreement with previous reported calculations.<sup>5,6</sup> It can be noticed that the position of O(SiAl<sub>2</sub>) seems not to be very sensitive to the coordination of the aluminum site. To examine whether tri- and tetracoordinated oxygens can be easily discriminated from O[2] sites, the NMR experimental parameters

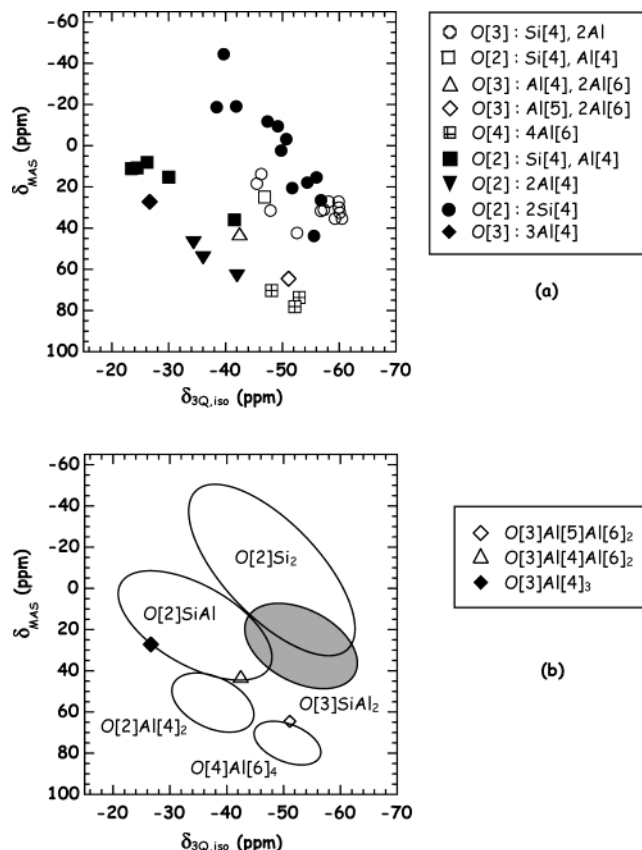


**Figure 3.** Quadrupolar coupling constant ( $C_Q$ ) as a function of the chemical shift of oxygen sites (a) in the three polymorphs of  $SiAl_2O_5$  and  $\alpha-Al_2O_3$ . (b) Compilation of experimental data (filled symbols) for SiOSi, SiOAl, and AlOAl sites summarized in Table 2. Coordination of the sites is indicated between hooks.

obtained for SiOSi sites in  $SiO_2$  polymorphs,<sup>11</sup> wallastonites,<sup>33</sup>  $Mg_2SiO_6$ ,<sup>33</sup>  $CaAl_2Si_2O_8$ ,<sup>2</sup> and an aluminosilicate glass;<sup>34</sup> for SiOAl sites in zeolites,<sup>35</sup>  $CaAl_2Si_2O_8$ ,<sup>2</sup> and an aluminosilicate glass;<sup>34</sup> and for Al—O—Al and  $OAl_3$  sites in  $CaAl_4O_7$ <sup>31</sup> are reported in Figure 3b in a two-dimensional ( $\delta$ ,  $C_Q$ ) space. A detailed compilation of the experimental data reported in Figure 3 are summarized in Table 2. Si—O—Si, Si—O—Al, and Al—O—Al sites appear in three relatively distinct areas although they show rather similar chemical shift values: this discrimination is indeed possible thanks to different  $C_Q$ . However, the  $OSiAl_2$  area tends to overlap with those of Si—O—Si and Si—O—Al, which strongly suggests that it would be difficult to distinguish the three-coordinated oxygens from Si—O—Al by  $^{17}O$  NMR due to very similar EFG and chemical shift values. On the other hand, tetracoordinated  $OAl_4$  sites seem to be relatively distinguishable thanks to small quadrupolar coupling constants and relatively high chemical shift values. Moreover, the position of these sites in kyanite is relatively close to the one of  $\alpha-Al_2O_3$  suggesting a small dispersion of these environments.

Equivalent correlations using the  $\eta$  parameter do not bring any additional information. Moreover,  $\eta$  is a parameter usually difficult to determine accurately experimentally due to the poor signal-to-noise ratio observed with  $^{17}O$  spectra.

An elegant way to deal with the quadrupolar broadening is to perform a multiple quantum (MQ) NMR experiment,<sup>36</sup> which significantly improves the resolution of sites and helps in evaluating their quadrupolar parameters. MQMAS NMR is indeed a two-dimensional technique removing the second-order contribution to the quadrupolar broadening but retaining conventional single quantum information. We therefore calculated



**Figure 4.**  $^{17}O$  NMR 3QMAS spectra for a magnetic field of 9.4 T corresponding to a frequency of 54.24 MHz for oxygen-17 computed from (a) the calculated coordinates (open symbols) of the  $SiAl_2O_5$  and  $\alpha-Al_2O_3$  samples and the experimental data (filled symbols) for SiOSi, SiOAl, and AlOAl sites summarized in Table 2. (b) Contour plots for the SiOSi, SiOAl, AlOAl,  $SiAl_2$ , and  $OAl_4$  sites. Coordination of the sites is indicated between hooks.

**TABLE 2:**  $^{17}O$  Chemical Shift Values ( $\delta$ ), Quadrupolar Coupling Constants ( $C_Q$ ), Asymmetry Parameters ( $\eta$ ), and Quadrupolar Coupling Products [ $P_Q = C_Q(1 + \eta^2/3)^{1/2}$ ] Reported in the Literature for Various O[2] Environments (Si—O—Si, Si—O—Al, and Al—O—Al) and the O[3] Tricoordinated Site in Grossite  $CaAl_4O_7$

site	$\delta$ (ppm)	$C_Q$ (MHz)	$\eta$	$P_Q$ (MHz)	ref
Si—O—Si					
cristobalite $SiO_2$	37	5.20	0.18	5.23	11
coesite $SiO_2$	29	6.05	0.0	6.0	11
	41	5.43	0.16	5.42	11
	57	5.45	0.17	5.42	11
	53	5.52	0.17	5.53	11
	58	5.16	0.29	5.22	11
$Mg_2Si_2O_6$	70			5.1	33
$Ca_3Si_3O_9$	75			4.8	33
	67			4.7	33
$CaMgSi_2O_6$	69	4.39	0.36	4.48	33
$CaAl_2Si_2O_8$	50	5.5	0	5.5	2
glass NaAlSiO <sub>8</sub>	49	5.1	0.15	5.1	34
Si—O—Al[4]					
$CaAl_2Si_2O_8$	61			3.5	2
glass NaAlSiO <sub>8</sub>	33	3.5	0	3.5	34
zeolite Na-A	32	3.2	0.2	3.2	35
zeolite Na-Y	31	3.1	0.2	3.1	35
zeolite Ba, Na-Y	40	3.4	0.4	3.5	35
Al[4]—O—Al[4]					
$CaAl_4O_7$	71.6	1.9	0.7	2.0	31
	61.5	1.8	0.5	1.9	31
	56.8	2.1	0.5	2.2	31
O[3]:3Al[4]					
$CaAl_4O_7$	40.6	2.5	0.4	2.5	31

the 3QMAS spectrum corresponding to the different oxygen sites (Figure 4) using Stebbin's convention.<sup>37</sup> The objective is



to evaluate which type of oxygen environments can be clearly distinguished experimentally. In a two-dimensional 3QMAS spectrum, each  $^{17}\text{O}$  site gives rise to a sharp resonance in the  $\delta_{3\text{Qiso}}$  dimension at the position:

$$\delta_{3\text{Qiso}} = -17/31\delta_{\text{iso}} + 10/31\delta_{\text{iso}}^{2\text{Q}}$$

and a broad MAS spectrum in the MAS dimension with a center of gravity given by:

$$\delta_{3\text{QMAS}} = \delta_{\text{iso}} + \delta_{\text{iso}}^{2\text{Q}}$$

where  $\delta_{\text{iso}}$  is the isotropic chemical shift value and  $\delta_{\text{iso}}^{2\text{Q}}$  is the second-order quadrupolar shift given for spin 5/2 by  $6000P_Q^2/\omega\omega^2$  with  $\omega$  the Larmor frequency and  $P_Q = C_Q(1 + \eta^2/3)^{1/2}$ .

The corresponding two-dimensional spectrum confirms the previous results: Si–O–Si, Si–O–Al, and Al–O–Al sites appear in three relatively distinct areas, but the O(SiAl<sub>2</sub>) area overlaps with those of Si–O–Si and Si–O–Al. OAl<sub>4</sub> is grouped at the bottom of the map while OAl<sub>3</sub> sites exhibit a position very sensitive to the coordination of the aluminum atoms. The OAl[4]<sub>3</sub> environment appears very close to the area of Si–O–Al, OAl[4]Al[6]<sub>2</sub> appears at the border between Si–O–Al and Al–O–Al sites, while the OAl[5]Al[6]<sub>2</sub> environment is close to the OAl<sub>4</sub> region. As a conclusion, it appears that all kinds of tricoordinated oxygen atoms (OSiAl<sub>2</sub> and OAl<sub>3</sub> with Al 4-, 5-, or 6-fold coordinated) cannot be clearly distinguished by running a 3QMAS NMR experiment. Nonetheless, OAl<sub>3</sub> sites are relatively well-distinguished in a two-dimensional ( $\delta$ ,  $C_Q$ ) space thanks to intermediate  $C_Q$  values ( $2.5 \leq C_Q \leq 3$  MHz) and could therefore possibly be univocally identified with other techniques than 3QMAS NMR.

## Conclusion

We have shown that calculations using DFT and GIPAW method under periodic boundary conditions are able to reproduce with high accuracy the  $^{29}\text{Si}$  and  $^{27}\text{Al}$  NMR parameters in the three polymorphs of SiAl<sub>2</sub>O<sub>5</sub>. Moreover,  $^{17}\text{O}$  NMR parameters could be predicted even though they have not yet been measured experimentally due to the very low abundance of this nucleus. The  $^{17}\text{O}$  quadrupolar coupling constants ( $C_Q$ ) and asymmetry parameters ( $\eta$ ) obtained for all sites are in good agreement with those previously calculated, and the corresponding chemical shift values are reported for the first time. It appears very difficult to distinguish the different tricoordinated oxygen atoms present in these structures (OSiAl<sub>2</sub> and OAl<sub>3</sub>) from X–O–X (X = Si, Al) sites by  $^{17}\text{O}$  NMR due to relatively similar EFG and chemical shift values. The position of OSiAl<sub>2</sub> sites appears not to be very sensitive to the coordination of the aluminum site while the chemical shift value of Al<sub>3</sub> environments changes

significantly with the coordination of the different aluminum atoms. Finally, tetracoordinated OAl[6]<sub>4</sub> oxygen sites can be clearly distinguished from X–O–X (X = Si, Al) environments on a 3QMAS spectrum.

## References and Notes

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