JOURNAL OF Materials CHEMISTRY

# Two-dimensional $^{23}$Na MQ MAS NMR study of layered silicates

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The two-dimensional multiple-quantum MAS (2D MQ MAS) NMR method was applied to $^{23}$Na in the hydrous layered silicates makatite, kanemite, octosilicate, magadiite and kenyaite in order to obtain precise information about the coordination structure of sodium ions in the inter-layer spaces. The makatite spectrum with high-power $^{1}$H decoupling clearly showed the existence of three different sites for sodium ions, in agreement with the structure derived from single-crystal X-ray diffraction. Lineshape fitting was performed for the cross sections of the 2D spectrum for the three sites. The derived $^{23}$Na NMR parameters indicate the value of the isotropic chemical shift to describe the coordination number of sodium ions in this type of compound. In the kanemite 2D spectra, well resolved signals from three different sites for sodium ions were also observed but only because of mixed sample composition. Two of the resonances were assigned to environments which we believe can best be described as $NaHSi_2O_5 \cdot 3H_2O$ and $NaHSi_2O_5 \cdot 4H_2O$, respectively, from a comparison of the spectra of two separately synthesized samples and by contrasting the results with those of samples dried under vacuum at room temperature for 6 h. The sodium ions in the third site are coordinated by more water molecules than in the other two sites. In all three sites, sodium ions were expected from their chemical shifts to have six-coordinated octahedral coordination. Although the structure of the samples changed reversibly by drying under vacuum at room temperature and re-moisturizing, drying the sample under vacuum at 100 °C resulted in structural change irreversibly altering the 2D NMR spectra. Octosilicate, magadiite and kenyaite showed only one sharp peak in their 2D spectra, and octahedral coordination with relatively high symmetry was deduced for each of these silicates. Samples of octosilicate and magadiite dried under vacuum at room temperature showed reversible changes in their 2D spectra, and the observed broadened signals were deduced to be due to the formation of less symmetrical coordination sites of sodium ions by the removal of water molecules.

## Introduction

Makatite, kanemite, octosilicate, magadiite and kenyaite are thought to be related silicates with typical empirical formulae, $Na_2O \cdot (4\text{–}20)SiO_2 \cdot (5\text{–}10)H_2O$. All of them have a layered structure containing sodium ions between the inter-layer spaces.[1–4] The inter-layered sodium ion undergoes facile ion exchange,[1,4,5] and this promotes the use of these layered silicates as catalysts and in detergent systems. For understanding the mechanism of the ion exchange and the chemical properties, it is important to know the structure around the sodium ions in the inter-layer space of these silicates.

However, the structure of only makatite has been fully resolved by single-crystal X-ray diffraction[1] due to the difficulty of obtaining single crystals with enough size for structure analysis. Sodium-23 NMR spectroscopy has been applied to the powdered samples,[5–8] but line broadening due to the quadrupolar interaction, which appears as a second-order effect even if the central transitions are selected, and the overlap of signals from different sites have hindered the derivation of precise information about the local molecular structure around the sodium ions. However, it has been suggested recently,[4,7] partly on $^{23}$Na NMR evidence, that the makatite structure is not directly related to those of the four other layered silicates in question.

Recently, Frydman and Harwood demonstrated that a two-dimensional multiple-quantum MAS (2D MQ MAS) method can result in isotropic NMR spectra for half-integer quadrupolar nuclei,[9,10] and our preliminary examination of makatite[11] showed high potential for this new method of studying $^{23}$Na spectra of layered silicates with high-power $^{1}$H decoupling. Therefore we applied the 2D MQ MAS method for all five layered silicates to gain information about the microscopic coordination structure of sodium ions. We have also examined the effect of drying on these compounds and discuss the structural changes around the sodium ions.

## Experimental

The sources of the layered silicates used in this study are as follows: makatite was supplied by courtesy of Leslie Dent-Glasser of the Department of Chemistry, Aberdeen University; two separately synthesized kanemites, octosilicate and magadiite were supplied from Unilever Research, Port Sunlight Laboratories; and kenyaite was supplied from Cureton Mineralogical Co.

NMR measurements were performed for the samples as received. NMR spectra were also obtained for samples dried at room temperature under vacuum for 6 h for the two kanemites, octosilicate and magadiite, and for one kanemite sample dried at 100 °C under vacuum for 10 h. After the measurements, these dried samples were kept under moisture-saturated conditions at room temperature for a week and then re-examined in order to check the reversibility of the sample properties.

Two-dimensional triple-quantum $^{23}$Na MAS NMR spectra were recorded at 52.94 MHz on a Chemagnetics CMX200 spectrometer. The spectrometer was fitted with a Chemagnetics HX probehead using 7.5 mm o.d. rotors spinning at rates between 5 and 6 kHz. The $^{79}$Br signal of KBr was used to calibrate the magic angle, and $^{23}$Na spectra were referenced with respect to an aqueous NaCl solution (1 mol dm$^{-3}$).

A two-pulse sequence[10,11] and a three-pulse *z*-filtered sequence[12] shown in Fig. 1 were used.[13] In the former case the nutation rate of rf pulses was set to 83.3 kHz, with typical pulse durations of 9 and 3 μs for the first and second pulses respectively. In the latter, the nutation rates of the first and second pulses were set to 83.3 kHz and that of the third pulse

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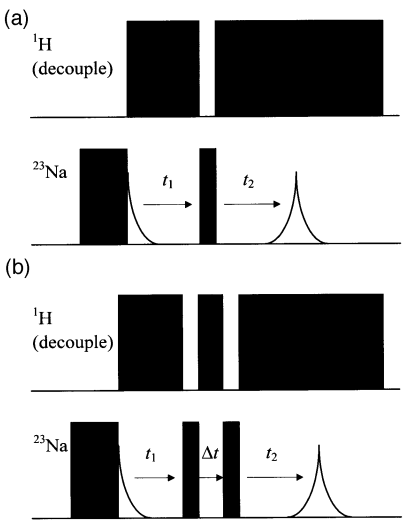

**Fig. 1** Radiofrequency pulse sequences used for the two-dimensional MQ MAS experiments in this study: (a) two-pulse sequence; (b) three-pulse $z$-filtered sequence

was set to 12.5 kHz, with typical pulse durations of 8, 3 and 8 μs for the first, second and third pulses respectively. The delay between the last two pulses was kept as 10 μs. The high-power $^1$H decoupling was performed by setting an irradiation frequency at 200.13 MHz with an rf field strength equivalent to 62.5 kHz. A rotor-synchronized acquisition method in the $t_1$ domain[14] was also used in some measurements in combination with the three-pulse $z$-filtered sequence in order to obtain accurate lineshapes of the cross sections in the 2D spectra and to shorten the measurement time.[13]

To produce pure absorption-mode lineshapes in the 2D spectra, the hypercomplex method was applied for data collection, and the data were processed as reported previously.[11,13] Shearing was applied in all cases before spectra were plotted or analysed.

Lineshape fitting for the cross sections of 2D spectra broadened by second-order quadrupolar interactions was performed by the non-linear least-squares method with the procedure reported previously,[13] which uses the information in the isotropic dimension of the 2D spectra as a constraint. Lineshapes are simulated using the same Gaussian broadening parameter (*ca.* 200 Hz) as was applied to the experimental data in the $\nu_2$ dimension.

## Results

### Makatite

As reported in a short communication,[11] the 2D MQ MAS method without $^1$H decoupling gave a 2D NMR spectrum showing only one $^{23}$Na peak with rather broadened lineshapes in both the MAS frequency dimension (derived from $t_2$—see Fig. 1) and the isotropic dimension (derived from $t_1$—see Fig. 1). However, when high-power $^1$H decoupling was applied, a substantial improvement in the spectral resolution was observed, as exhibited in Fig. 2. In this spectrum, the existence of three different sites for sodium ions in makatite, with an approximately 1 : 1 : 2 intensity ratio, is clearly shown from the projection onto the isotropic axis, with good resolution. From the cross sections at the corresponding peaks for sites 1, 2 and 3, the NMR parameters for each $^{23}$Na site were obtained by lineshape fitting, and the derived parameters are listed in Table 1.

Apart from these three peaks, a weak signal was observed in the 2D spectrum at $\delta \approx -5$ (in the MAS dimension) and $\nu_1'$/kHz$\approx 0.8$ (in the isotropic dimension). This minor peak is considered to be due to impurities included in the powdered makatite sample, in which the sodium ions have different coordination structure from those in makatite, as will be discussed later.

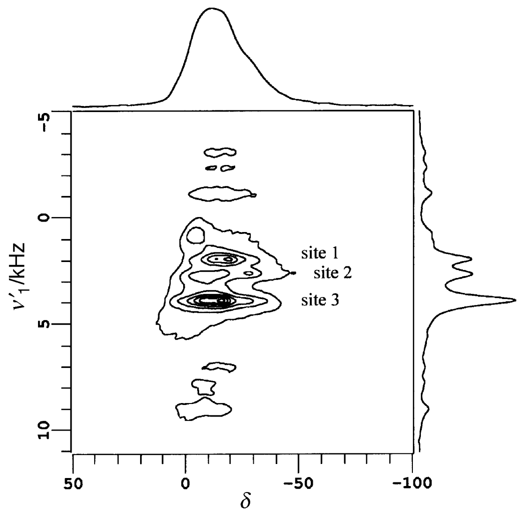

**Fig. 2** Two-dimensional triple-quantum $^{23}$Na MAS spectrum of makatite with $^1$H decoupling. The 2D spectrum shows spinning sidebands in the isotropic ($\nu_1'$) dimension with separations of the spinning rate, $\nu_{\text{rot}} = 5$ kHz, from the centrebands.

**Table 1** Sodium-23 NMR parameters for layered silicates obtained by fitting the triple-quantum-filtered single-quantum MAS cross-section lineshapes in 2D MQ MAS spectra

| silicate | site | $\delta^{\text{cs}\,a}$ | $\chi$/MHz | $\eta$ |
|---|---|---|---|---|
| makatite | site 1 | $0 \pm 1$ | $1.3 \pm 0.1$ | $0.6 \pm 0.1$ |
|  | site 2 | $1 \pm 1$ | $1.5 \pm 0.1$ | $0.4 \pm 0.1$ |
|  | site 3 | $8 \pm 1$ | $1.4 \pm 0.1$ | $0.6 \pm 0.1$ |
| kanemite | site 1 | $0 \pm 1$ | $1.7 \pm 0.1$ | $0.7 \pm 0.1$ |
|  | site 2 | $2 \pm 1$ | $2.0 \pm 0.1$ | $0.7 \pm 0.1$ |
|  | site 3 | $-1 \pm 1^c$ | $0.6 \pm 0.1^d$ | — |
| octosilicate |  | $-0.7 \pm 0.3^c$ | $0.48 \pm 0.05^d$ | — |
| octosilicate$^b$ |  | $-6 \pm 1$ | $2.4 \pm 0.1$ | $0.7 \pm 0.1$ |
| magadiite |  | $-0.9 \pm 0.3^c$ | $0.61 \pm 0.05^d$ | — |
| kenyaite |  | $-0.5 \pm 0.3^c$ | $0.60 \pm 0.05^d$ | — |

[a] True isotropic chemical shift, free of second-order quadrupolar effects, obtained from fitting the cross sections in the MAS dimension. [b] The sample dried under vacuum at room temperature for 6 h. [c] These values are directly calculated from the peak position in the 2D spectrum by using the relations $9\nu_1' = 34\nu^{\text{CS}} - 60\nu_0{}^{\text{Q}}$ and $\langle \nu_2 \rangle = \nu^{\text{CS}} + 3\nu_0{}^{\text{Q}}$, where $\nu_0{}^{\text{Q}} = -(3+\eta^2)\chi^2/360\nu_{\text{L}}$.[10,13] [d] These values are quadrupole coupling parameters $\chi(1+\frac{1}{3}\eta^2)^{1/2}$ directly calculated from the peak position in the 2D spectrum by using the relations cited above.

### Kanemite

In the present study, we used two different kanemite samples, named kanemite A and kanemite B, which were synthesized separately. Fig. 3(a) and (b) show the $^{23}$Na MQ MAS spectra with $^1$H decoupling for kanemites A and B, respectively. In the 2D spectrum of kanemite A, the existence of two principal sites (sites 1 and 2) and one minor site (site 3) was observed. When the measurement was performed without $^1$H decoupling, as shown in Fig. 3(c), only one broadened peak was seen in the 2D spectrum, at the frequency position corresponding to site 2. In the case of kanemite B, the spectrum [Fig. 3(b)] showed the existence of sites 2 and 3, with just a hint of the existence of site 1.

On the other hand, the 2D MQ MAS spectra changed drastically in both the samples of kanemite A and kanemite B after they were dried under vacuum at room temperature for 6 h. The dried samples gave almost identical 2D spectra. Fig. 4(a) shows the result for kanemite B. In this spectrum,

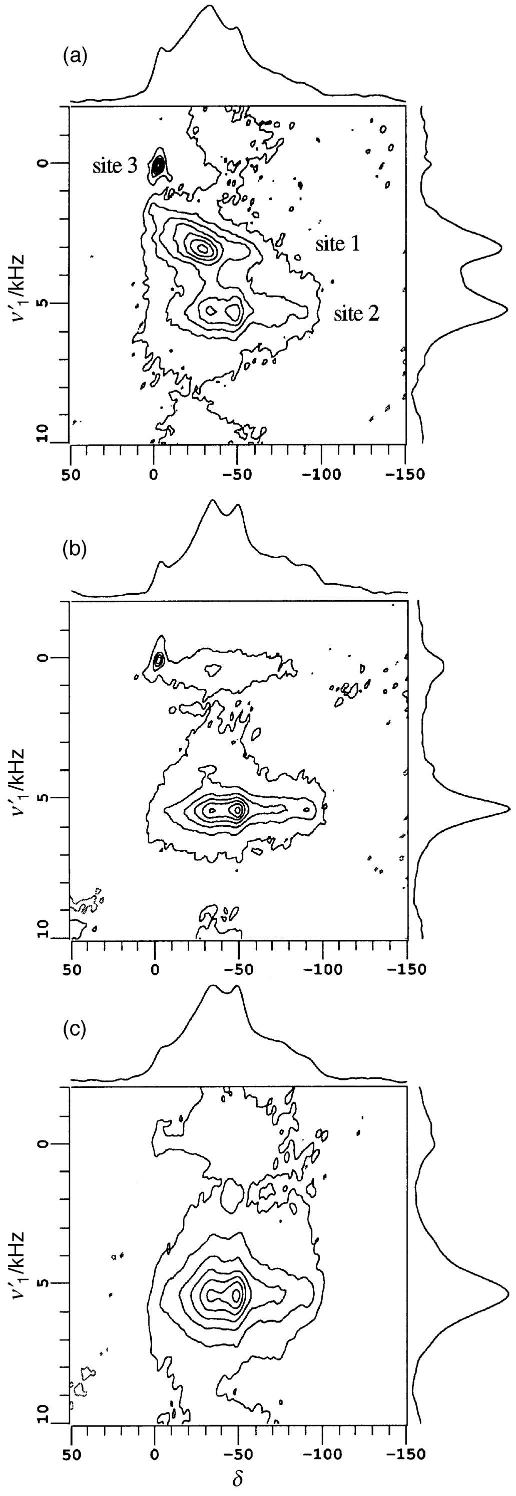

**Fig. 3** Two-dimensional triple-quantum $^{23}$Na MAS spectra of (a) kanemite A with $^{1}$H decoupling, (b) kanemite B with $^{1}$H decoupling, and (c) kanemite A without proton decoupling. The 2D spectra show spinning sidebands in the isotropic ($\nu_1'$) dimension with separations of the spinning rates, $\nu_{\mathrm{rot}} = 6$ kHz for (a) and (c) and 5 kHz for (b), from the centrebands.

only the signal from site 1 was observed, while the signals from sites 2 and 3 were eliminated. However, after the dried sample of kanemite B was kept under moisture-saturated conditions at room temperature for a week, the spectrum reverted to that of the sample without drying, as shown in Fig. 4(b), in which the peak from site 2 was clearly observed, with some small indication of signals from sites 1 and 3. The dried sample of kanemite A showed a similar spectral change

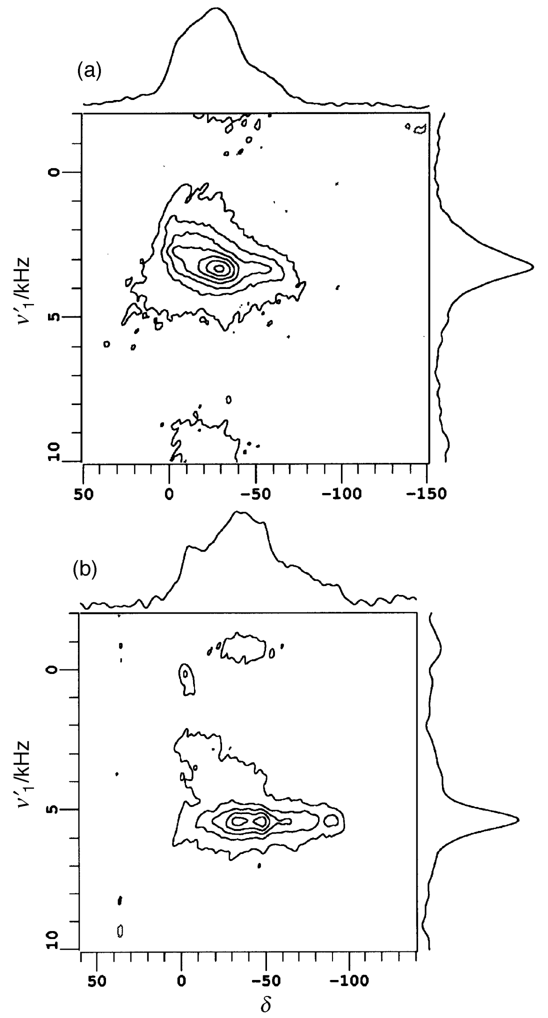

**Fig. 4** Two-dimensional triple-quantum $^{23}$Na MAS spectra of kanemite B with $^{1}$H decoupling: (a) dried sample under vacuum at room temperature for 6 h; (b) re-moisturized sample. The 2D spectra show spinning sidebands in the isotropic ($\nu_1'$) dimension with separations of the spinning rate, $\nu_{\mathrm{rot}} = 6$ kHz, from the centreband.

from the re-moisturization, and almost the same spectrum was observed to that of re-moisturized kanemite B.

Fig. 5(a) and (b) show triple-quantum-filtered single-quantum MAS cross-sections for site 2 in as-received kanemite B and site 1 in kanemite B dried under vacuum at room temperature, respectively, along with the best-fit simulations. The $^{23}$Na NMR parameters obtained by lineshape fitting are listed in Table 1. For site 3, the $^{23}$Na isotropic chemical shift and the quadrupolar parameter $\chi(1+\frac{1}{3}\eta^2)^{1/2}$ were directly calculated from the peak position in the 2D spectrum of $\delta = -4$ and $\nu_1'/\mathrm{kHz} = 0.16$, using[10,13] the relations $9\nu_1' = 34\nu^{\mathrm{CS}} - 60\nu_0^{\mathrm{Q}}$, where $\nu_0^{\mathrm{Q}} = -(3+\eta^2)\chi^2/360\nu_{\mathrm{L}}$, and $\langle\nu_2\rangle = \nu^{\mathrm{CS}} + 3\nu_0^{\mathrm{Q}}$ (assuming $\langle\nu_2\rangle = \nu_2$ at the peak).

When kanemite A was dried under vacuum at 100 °C for 10 h, all the signals from sites 1, 2 and 3 disappeared, and a new peak was observed in the 2D spectrum as shown in Fig. 6(a). This change was irreversible, and even after re-moisturization the sample exhibited a different spectral pattern from those of samples as-received, dried under vacuum at room temperature, and re-moisturized, as shown by Fig. 6(b).

### Octosilicate, magadiite and kenyaite

All these three samples showed only one sharp peak each, with similar positions in their 2D spectra, as exhibited in Fig. 7(a), (b) and (c). Although the spectrum of kenyaite shows another weak signal at the high frequency side in $\nu_1'$ of the sharp

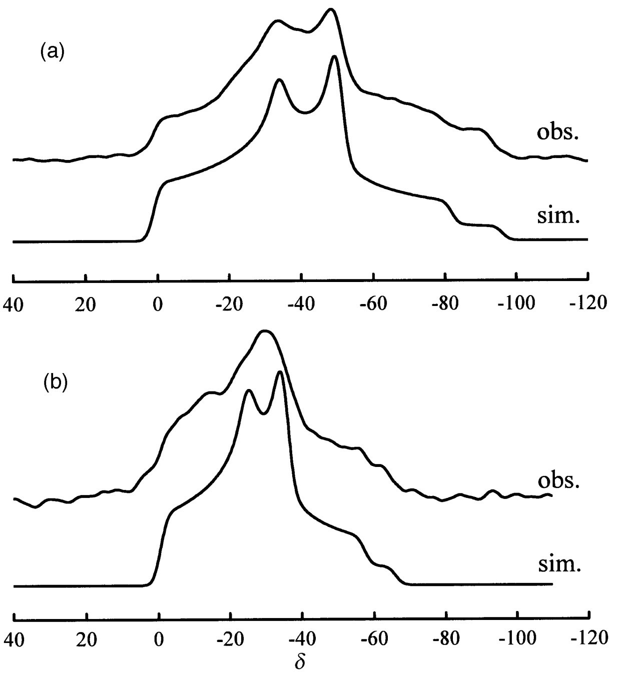

**Fig. 5** Triple-quantum-filtered single-quantum MAS cross sections at the peaks of the spectra in the isotropic ($\nu_1'$) dimension for (a) site 2 in as-received kanemite B, and (b) site 1 in kanemite B dried under vacuum at room temperature. The 2D spectra for these cross sections were acquired by a rotor-synchronized method in the $t_1$ domain obtained at a spinning rate of $\nu_{\text{rot}}=6$ kHz for accurate lineshapes. The best-fit simulations are also presented, along with the experimentally observed spectra.

intense peak, this is reasonably considered to be due to impurities included in the sample. This conclusion takes account of the facts that the kenyaite sample had its origin in minerals and that the sample was slightly coloured (dark green), whereas the other samples were white.

The cross-sections in the $\nu_2$ direction for the 2D spectra shown in Fig. 7 are relatively narrow and featureless, indicating that the quadrupole coupling constants are significantly smaller than those for makatite and kanemite. It is thus not feasible to fit the lineshapes with any accuracy. Therefore we have used the simpler approach of calculating the isotropic chemical shift and the effective quadrupole interaction parameter $\chi(1+\frac{1}{3}\eta^2)^{1/2}$ from the $\nu_1'$ frequency and the centre of gravity in the $\nu_2$ dimension.[10,13] The results are given in Table 1.

On the other hand, an octosilicate dried under vacuum at room temperature for 6 h exhibited a completely different 2D spectrum from that of the as-received sample [Fig. 8(a)]. Fig. 8(b) shows the cross-section for the peak in the $\nu_1'$ dimension with the best-fit spectrum, and the $^{23}$Na NMR parameters obtained are listed in Table 1. The lineshape of the cross section deviates significantly from theoretical expectation (probably arising, in part, from the low signal-to-noise ratio), resulting in the poor fitting by the simulated spectrum, and the signal is rather broadened also in the $\nu_1'$ isotropic dimension. A magadiite sample dried under vacuum at room temperature also lost the sharp intense signal in its 2D MQ MAS spectrum and showed an indication of a signal at a similar position to that of dried octosilicate, although the spectrum is not shown because of its poor signal-to-noise ratio.

For both dried octosilicate and dried magadiite, the re-moisturized samples gave identical 2D spectra to those of the as-received samples, implying that the structural change is reversible.

## Discussion

Among the five kinds of hydrous layered silicates studied here, the structure of only makatite, $Na_2Si_4O_8(OH)_2\cdot 4H_2O$ ($Na_2O\cdot 4SiO_2\cdot 5H_2O$), has been fully resolved by single-crystal X-ray diffractometry.[1] A schematic diagram of the makatite structure is shown in Fig. 9. Two of the three kinds of sodium ions are coordinated by six water oxygens and the other is coordinated by two water oxygens and three silanol oxygens.

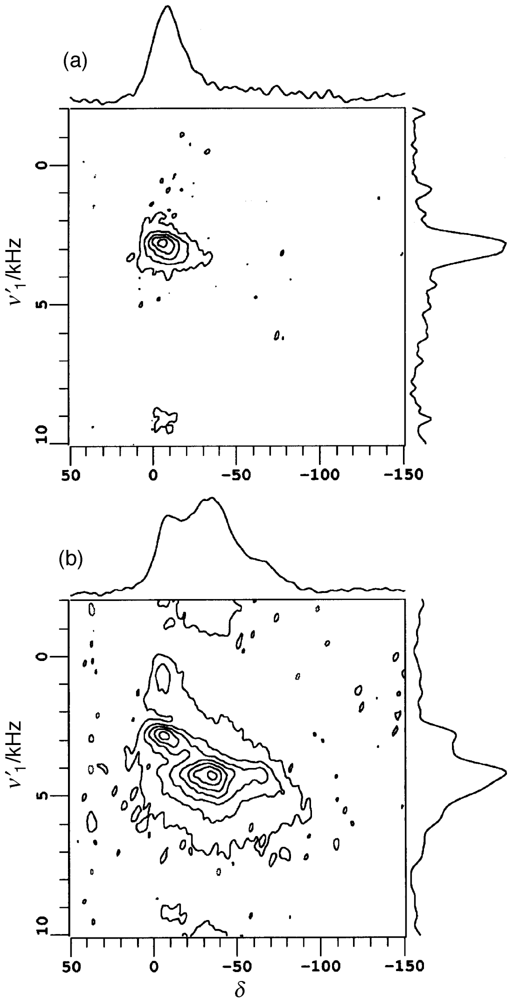

**Fig. 6** Two-dimensional triple-quantum $^{23}$Na MAS spectra of kanemite A with $^1$H decoupling: (a) sample dried under vacuum at 100 °C for 10 h; (b) re-moisturized sample. The 2D spectra show spinning sidebands in the isotropic ($\nu_1'$) dimension with separations of the spinning rate, $\nu_{\text{rot}}=6$ kHz, from the centrebands.

In the present work these three distinct sites for sodium ions were clearly resolved by the $^{23}$Na 2D MQ MAS method (Fig. 2). Sites 1 and 2 are assignable to two octahedrally coordinated environments and site 3 to the pentacoordinated one by virtue of the 1:1:2 relative intensity in the projection onto the isotropic axis. Although the hexacoordinated sodium ions seem to have higher local symmetry than the pentacoordinated ions, no large differences are observed in the quadrupolar coupling constants, $\chi$, or the asymmetry parameters, $\eta$. The relatively large $\chi$ and $\eta$ values of sites 1 and 2 are considered to arise from the differences of the six water oxygens in their coordinating features; one water oxygen is coordinated to only one sodium ion, while the others bridge two sodium ions. Some of the water molecules are expected to be hydrogen bonded to silicate layers in different ways.[1] However, considerable differences are observed in the isotropic chemical shift, $\delta^{\text{CS}}$, between the pentacoordinated sodium ions ($\delta^{\text{CS}}=8$) and the hexacoordinated ones ($\delta^{\text{CS}}=0$–$1$). This tendency of larger chemical shifts for pentacoordinated than for hexacoordinated sodium ions has also been reported for non-layered sodium silicates,[15] and thus the result obtained here suggests the possibility of using the isotropic chemical shift to distinguish

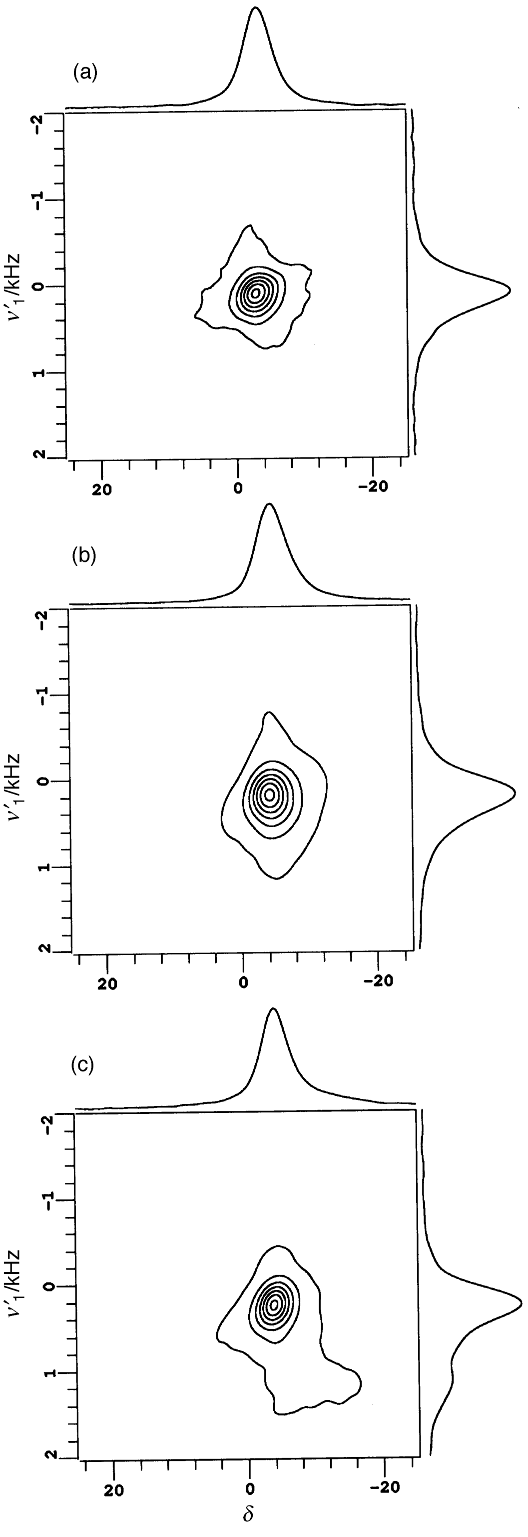

**Fig. 7** Two-dimensional triple-quantum $^{23}$Na MAS spectra with $^1$H decoupling for (a) octosilicate, (b) magadiite and (c) kenyaite. All the spectra were obtained at a spinning rate of $\nu_{rot} = 6$ kHz and acquired by a rotor-synchronized method in the $t_1$ domain.

the coordination number of sodium ions in these kinds of compounds, provided resolved spectra with true isotropic shifts can be obtained.

It should be noted here that the two different hexacoordinated sodium ions were clearly distinguished in the 2D MQ MAS spectrum, although they have quite similar surroundings in the crystal lattice. This result demonstrates the validity and the high performance of the 2D MQ MAS method combined with $^1$H decoupling for these kinds of compounds.

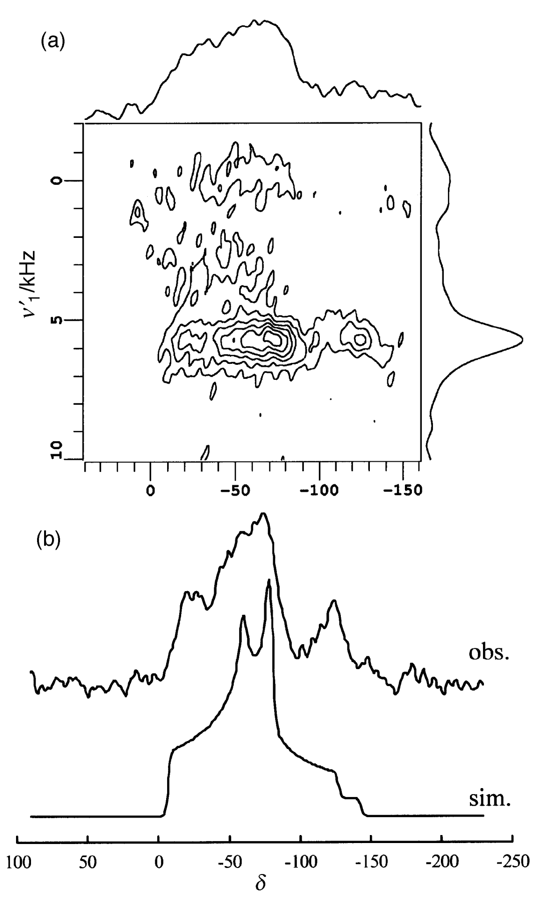

**Fig. 8** Two-dimensional triple-quantum $^{23}$Na MAS spectrum of octosilicate dried under vacuum at room temperature for 6 h (a), and triple-quantum-filtered single-quantum MAS cross section obtained from the 2D spectrum at the peak of the spectrum in the isotropic ($\nu_1'$) dimension, along with the best-fit simulation (b)

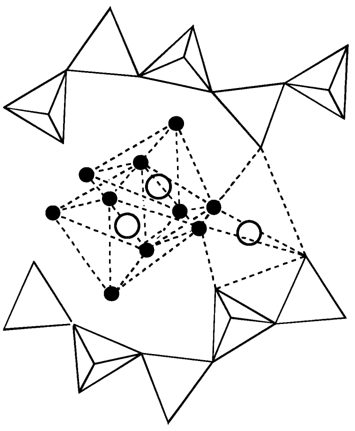

**Fig. 9** A schematic diagram of the makatite structure, derived from that in ref. 1, showing $SiO_4$ tetrahedra, water oxygen atoms (●) and sodium ions (○)

The two kanemite samples, kanemite A and kanemite B, showed rather different 2D MQ MAS spectra from each other in the as-received condition (Fig. 3). However, after the samples were dried under vacuum at room temperature and also after re-moisturization, they gave almost identical spectra.

Although kanemite has been considered to have a chemical formula of $NaHSi_2O_5 \cdot 3H_2O$ ($Na_2O \cdot 4SiO_2 \cdot 7H_2O$), the amount of water included in the sample depends on how it is prepared. It has been reported that the air-dried sample at room temperature after the synthesis has the formula $NaHSi_2O_5 \cdot 4.4H_2O$, and that the sample loses some of its water molecules to give $NaHSi_2O_5 \cdot 3H_2O$ by drying under vacuum at room temperature.[6]

This change in the number of incorporated water molecules has also been confirmed for the kanemite samples used here by thermogravimetry.[16] Therefore, the as-received samples of kanemite A and kanemite B are considered to have a chemical formula of $NaHSi_2O_5 \cdot (3+\alpha)H_2O$ ($\alpha<1$) and $NaHSi_2O_5 \cdot (4+\beta)H_2O$ ($\beta<1$), respectively, and the difference in the amount of water between the two samples is considered to originate in the different storage conditions. The formula of the samples was changed to $NaHSi_2O_5 \cdot 3H_2O$ by drying under vacuum at room temperature, but recovered to $NaHSi_2O_5 \cdot (4+\beta)H_2O$ after re-moisturization. Since the dried samples showed a strong signal only from site 1 in the $^{23}Na$ 2D MQ MAS spectra, whereas the re-moisturized samples showed an intense signal only from site 2 (Fig. 4), sites 1 and 2 are assignable to sodium ions in $NaHSi_2O_5 \cdot 3H_2O$ and $NaHSi_2O_5 \cdot 4H_2O$ formulations, respectively, so sodium ions in the re-moisturized sample would be coordinated to more water molecules (corresponding to the excess value of $\beta$ in the chemical formula), giving rise to site 3.

It has been suggested[4] that kanemite has a structure related to that of $KHSi_2O_5$ (where the silicate layers are connected by hydrogen bonding of the Si-O-H-O-Si type and potassium ions are coordinated by four silicate oxygens[17]), rather than to that of makatite. The present results confirm there are substantial differences between makatite and kanemite. However, by comparison with the results for makatite, sodium ions in sites 1 and 2 of kanemite are considered to have hexacoordinated structures from their chemical shifts. Therefore, some of four silicate oxygens coordinating the sodium ions in the case of $KHSi_2O_5$ are exchanged by water oxygens, resulting in three and four coordinating water molecules per sodium ion in kanemite, and the octahedral coordination structures of such sodium ions are expected to be rather distorted, as judged by the $\chi$ and $\eta$ values. In the $^{23}Na$ 2D MQ MAS measurement for kanemite A without $^1H$ decoupling, only the signal from site 2 was clearly observed [Fig. 3(c)]. This result is another[11] good example showing the high efficiency of $^1H$ decoupling when applied with the 2D MQ MAS method, and indicates that the sodium ions in $NaHSi_2O_5 \cdot 4H_2O$ probably have a more mobile coordination structure than that in $NaHSi_2O_5 \cdot 3H_2O$.

Recently, $^{23}Na$ 2D triple-quantum MAS NMR spectra of kanemite have been reported by Hayashi.[18] The measurement of the spectra was performed without $^1H$ decoupling, and the spectrum for the sample dried at 20 °C in air showed only one peak, in agreement with our present results. He assigned the signal to his 'component I', with the NMR parameters of $\delta^{CS}=2.9$, $\chi/MHz=2.05$ and $\eta=0.63$, which were evaluated by spectral simulation for ordinary 1D MAS NMR spectra with $^1H$ decoupling. Hayashi's component I is considered to correspond to the site 2 in this paper, assigned to the environment for sodium ions in $NaHSi_2O_5 \cdot 4H_2O$.

The signal from site 3 showed a much narrower lineshape, corresponding to a smaller $\chi$ value, than those of sites 1 and 2, and the chemical shift suggests a hexacoordinated structure for the site. Thus the sodium ions would have an octahedral coordination structure in site 3, with higher local symmetry than in sites 1 and 2 because of coordination by excess water molecules.

Although $NaHSi_2O_5 \cdot 3H_2O$ recovered its formula of $NaHSi_2O_5 \cdot (4+\beta)H_2O$ by re-moisturization, the sample dried under vacuum at 100 °C showed irreversible structural change so that the re-moisturized sample exhibited a new signal with a different position from those of sites 1, 2 and 3 (Fig. 6). This result strongly suggests that the drying procedure under vacuum at 100 °C brings structural changes not only in the coordination structure of sodium ions but also in the silicate layer, drastically changing the whole structure of kanemite irreversibly. This structural change can be considered as a reflection of the rather labile property of kanemite silicate monolayers, which also change their structure by exchange of sodium ions with protons.[4]

Octosilicate, magadiite, and kenyaite have nominal chemical formulae of $Na_2O \cdot 8SiO_2 \cdot 10H_2O$, $Na_2O \cdot 14SiO_2 \cdot 10H_2O$ and $Na_2O \cdot 20SiO_2 \cdot 10H_2O$, respectively. They showed only one sharp peak in their $^{23}Na$ 2D MQ MAS spectra (Fig. 7). From the similarity of the peak positions in the 2D spectra and of the lineshapes of the cross sections, the coordination structures of sodium ions in these three layered silicates are considered to be very similar, and the sodium ions presumably have hexacoordinated structures with relatively high symmetries, as shown by their chemical shifts of *ca.* $-1$ ppm and small quadrupole coupling parameters.[15] Approximate values of $\chi(1+\frac{1}{3}\eta^2)^{\frac{1}{2}}$ can be obtained from the peak positions in the 2D spectra[10,13] (Table 1). However, our attempts to fit the cross-sections suggest that the asymmetry factor is in an intermediate range, so that coordination both of water oxygens and of silicate oxygens to the sodium ions and/or differences of coordinating water molecules may occur; some water may be coordinated to only one sodium ion while others may coordinate two sodium ions as bridging ligands.[19] Some water molecules may be hydrogen bonding to silicate layers to different extents. The variations in $\delta^{CS}$ and the quadrupole coupling parameter among them seem to indicate differences in the silicate-layer structures, and thus in the inter-layer space where the sodium ions and water molecules exist.[2,3]

On the other hand, sharp signals were observed in the 2D spectra of makatite and kanemite at similar positions to those of octosilicate, magadiite and kenyaite. In kanemite, such a signal was assigned to site 3, so this is considered to have a similar coordination to those in octosilicate, magadiite and kenyaite. In the case of makatite, the signal is considered to be due to an impurity in which more water molecules coordinate to sodium ions, resulting in a more symmetrical coordination structure, such as is realized in octosilicate, magadiite and kenyaite.

By drying octosilicate and magadiite, the 2D spectra changed substantially, and a signal broadened by quadrupolar interaction was observed for both samples. This spectral change is deduced to be the result of lowering the coordination symmetry of sodium ions, produced by the removal of coordinating water molecules. A large deviation from the theoretical expectation was observed for dried octosilicate in the lineshape of the cross section, with spectral broadening in the $\nu_1'$ isotropic dimension. Since the triple-quantum excitation is anisotropic and depends on the orientations of the crystallites, the molecular orientation dependence could be a possible origin of the deviation in practice. However, the anisotropic effect has been shown to be sufficiently small under the present experimental conditions by a measurement for sodium oxalate ($Na_2C_2O_4$), which has a relatively large quadrupolar coupling constant of $\chi/MHz=2.52$.[13] Therefore, the lineshape deviation in the dried octosilicate is considered to indicate that there is a distribution in the coordination of sodium ions (*i.e.* in $\delta^{CS}$, $\chi$ and $\eta$), and the observed signal is concluded to be a composite from slightly differing sites.

## Concluding remarks

To obtain the structural information about the coordination of sodium ions, we applied the 2D MQ MAS NMR method for the first time to $^{23}Na$ in five different layered silicates. As a consequence, well resolved 2D spectra were observed for all the samples. For makatite and kanemite the 2D spectra enable us to evaluate accurate $^{23}Na$ parameters by lineshape fitting to the cross sections for each sodium site, because the signals are better resolved than for 1D MAS spectra, and the coordination structures of sodium ions in the inter-layer spaces are discussed in detail according to the parameters obtained.

It should be noted here that the existence of three different sites in makatite is shown definitively for the first time by NMR. Furthermore, three different sites were newly observed in kanemite, and the site corresponding to $NaHSi_2O_5 \cdot 4H_2O$ was distinguished from that to $NaHSi_2O_5 \cdot 3H_2O$. Such conclusions are not possible by ordinary MAS NMR because of overlapping of the signals.[6,7]

The results described here indicate the high performance of the $^{23}Na$ 2D MQ MAS NMR method, when used in conjunction with high-power proton decoupling, and this technique should be valuable for structural studies of other minerals, ceramics and bio-materials, where sodium ions play an important role for their chemical and physical properties.

We thank the UK EPSRC for research grants GR/H96096 and GR/J97557. One of us (M.H.) is grateful to the Ministry of Education, Science, Culture, and Sports of Japan for financial support. We also thank G. McGeorge and A. Nordon for assistance with spectrometer operation.

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*Paper* 7/07764E; *Received* 28*th October*, 1997