A Study of the Layered Alkali Metal Silicate, Magadiite, by One- and Two-Dimensional 1H and 29Si NMR Spectroscopy

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The layered alkali metal silicate magadiite is analysed by solid-state MAS/NMR techniques, showing that there is strong hydrogen bonding (but not in sodium-free forms) and that the hydrogen-bonded proton is the principal source of cross-polarisation for all types of silicon.

The five known hydrated layered alkali metal silicates have potential uses as catalyst supports or novel absorbents. Of these, magadiite ($Na_2O \cdot 10SiO_2 \cdot 14H_2O$) is the most heavily researched. Though it has never been fully resolved, its layer structure (Fig. 1) is well established. Magadiite has a basal spacing of ca. 15.6 Å, as measured by powder X-ray diffraction.[1] Previous 29Si NMR results have shown that the silicon atoms in the silicate layer are type Q^3 [-Si(OSi)$_3$] and Q^4 [Si(OSi)$_4$] only.[2] Several authors have predicted the structure of the silicate layer from quantitative 29Si NMR experiments.[3-5] The interlayer space probably consists of aqueous proton and sodium species, flanked by siloxide (-Si-O$^-$) or silanol (-Si-OH) groups.[6] Here, we report the first high-resolution proton spectra, and use two-dimensional methods to establish the mechanism for cross polarisation.

Fig. 2 shows a two-dimensional 29Si–1H heteronuclear correlation spectrum (via cross polarisation) for a carefully dried sample of magadiite. One-dimensional projections are given along each axis. These have the same number of peaks and chemical shifts as conventional one-dimensional 1H and 29Si single-pulse spectra. However, the relative intensities of the signals are not quantitative as, in both cases, they depend on the efficiency of cross polarisation. The 1H signal at δ 3.5 and the Q^4 29Si peaks are under-represented in the two dimensional spectrum. The 1H projection spectrum (Fig. 2) consists of two peaks at δ 3.5 and 14.9. The 1H MAS NMR spectrum of undried magadiite also consists of two centre-band signals with slightly shifted, broader lines. The peak at δ 3.5 can be attributed to water molecules, whereas the one at δ 14.9 must arise from strongly hydrogen-bonded protons, which presumably involve -Si-OH groups in unusual environments. In this work, similar high-frequency 1H shifts have also been observed in samples of kanemite, octosilicate and kenyaite. 1H NMR spectra of virtually sodium-free, acid-treated samples of magadiite have no signals at a high chemical shift. Therefore, strong hydrogen-bonding in layered alkali metal silicates seems to depend on the presence of sodium, implying -Si-OH···⁻O-Si- groups, as observed in potassium hydrogen silicate, $KHSi_2O_5$.[7] Such bonding may be crucial in matters of ion-exchange and pillaring for these systems. A value of 2.52 Å can be calculated for the -O-H···O- distance using the linear relationship between bond length and chemical shift of Eckart et al.[8] Such high 1H NMR chemical shifts have been observed previously in a few silicates.[7,9-11] The 29Si projection spectrum consists of four
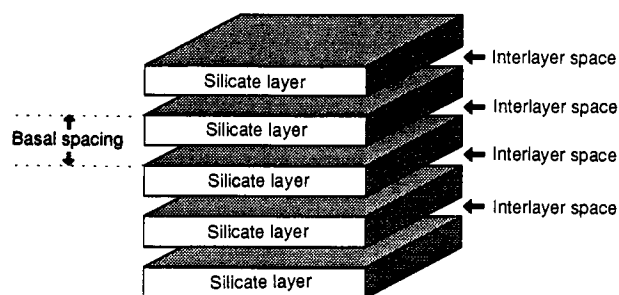
peaks at δ -99.2, -109.5, -111.2 and -113.6. The peaks can be confidently assigned to one Q^3 site and three Q^4 sites, respectively.[2] It has been proposed that the three Q^4 sites may differ by their average Si-O-Si bond angles.[3]

There are five centre-band peaks in the two-dimensional 1H, 29Si heteronuclear correlation spectrum. It is clear that the hydrogen-bonded site is the main source of cross polarisation to all the silicon atoms (including, interestingly, the Q^4 site), presumably because of its relative rigidity and proximity to the silicon atoms. The intensity of the peaks in the two-dimensional spectrum is a measure of the selectivity and efficiency of the 1H, 29Si cross-polarisation. As the Q^3 peaks are more intense, coupling to these sites is more efficient. Spin diffusion (or proton exchange) between the two types of proton site is clearly negligible over the timescale of the cross polarisation (8 ms). Magadiite must be dried for this selectivity to be observed; with undried magadiite, both protons apparently cross polarise to all silicon sites. In dried magadiite, spin diffusion/proton exchange is slower, as the 1H NMR lines are sharper, with less overlap. We have used two-dimensional 1H–1H correlation experiments to confirm this situation for layered alkali metal silicate samples: significant exchange is seen in a time of 8 ms for undried magadiite, but not for dried material.

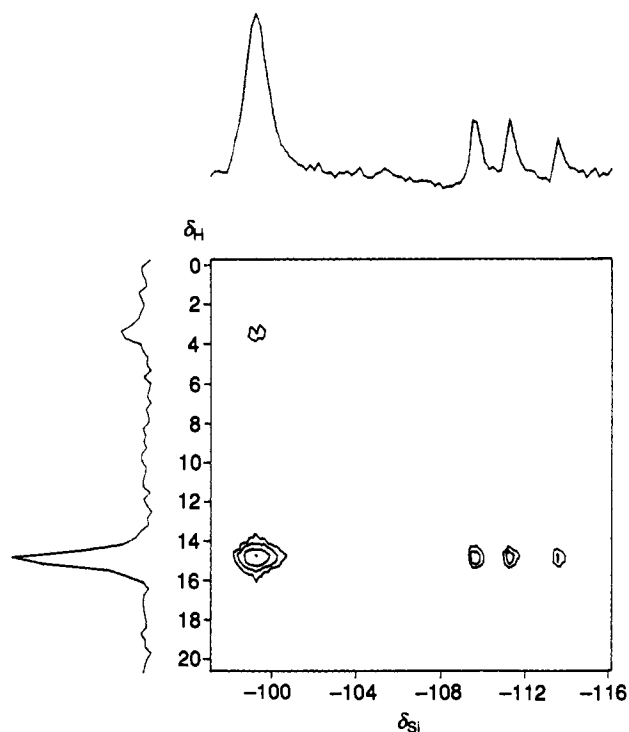Magadiite, therefore, contains protons which are strongly

Fig. 2 Two-dimensional 1H–29Si correlation spectrum (contour mode) of carefully-dried magadiite. Experimental conditions: recycle time 0.5 s, contact time 8 ms, number of experiments 128, number of transients per t_1 point 432, spinning rate 4.87 kHz. 1H and 29Si projections are shown along the axes.

Fig. 1 A schematic diagram of a layered alkali metal silicate

hydrogen bonded, and only such protons cross polarise efficiently to silicon atoms. Moreover, the behaviour of magadiite (and also kenyaite) on $^1H \rightarrow$ ^{23}Na cross polarisation[4,12] suggests that one type of sodium site (out of two) is within the silicate layer, with no neighbouring protons. A water-free magadiite silicate layer, with provision for isolated sodium sites and hydrogen bonding, may be postulated from these results. These conclusions must be considered in any proposals for the structure of magadiite.[3–5]

The natural magadiite sample was obtained from the Cureton Mineralogical Company, Tuscon, Arizona. The sample was dried by storage in a dry-box, in an atmosphere of oxygen-free nitrogen, circulating through P_2O_5 and molecular sieve 4 Å drying towers. The dried sample still contains at least 10% of hydration water by weight, as measured by TGA. The spectrum was acquired on a Varian VXR300 spectrometer fitted with a Doty 7 mm MAS probe. Transmitter frequencies of 299.949 and 59.584 MHz were used for the ^1H and ^{29}Si channels, respectively. Chemical shifts were referenced with tetramethylsilane. Tetra(*tert*-butyl)silane was used to obtain a Hartmann–Hahn match for ^{29}Si cross polarisation. The two-dimensional $^1H–^{29}Si$ heteronuclear correlation NMR spectrum was obtained using the pulse sequence of Vega[13] and Fyfe *et al.*[14] The $^1H–^1H$ exchange spectra were acquired using the method of Szeverenyi *et al.*[15] All spectra were recorded at ambient probe temperature.

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