Ordering of Silicate Layers by Hydrogen-Bonding Networks: Solid State NMR Investigation of the Perfect Three-Dimensional Registration in the Layer Silicate RUB-18

Ingo Wolf,[†,*] Hermann Gies,[†] and Colin A. Fyfe[‡]

Institut für Mineralogie, Ruhr-Universität Bochum, D-44780 Bochum, Germany, and Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1

Solid state ^{1}H and ^{29}Si NMR spectroscopies were applied to the layer silicate RUB-18 in order to investigate the hydrogen bonding network providing the three-dimensional ordering of the silicate layers. Two ^{1}H NMR signals corresponding to water molecules and strongly hydrogen-bonded silanol groups were resolved, the relative intensities of which are in good agreement with the recently proposed structure. By means of two-dimensional heteronuclear correlation NMR, the protons in hydroxyl groups are clearly identified as the source of polarization transfer to the ^{29}Si nuclei of the silicate layer. The dynamics of the exchange process between the protons in hydroxyl groups and those in the water molecules were investigated by two-dimensional ^{1}H exchange spectroscopy, giving insight into the nature of the exchange process—chemical exchange or spin diffusion. In addition, the ratio of exchanging protons of the two species has been found to differ from the stoichiometric ratio. ^{29}Si cross-polarization/magic angle spinning (CP MAS) NMR spectra taken at temperatures down to 140 K lead to enhanced resolution in the spectral region of Q^4 silicons, whereas the signal from Q^3 silicons remains unaffected. The potential applicability of solid-state NMR methods for measuring internuclear distances in this material is discussed.

Introduction

Layered sodium silicates are a group of materials that has been of considerable interest in the recent past especially in the area of heterogeneous catalysis.[1] The exchangeable intercalate cations and water molecules have been replaced with a variety of inorganic and organic cations and solvent molecules in order to modify and functionalize these materials for various applications.[2,3] Although their physical and chemical properties have been well studied, their crystal structures are mostly unknown and their frameworks are discussed only in terms of models proposed from crystal chemical reasoning:[3] Of the ∼10 layered sodium silicate hydrates known, only the structure of makatite is fully described by a single-crystal diffraction study. Moreover, most often the diffraction patterns of these materials are broad, indicative of the presence of two-dimensional (2D) order within the layers, but with incomplete or even no ordering in the third dimension orthogonal to the layers. In some cases, however, through fortuitous choice of interlayer cation and synthesis conditions, materials with perfect three-dimensional (3D) order were produced where the interactions of the interlamellar species bring the layers into perfect registration with each other. Such a situation was found for the layer silicate RUB-18 (Figure 1). The structure is built from anionic silicate sheets containing silanol bearing Q^3 [SiO$_3$OH]-tetrahedra and three-dimensionally connected Q^4 [SiO$_4$]-tetrahedra in the ratio 1:1. Neighboring layers are stacked along a 4_1 screw axis with the sodium hydrate polyhedron intercalated between the layers. From the oxygen−oxygen distances involving the oxygens of the hydrate water and the silanol groups calculated from the structure analysis (Figure 1), it is likely that the presence of considerable hydrogen

bonding is the driving force behind the ordering of neighboring layers (Figure 1). However, this hydrogen-bonding region shows poor scattering behavior in the X-ray experiment; most importantly, the hydrogen atoms involved cannot be located by this method.

NMR spectroscopy has often been used as a complementary analytical technique in the elucidation of silicate crystal structures. In particular, in zeolite structure analysis, the long-range periodicity of the silicate framework was analyzed with high-resolution X-ray powder diffraction (XRD) techniques, whereas the local symmetry of the framework and the ordering of guest- and sorbate species was examined with NMR spectroscopic experiments. For RUB-18, ^{1}H, ^{23}Na, and ^{29}Si NMR experiments are ideally suited to probe the ordering of the intercalated water and to investigate the hydrogen-bonding network. NMR experiments can yield information not only on the static structure of the material but also on the dynamics of any proton exchange between intercalated water and the surface silanol-groups of the silicate layer. Because almost all physical and chemical properties of the material involve the proton interactions, their detailed characterization is of particular importance. It is hoped that the information gained from the study of the hydrogen-bonding network in this highly ordered material will provide insight into the organization of less highly ordered materials.

Note that this layered silicate also can be looked upon as a model for external silicate surfaces. Because of the crystallinity of the material, the study can be carried out with conventional volume-analytical techniques, in particular XRD and NMR. Of particular interest in this context is the termination of the silicate layer with silanol groups and its interaction with and ordering of surface hydrate water.

We report here on ^{1}H and ^{29}Si NMR spectroscopic experiments of RUB-18, probing the local environment of the silicate

---

* To whom correspondence should be addressed.
† Ruhr-Universität Bochum.
‡ University of British Columbia.

5934 *J. Phys. Chem. B, Vol. 103, No. 29, 1999*

Wolf et al.
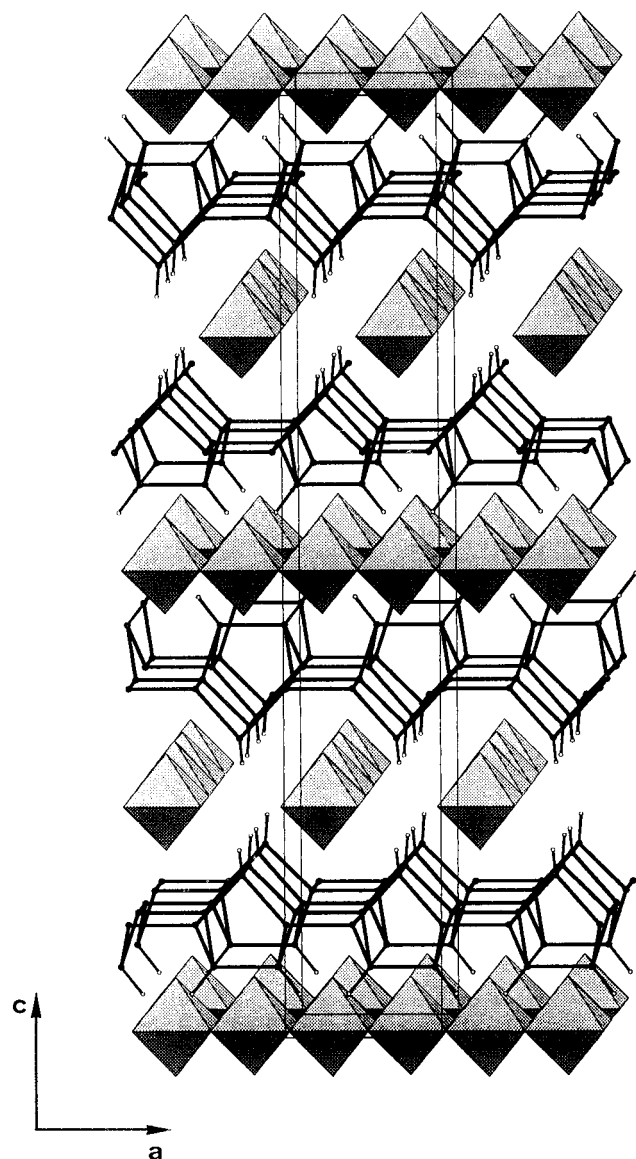
Figure 1. Crystal structure of RUB-18. Silicate layers are represented as skeleton model showing only the silicon atoms. Oxygen atoms are located in the middle of the Si−Si connections. Sodium cations are octahedrally coordinated by water forming edge-sharing one-dimensional chains.

layer and the hydrate water. In addition, the experiments also provide information about the proton spin diffusion and the chemical exchange between the silanol groups of the silicate layers and the protons of the intercalated hydrate water.

Experimental Section

The synthesis and lattice structure of RUB-18 were well described elsewhere.[4] For some experiments in the present study, the material needed to be deuterated. This was done by heating the sample in pure D_2O at 100 °C. The necessity of using elevated temperatures reflects the strength of the interactions within the hydrogen-bonding network. The degree of exchange was determined by ^1H magic angle spinning (MAS) NMR using a weighed amount of silicon rubber (poly(dimethylsiloxane)), as an internal reference.

All NMR experiments were carried out using a Bruker ASX 400 spectrometer. Experiments that required high spinning rates, such as ^1H MAS and ^1H nuclear Overhauser enhancement spectroscopy (NOESY) were run at 10 kHz using a standard 4

NOESY:
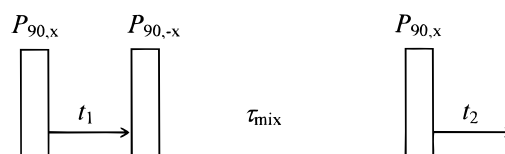
2D CP:
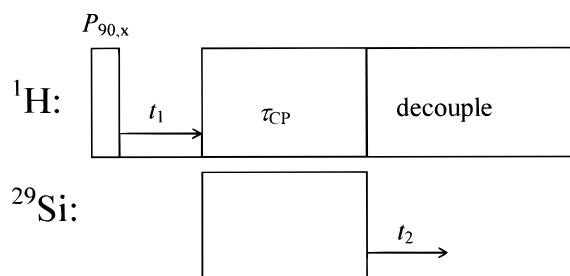
Figure 2. Pulse schemes used for 2D NMR experiments. The NOESY or exchange sequence produces homonuclear correlated spectra giving rise to off-diagonal intensities at positions where nuclei undergo chemical exchange or spin diffusion during the mixing time τ_m. The 2D CP sequence reveals heteronuclear correlation intensities at positions of spins between which polarization is being transferred.

mm MAS probe, whereas all ^{29}Si NMR experiments both with and without cross polarization (CP) from protons were done at spinning rates of ca. 3 kHz using a standard 7 mm MAS probe. ($^1H/^{29}Si$ CP; the Hartmann−Hahn condition was set on Q_8M_8 and then on the sample itself; pulse lengths of 90° pulses were between 5 and 7 μs.) Low-temperature experiments were performed using nitrogen gas and the standard Bruker VT unit. Chemical shifts of ^1H and ^{29}Si were referenced to tetramethylsilane (TMS).

In addition to conventional pulse MAS and CP MAS experiments, two-dimensional $^1H/^{29}Si$ CP and $^1H/^1H$ NOESY experiments were performed using the pulse sequences of Figure 2. Further descriptions of the experiments and the parameters used are given in the figure captions and at appropriate points in the text.

Results and Discussion

The ^1H MAS NMR spectrum of RUB-18 shows two well-separated signals centered at 3.5 and 15.9 ppm (Figure 3). Their intensity ratio is 8:1 which corresponds exactly to the relative concentrations of the protons in water molecules and silanol groups as proposed in the structure refinement.[4] Therefore, the 3.5 ppm peak can be assigned to intercalate water and the 15.9 ppm signal to SiOH groups terminating the silicate layers. A chemical shift of 15.9 ppm for protons in hydroxyl groups is quite unusual. One can, however, account for this, if the hydrogen is involved in a strong hydrogen bond to a neighboring oxygen. For a series of compounds with strong hydrogen bonds the relationship between the proton chemical shift and the X-ray or neutron diffraction analysis of the O−H···O geometry was investigated. The correlation between hydrogen bond lengths as determined from diffraction studies and ^1H chemical shift[5] predicts a bridging H···O bond length in the range of ca. 1.5− 1.6 Å for RUB-18. Also, the large negative chemical shift anisotropy parameter of −31 ppm obtained for the 15.9 ppm signal from the low-speed ^1H MAS NMR spectrum (see Figure 3) is consistent with there being an additional hydrogen bond,
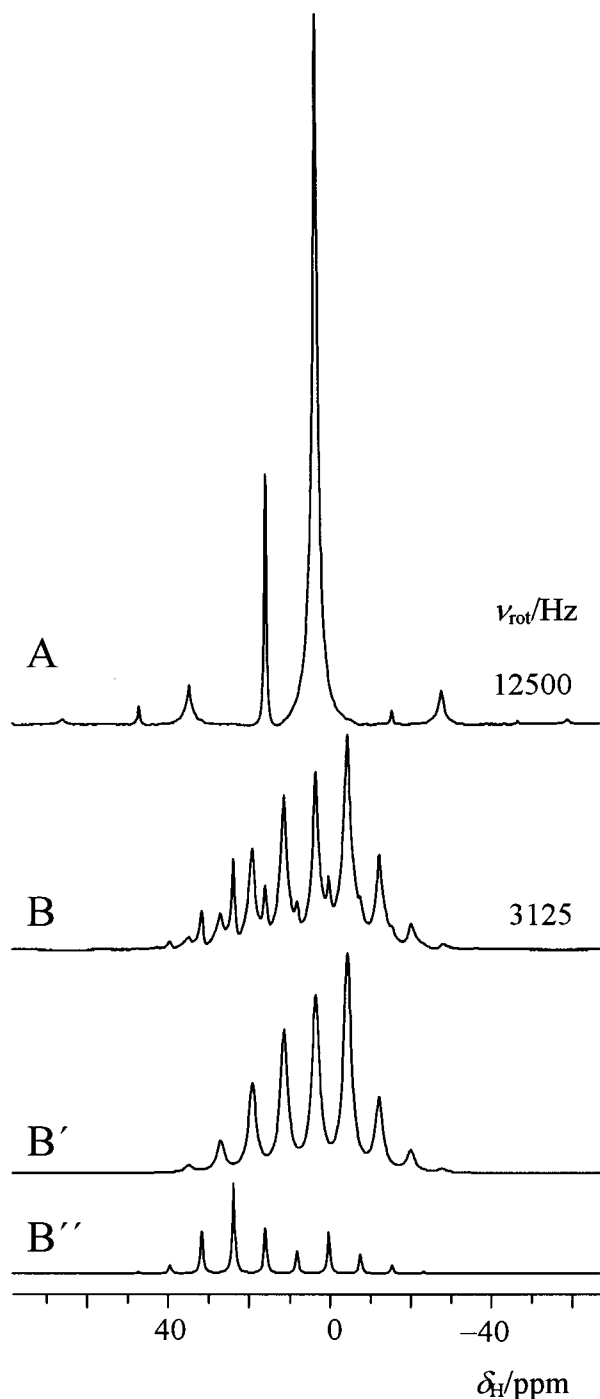
Figure 3. [1]H MAS spectra of RUB-18 measured at spinning rates of 12.5 kHz (A) and 3125 Hz (B). The simulated line shapes given in (B′) and (B″) are the two components of a chemical shift anisotropy (CSA) sideband fit to spectrum (B).

although the correlation found in ref 5 between chemical shift anisotropies and H···O bond lengths is less well defined.

Distance determinations in NMR are always based on measuring dipolar couplings between nuclei. Because these interactions scale with the reciprocal cubic root of the distance, NMR usually produces quite accurate distances from only moderately accurate experimental data. Methods of choice include CP[6] with variable contact times,[7] rotational echo double resonance (REDOR),[8] or transferred echo double resonance (TEDOR).[9] It is, however, important to ensure that the nuclei of specific interest are present as isolated spin pairs, i.e., any dipolar couplings to additional nuclei may be neglected, and that the internuclear distances are fixed during the NMR

experiment. Otherwise, the theoretical descriptions of the effect of dipolar couplings are no longer unambiguous.

The first step in this study to support the assignment of the proton NMR signals was a 2D CP experiment correlating ^{1}H and [29]Si chemical shifts to clearly identify the polarization source. The ^{29}Si MAS NMR spectrum of RUB-18 consists of two signals of equal intensity (Figure 4A), assigned to the Q^3 and Q^4 silicons of the silicate layers.[4] On applying the ^{1}H/[29]Si CP sequence, the intensity ratio is increased in favor of the Q^3 silicon signal. 2D ^{1}H/[29]Si CP spectra were obtained, by waiting an incremented time between the initial [1]H 90° excitation pulse and the polarization transfer pulse of the CP sequence (Figure 2B), thus allowing the ^{1}H spin system to evolve prior to transferring magnetization to the [29]Si spins.[10,11] The resulting 2D data matrix directly correlates those ^{1}H and [29]Si nuclei between which CP takes place (Figure 4B). The figure illustrates that only the protons giving rise to the signal centered at 15.9 ppm cross polarize efficiently to [29]Si at a contact time of 20 ms. This confirms our earlier assignments of the resonances in the ^{1}H MAS spectrum. The complete lack of intensity in the ^{1}H projection in the range of the intercalate water proton signals suggests that these are sufficiently remote from silicon and/or have sufficient mobility so as not to interfere with the dipolar coupling between the protons of the silanol groups and the [29]Si nuclei. However, the result of the experiment does not exclude the presence of some homonuclear dipolar coupling and/or chemical exchange between the two proton species which could affect experiments with very long evolution times. The method of choice for investigating these two effects with NMR is 2D exchange spectroscopy making use of the NOESY sequence.[12,13] The experiment is shown in Figure 2A: Three 90° pulses are applied, with an incremented delay between the first and the second pulses. The second pulse returns the magnetization to the *z* axis and the state of the proton spin system evolution is conserved during a fixed delay allowing exchange processes to take effect. The application of the third 90° pulse returns the magnetization to the *x,y* plane where it is detected during t_2. As long as the time constant(s) of the exchange process(es) is longer than the spin−spin relaxation time and not (much) longer than the spin−lattice relaxation time, the NOESY experiment will produce a 2D spectrum where any exchange processes are reflected in the presence of off-diagonal correlation peaks at the cross sections of the signals of exchanging species. For isolated spin pairs, exchange rates may be derived from the integrated signal intensities of the diagonal and off-diagonal peaks, depending on the relative spin concentrations and the applied mixing time used.[12,13] More accurate results can be obtained from a series of NOESY spectra with different mixing times and activation energies can be determined from experiments carried out at different temperatures.

There are two basic mechanisms by which spin exchange between nuclei in different sites can occur: direct exchange via dipolar interactions between them and chemical exchange of the nuclei themselves between the sites. The former should have little direct temperature dependence, whereas the latter should show a clear Arrhenius-type behavior. The absolute contribution from dipolar based spin-diffusion may be minimized by dilution of the observed spins achieved in the present case by exchange of the OH-functionalities with deuterium by reaction with D_2O.

The 2D ^{1}H NOESY spectrum shown in Figure 5 is of a 90% deuterium-exchanged sample at a mixing time of 20 ms; it is obvious that there is considerable exchange on that time scale. The time constant of the exchange process can be obtained from

A

B
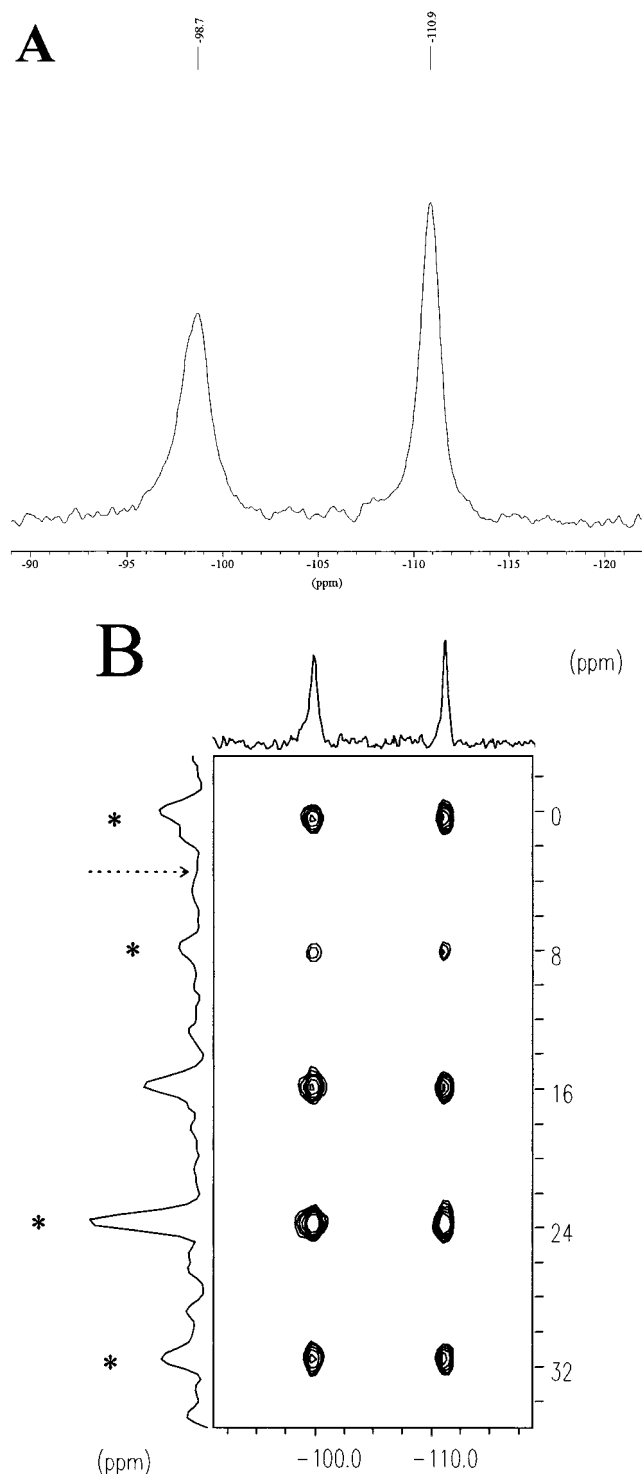
Figure 4. (A) ^{29}Si MAS spectrum of RUB-18 showing Q_3 and Q_4 sites as indicated. This spectrum serves to reference the F2 dimension of the 2D plot. (B) 2D ^{1}H/^{29}Si CP spectrum showing ^{1}H to ^{29}Si connectivities. The contact time was 20 ms. The ^{1}H spectrum in the F1 dimension is a projection and shows resonances from only those protons which are involved in the coherence transfer to ^{29}Si. From the isotropic chemical shift value of 16 ppm these are identified as silanol protons as indicated. Asterisks (*) indicate spinning sidebands and the position of the nonobserved isotropic chemical shift of the coordinated waters is indicated by the dashed arrow.

the peak intensities of a series of 2D NOESY spectra with mixing times from 0.5 to 50 ms. The kinetics can be described in terms of the ratio of cross-peak vs diagonal peak intensities I_{CROSS}/I_{DIAG}. Assuming a first-order two-site exchange with
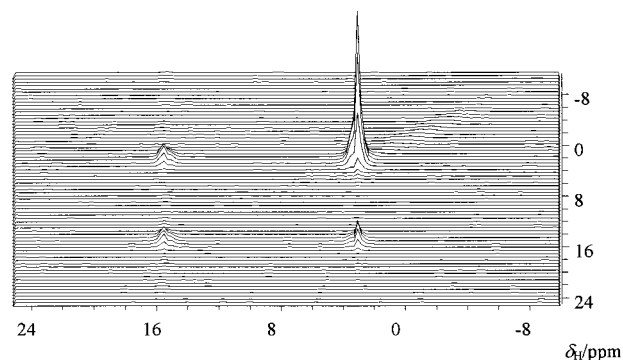
Figure 5. ^{1}H NOESY spectrum of RUB-18 (90% deuterated) recorded at 20 ms mixing time. There is considerable intensity at the cross sections of the two resonance positions because of both chemical exchange and spin diffusion.

TABLE 1: Temperatures, Chemical Exchange Rates (k), Dipolar Rates (R_D), and χ_A/χ_B Ratios from ^{1}H NOESY MAS Spectra of 90% Deuterated RUB-18

$T/°C$	k/s^{-1}	R_D	$\chi_A{:}\chi_B$
23	94	0	4,0
40	147	0	4,2
50	234	0	4,3
60	283	0	4,4
70	552	0	4,4
75	728	0	4,6
80	709	0	4,8
100	1239	0	8,0

unequal occupancies of the sites, we obtain from ref 12

$$\frac{I_{CROSS}}{I_{DIAG}} = \frac{-2\chi_A\chi_B\dfrac{R_C}{D}\sinh(D\tau_m)}{\cosh(D\tau_m) - (\chi_A - \chi_B)\dfrac{\delta}{D}\sinh(D\tau_m)} \quad (1)$$

where τ_m is the mixing time and χ_A and χ_B denote the molar fractions of the protons in water molecules (A) and the protons in hydroxyl groups (B), respectively, which are involved in the exchange process. The constants R_C, δ, and D contain the rates of chemical exchange k and of spin diffusion R_D as follows (assuming T_1 relaxation of both species to be equal):

$$R_C = R_D - k \quad (2)$$

$$\delta = (\chi_B - \chi_A)(2R_D + k) \quad (3)$$

$$D = \sqrt{\delta^2 + \chi_A\chi_B R_C^2} \quad (4)$$

A detailed description of the derivation of eq 1 as well as the analysis of the data from 2D exchange experiments is in preparation.[14]

To provide a complete description of the kinetics and also the mechanism of the exchange process, a detailed study was made of a sample which was 90% deuterium exchanged in order to minimize possible contributions from dipolar-based spin diffusion. 2D exchange experiments were carried out at eight temperatures between 23 and 100 °C as indicated in Table 1. At each temperature, six 2D exchange spectra were recorded at mixing times between 0.4 and 50 ms and the ratios of the diagonal to cross-peak intensities were determined for each mixing time at each temperature.

In eq 1, there are three independent parameters which determine the ratio of the diagonal and cross-peak intensities: the mole fraction χ_A ($\chi_B = 1 - \chi_A$), the chemical exchange

rate k and the spin diffusion rate R_D. By keeping χ_A and χ_B fixed at the values expected from their stoichiometric ratio, it was possible to obtain an approximately Arrhenius relationship between log k and temperature if a specific constant (and arbitrary) R_D value was chosen. However, the fit is not exact, the R_D value is surprisingly large for the degree of exchange and the procedure is not entirely satisfactory.

Another possibility, which is not relevant in solution exchange studies, is that because the sample is crystalline and the various functionalities have only limited, if any, motional freedom, not all of the hydrogens on the coordinated water molecules are involved in the exchange; that is, χ_A and χ_B may be different from the stoichiometrically determined values. If all three parameters χ_A, k, and R_D are allowed to vary, nonzero values are found for each, but the R_D values are always close to zero, more in line with what is expected from the extent of deuteration. On the basis of this information, all the data were fitted to eq 1 assuming that R_D was exactly zero throughout the temperature range and χ_A and k were variables. The resulting fits were of the same accuracy or better as with all three parameters given free. The contribution of the spin diffusion to the exchange process should be independent of the temperature. Thus, the resulting chemical exchange rates are expected to form a straight line in an Arrhenius plot versus temperature. The rate constants from a series of ^{1}H NOESY experiments on 90% deuterated RUB-18 are given in Table 1 and their logarithms are plotted vs the reciprocal of temperature in Figure 6A. In this Arrhenius plot the data fit well to a straight line with a slope corresponding to an activation barrier of $E_a = 33 \pm 2$ kJ mol^{-1}. To quench the exchange rate well below 50 s^{-1} (which corresponds to an exchange time of longer than 20 ms), the working temperature should be kept below room temperature. The open circle in Figure 6A marks the predicted 0 °C point in the linear fit, giving a value of $k \approx 26$ s^{-1}.

In this model, the χ_A value remains approximately constant between 4.0 and 4.6 up to 75 °C (Table 1) indicating that only two of the four coordinated water molecules are involved in the exchange over this extended temperature range. This is reasonable in light of the crystal structure (Figure 1) where two of the coordinated waters have their hydrogen atoms pointing into cavities in the silicate layers away from the bridging hydroxyls. At temperatures closer to 100 °C where dehydration occurs, the number of hydrogens involved approaches 8.0 as might be expected from the greatly increased mobility suggested by the eventual dehydration.

As a final test of the correctness of this model, a sample was exchanged to a level of 95% and the exchange process was investigated at room temperature. There was no effect at all on the exchange rates compared to the previous data from the 90% exchanged material, proving decisively that there is no contribution from spin diffusion.

The ^{29}Si nucleus is known to be extremely sensitive to its local environment. In a perfectly ordered crystal, every crystallographically inequivalent Si position results in a unique individual resonance position. The presence of other chemical elements occupying tetrahedral positions in a silicate lattice usually gives rise to considerable line broadening and resonance shifts. It is anticipated then, that the resonance position of the Q^3 silicons should be sensitive to the actual orientation of the hydrogen bond within each of the Si−O−H···O−Si bridges containing a ^{29}Si nucleus. The fact that no splitting of the ^{29}Si resonance because of Q^3 is observed at room temperature suggests that there are thermally activated jumps of the protons between the two possible orientations. Figure 7 shows ^{29}Si CP
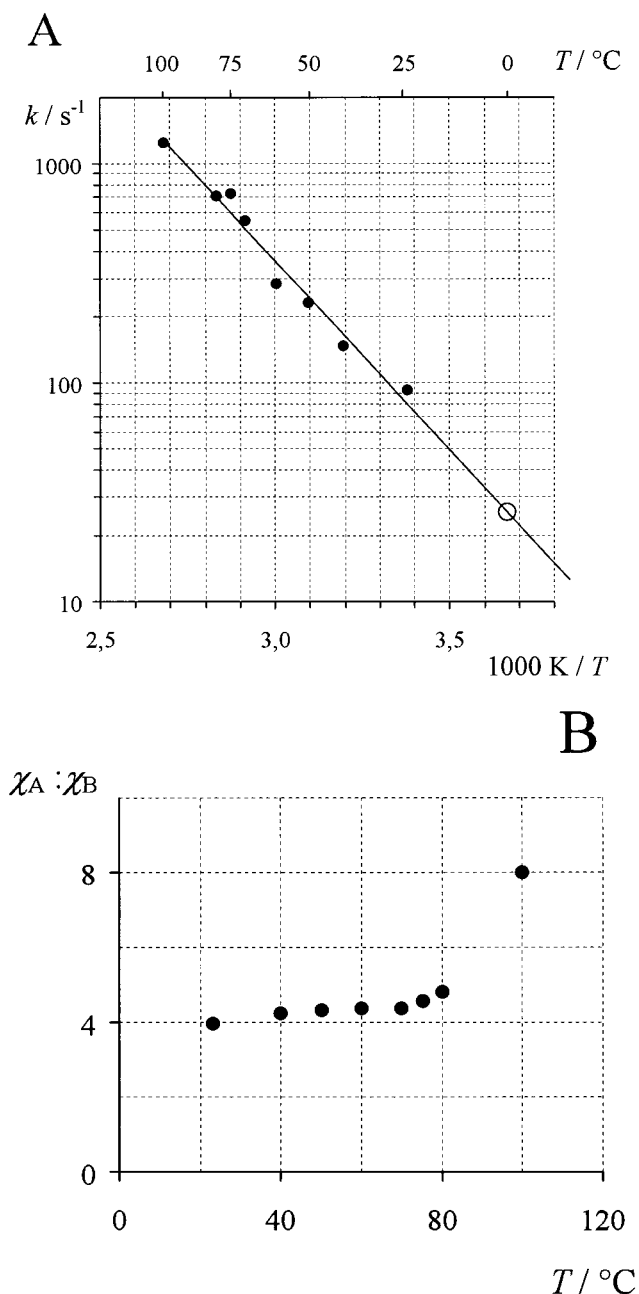

Figure 6. (A) Arrhenius plot of exchange rates vs the reciprocal of temperature from ^{1}H NOESY spectra of 90% deuterated RUB-18. For convenience, the T values in °C are given at the top axis. The straight line is a linear least-squares fit to the data giving an activation barrier of $E_A = 33$ kJ mol^{-1}. The open circle marks the 0 °C point in the linear fit. (B) Ratios χ_A/χ_B of molar fractions of exchanging protons in water molecules vs protons in hydroxyl groups plotted vs temperature.

MAS spectra of RUB-18 acquired at temperatures down to 140 K. Whereas the Q^4 resonance obviously starts to show signal splitting into several peaks, no changes in the Q^3 signal are obvious. Because we assume the hydrogen bond to be very short from its large resonance shift, we should expect a rather low activation barrier between the two orientations. Therefore, that motion may be well frozen out on the ^{29}Si shift scale only below 140 K. On the other hand, the short hydrogen bond might not necessarily lead to a sufficient separation of the two ^{29}Si resonance positions that they are resolved in the spectra.

Conclusions

The hydrogen bonding network responsible for the three-dimensional registration of the silicate sheets in RUB-18 was

T / K
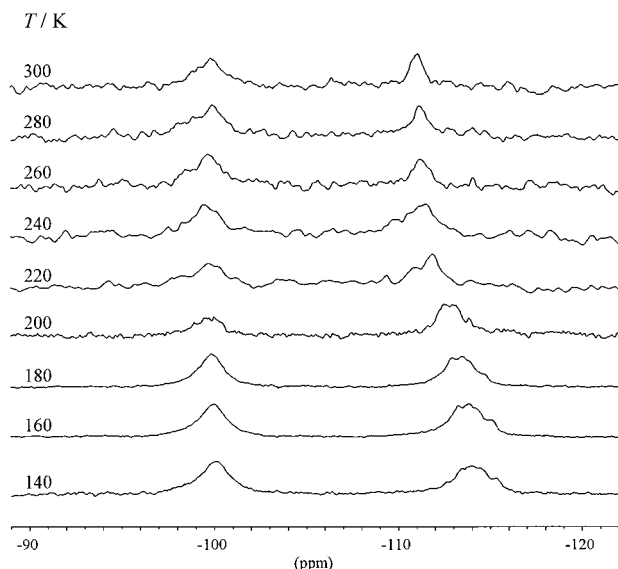
Figure 7. ^{1}H/^{29}Si CP MAS spectra of RUB-18 recorded at temperatures as indicated at the left. Whereas no splitting of the Q^3 signal into two separate lines could be observed, the Q^4 signal appears to split into several lines at low temperatures.

studied by ^{1}H and ^{29}Si NMR spectroscopies. The proton MAS spectra exhibit two well-defined resonances with ratios of 8:1 which can be assigned to the hydrate water and the layer hydroxyls in Si−OHLO−Si units, respectively. This assignment was confirmed by 2D ^{1}H/^{29}Si CP MAS spectra which also define the lattice hydroxyls as the dominant polarization source. The exchange process between the two proton types was described

on the basis of 2D NOESY experiments on a 90% deuterium-exchanged sample. It was found that the activation barrier of the chemical exchange is 33 kJ/mol, and that not all hydrogens need to be involved in the exchange. By applying the presented methodology it should be possible to find similar exchange behavior in other solid systems as well.

These measurements define the behavior of the H-bonding network and provide the foundation for further NMR spectroscopic investigations both of RUB-18 and also less highly ordered layered materials.

References and Notes

(1) Rieck, H. P. *Nachr. Chem. Technol. Lab.* **1996**, *44*, 699−704.
(2) Bergk, K. H.; Schwieger, W.; Porsch, M. *Chem. Technol.* **1987**, *39*, 459−466.
(3) Bergk, K. H.; Schwieger, W.; Porsch, M. *Chem. Technol.* **1987**, *39*, 508−514.
(4) Vortmann, S.; Rius, J.; Siegmann, S.; Gies, H. *J. Phys. Chem. B* **1997**, *101*, 1292−1297.
(5) Jeffrey, G. A.; Yeon, Y. *Acta Crystallogr.* **1986**, *42*, 1986 410−413.
(6) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(7) Fyfe, C. A.; Lewis, A. R.; Chézeau, J. M.; Grondey, H. *J. Am. Chem. Soc.* **1997**, *119*, 12210.
(8) Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196.
(9) Hing, A. W.; Vega, S.; Schaefer, J. *J. Magn. Reson.* **1992**, *96*, 205.
(10) Caravatti, P.; Bodenhausen, G.; Ernst, R. R.; *Chem. Phys. Lett.* **1982**, *89*, 363.
(11) Fyfe, C. A.; Grondey, H.; Mueller, K. T.; Wong-Moon, K. C.; Markus, T. *J. Am. Chem. Soc.* **1992**, *114*, 1992 5876.
(12) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.
(13) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford University Press: Oxford, 1987.
(14) Wolf, I. To be submitted for publication.