Synthesis and characterization of the layered sodium silicate ilerite

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Received 11 February 2000; received in revised form 16 May 2000; accepted 19 May 2000

Abstract

A sodium ilerite, molar ratios 1Na2O:8.2SiO2:10.2H2O, was obtained with a good crystalline structure and characterized by several NMR techniques in addition to X-ray diffraction (XRD). The X-ray pattern of the as-synthesized ilerite is in very good agreement with the structure proposed by Gies and coworkers. The narrow 29Si MAS NMR signals (FWHM ≈ 3 ppm) indicate a good short-range order of the framework. The proton dynamics influences several 29Si NMR parameters. The 16 ppm signal in the 1H MAS NMR spectra is explained by a proton in a bridging position in the short (2.3 Å) O4–O4 bonding. The quadrupole coupling constant \( C_{QCC} \approx 100 \text{ kHz} \) with \( \eta = 0.2 \) for the 16 ppm signal, which was obtained from the 2H MAS NMR spectra, confirms this explanation. 17O NMR shows also a separate signal for SiOH groups but cannot resolve the three expected lines for SiOSi. PFG NMR detects a small mobile portion of water in the ilerite, which is located probably on the external surface of the crystallites. An intracrystalline diffusion coefficient of the intercalated water molecules of the order of magnitude \( 10^{-15} \text{ m}^2 \text{s}^{-1} \) was obtained by NMR tracer exchange experiments. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Layered sodium silicate; Ilerite; Synthesis; NMR; Diffusion

1. Introduction

Aluminum-free layered sodium silicates are materials with a two-dimensional (2-D) oriented condensed structure [1–3], which attracted attention for industrial applications because of their high ion-exchange selectivity and capacity, their properties as catalysts or catalyst supports [4,5] and their potential in creation of novel properties through intercalation of organic material [6–10]. Contrary to other microporous silicates like the well-crystallized zeolites, the crystal structures of layered silicates are mostly unknown, since diffraction patterns are often broad, showing the 2-D order of the layers but no ordering in the third dimension. In very few cases, materials with good three-dimensional (3-D) order were found or synthesized [11]. Complete structure analysis of a
material with the code name RUB-18 and the cell content \((\text{Na}_8\{\text{Si}_{32}\text{O}_{64}(\text{OH})_8\}\cdot32\text{H}_2\text{O})\), which should be identical with Na ilerite, was recently achieved by Gies and coworkers [12] by means of a special approach for the processing of X-ray powder data at moderate resolution. This layered sodium silicate was first synthesized by Iler [13]. We use the term ilerite introduced in 1979 by Wolf and Schwieger [14]. The name octosilicate was introduced for this layered sodium silicate by Schwieger et al. [15] in 1985 and also used by Borbely et al. [16]. Fig. 1 shows a model of hydrated sodium ilerite obtained by Cerius on the basis of the X-ray powder data of Gies and coworkers [12].

Solid-state and diffusion NMR techniques are well established for the investigation of microporous silicates, cf. Refs. [17–20]. A recent solid-state NMR study of RUB-18 [21] gives information about the hydrogen-bonding network, which provides the 3-D ordering of the ilerite layers. Two \(^1\text{H}\) MAS NMR signals corresponding to water and strongly hydrogen-bonded silanol groups have been resolved, and the dynamic hydrogen exchange between the two species was observed by exchange spectroscopy [21]. However, it was also shown by MAS NMR measurements in a temperature range between 150 and 300 K [22] that the structure of ilerite is drastically influenced by the synthesis procedure, the ion exchange and the thermal sample treatment in the range from 300 to 353 K. This paper focuses on the synthesis of a Na ilerite with a good crystalline structure and on its characterization by X-ray diffraction (XRD) and several NMR techniques.

2. Experimental

2.1. Synthesis

The layered silicate sodium ilerite was synthesized using colloidal silica (Chemiewerk Köstritz) with a SiO\(_2\) content of about 30\%, sodium hydroxide pellets (minimum 97\% NaOH, Aldrich) and de-ionized water as starting materials for the preparation of the reaction mixtures. The hydro-

![Fig. 1. Projection of the modeled structure of hydrated sodium ilerite. Three unit cells are displayed in a crystallographic c–a plane. The layers lie in the a–b plane. Black spheres denote oxygen atoms. Isolated black spheres denote the oxygen atoms of water molecules. White spheres are the silicon atoms, and gray spheres denote the sodium ions.](image-url)
thermal procedure used was based on that described in Ref. [3]. The dissolved sodium hydroxide (in one-third of the whole water amount) was added slowly under vigorous stirring to the diluted (one-third of the water amount) silicon compound (the remaining water was used to flush the NaOH containing flask). After mixing the components (≈15 min), the reaction mixture was homogenized by vigorous stirring for about 45 min. This final mixture was then dispersed into stainless-steel autoclaves. Crystallization of the sodium ilerite was performed at 373 K with a molar composition of the reaction mixture of 4SiO$_2$:1Na$_2$O:30H$_2$O. The crystallization time was 21 days. After removing the autoclave from the oven, the solid product was quenched in water, separated by filtration, washed with de-ionized water, and air-dried at room temperature.

2.2. $^{17}$O and $^2$H enrichment

Water which was 43% enriched in $^{17}$O or 99.8% enriched in $^2$H was used. The ilerite was immersed into 1 g of enriched water per gram of structural water and heated for 20 h in a sealed glass tube at 373 K. This treatment did not change the structure of the sodium ilerite, whereas a heating in an open tube would destroy the structure already at a temperature of 320 K [22]. $^1$H MAS NMR spectra of ilerite immersed into $^2$H$_2$O, which were measured some days after the heating procedure, showed that the D/H ratio is equal to one and no preferential deuteration of the species indicated by the lines at 16.6 and 3.7 ppm takes place.

2.3. Solid-state, multi-nuclear NMR experiments

NMR spectrometers MSL 500 and DMX 750 were used with magic-angle spinning in the range from 0 to 16.6 kHz. Quadrupole echo and Hahn echo pulse sequences were applied for $^2$H and $^1$H NMR measurements, respectively, in addition to the observation of the free induction decay (FID). The maximum non-selective nutation frequencies for the $^{17}$O {$^1$H} double resonance experiments ($v_L = 101.7$ (750) MHz, $v_{rot} = 10$ kHz) were 55 and 44 kHz for $^{17}$O and $^1$H, respectively. A $^{17}$O nutation frequency of 14.67 kHz was applied for the $^{17}$O {$^1$H} cross-polarization (CP) NMR experiment. The non-selective $^{17}$O nutation frequency in the single-resonance probe was 120 kHz. Triple-quantum experiments were performed by means of two strong pulses and an additional weak z-filter pulse and a MAS frequency of 17.5 kHz. A total ring-down delay of 7 μs after the z-filter pulse and a repetition time of 200 ms were used. A 24-phase cycle was applied twice with an additional 30° phase shift in between, in order to acquire the real and imaginary parts for the second Fourier transform. The widths of the first and second pulses were adjusted for maximum signal to 3.4 and 1.2 μs, respectively. The selective π/2 pulse length of the z-filter was adjusted to 50 μs by lowering the rf power. $^{29}$Si MAS NMR experiments were performed with and without $^1$H cross-polarization and with and without $^1$H de-coupling in the temperature range from 135 to 353 K. $^{23}$Na MAS NMR spectra were measured at 140 and 298 K. Values of the chemical shift are given to the usual references (TMS for $^1$H, $^2$H and $^{29}$Si; water for $^{17}$O; 1M NaCl for $^{23}$Na).

2.4. Pulsed field gradient and tracer exchange NMR experiments

$^1$H PFG NMR self-diffusion measurements were carried out by means of the home-built spectrometer FEGRIS 400 [23] operating at 400 MHz. Pulsed field gradient (PFG) of 24 T m$^{-1}$ amplitude and 800 μs duration, and the rf pulse sequence for a stimulated echo were applied [20]. NMR tracer exchange experiments [24] were performed on an ilerite sample additionally loaded with D$_2$O by observation of the $^1$H NMR intensity of the bulk water signal at 300 MHz (spectrometer Bruker MSL 300).

2.5. X-ray

X-ray powder diffraction patterns were obtained on a Philips vertical sample diffractometer using CuKα radiation operating with 48 kV. γ-Al$_2$O$_3$ served as an external standard to determine the crystallinity of the products.
3. Results and discussion

The composition of the prepared sodium ilerite was, expressed in molar ratios of the oxides, 1Na₂O:8.2SiO₂:10.2H₂O. Taking into consideration the $^{29}$Si MAS NMR results, which confirm the unit-cell composition proposed by Gies and co-workers [12], our as-synthesized sodium ilerite is specified by $\{(0.98\text{Na} + 0.02\text{H})\cdot 2\text{H}_2\text{O}\} \cdot \{\text{Si}_2\text{O}_5 \cdot \text{Si}_2\text{O}_4\} \cdot 2.3\text{H}_2\text{O}$. The different Si species Si₂O₅ and Si₂O₄ are the so-called Q³ and Q⁴ groups, respectively. The adsorbed 2.3 molecules of water are reversibly removable. Fig. 2 shows the XRD powder pattern of the as-synthesized sample and samples at different dehydration stages. The peak positions in the X-ray pattern of the as-synthesized ilerite (Fig. 2) are in very good agreement with literature data [12]. No additional peaks could be detected, which indicates the good quality of the synthesized ilerite. A thermal treatment of the ilerite causes a shift of the basal spacing from 11.2 to 9.6 Å due to a desorption of water from the interlayer space. Such a process is reversed when the ilerite sample is exposed to water after a treatment at temperatures up to 70°C, as shown in Fig. 2. A temperature treatment above 90°C leads to a structural collapse of the sodium ilerite. Fig. 3 shows that the powdered sodium ilerite product consists mostly of regularly shaped rectangular plate-like single crystallites.

$^{29}$Si MAS NMR spectroscopy gives a value of the Q³/Q⁴ ratio on the one hand and information of the near-order homogeneity of the framework structure on the other hand. A $^{29}$Si MAS NMR study of several ilerites [22], which were obtained from the Na ilerite by exchange with other cations (K⁺, H⁺, Li⁺, NH₄⁺, Ca²⁺, La³⁺), showed an increase of the full width at half maximum (FWHM) of both signals (Q³ signal at $\approx -100$ ppm, Q⁴ signal at $\approx -111$ ppm) in this sequence: 0.5 ppm (Na form), 2 ppm (K form), 5 ppm (NH₄ and Ca form). The increasing FWHM is due to a larger distribution of isotropic values of the chemical shift, which is caused by a decreasing short-range order of the framework structure. The narrow signals (FWHM = 0.3 ppm) in Fig. 4 indicate a good short-range order of the framework. The tetrahedral symmetry of the Q⁴ units (one silicon
atom is fourfold coordinated to OSi) yields a small chemical shift anisotropy, whereas for the Q3 units (one silicon atom is connected three times to OSi and once to OH) the anisotropy of about 40 ppm gives rise to spinning sidebands. Therefore, the MAS frequency of 10 kHz for the spectra in Fig. 4 is of advantage compared to a MAS frequency of 2 kHz (not shown): Firstly, the spinning frequency is higher than the chemical shift anisotropy of the Q3 signal and only two peaks (without spinning sidebands) at −100.2 and −111.4 ppm must be taken into consideration. Secondly, the lowering of the MAS frequency causes a broadening of the Q3 signal from 0.3 ($v_{\text{rot}} = 10$ kHz) to 1 ppm ($v_{\text{rot}} = 2$ kHz). The latter is a hint that $^1$H species with jump frequencies (between positions in the layer) of 1 kHz and below cause a dipolar interaction with the $^{29}$Si nuclei in Q3 position. The two signals of the $^{29}$Si MAS NMR spectra reflect several time-dependent spin interactions, including the longitudinal relaxation time $T_1$. The spectrum in Fig. 4B was acquired with a repetition delay of 30 s and yields a ratio Q3/Q4 = 1.7, whereas the spectrum 3A for a repetition delay of 150 s gives a ratio Q3/Q4 = 1.0 ± 0.05 in agreement with Refs. [12,21]. A measurement of the longitudinal relaxation time $T_1$ yields 140 and 280 s for the silicon atoms in Q3 and Q4 positions, respectively. Another effect can be observed by the $^1$H de-coupling (the decoupling field strength corresponds to a nutation frequency of 40 kHz) during the observation time. It broadens the Q3 line in $^{29}$Si CP MAS NMR and $^{29}$Si MAS NMR spectra by factors of about 4 at $v_{\text{rot}} = 10$ kHz. Also, the mixing time of the cross-polarization $^{29}$Si($^1$H) CP MAS NMR experiment reflects different time-dependent spin interactions for both $^{29}$Si signals. Spectra, which are not shown here, yield maximum signal amplitudes after mixing times of 1 and 5 ms for Q3 and Q4 units, respectively. All four effects, which were observed at room temperature, do not allow an exact quantification of the proton dynamics. But the experiments and the model of the hydrogen exchange between silanol groups and water molecules in the Na ilerite of Wolf et al. [21] gave quantitative results, e.g. an exchange rate of $\approx 100$ s$^{-1}$ at room temperature. This hydrogen exchange can explain all the above-mentioned effects of the spin dynamics.

The low-temperature $^{29}$Si CP MAS NMR spectrum in Fig. 4C shows only little change around $-100$ ppm. The broadening caused by de-coupling is less significant than at room temperature. However, the Q4 signal is drastically changed: A quartet consisting of lines at $-113.0$, $-113.7$, $-114.1$ and $-114.9$ ppm is obtained at 130 K instead of the singlet at $-111.4$ ppm at room temperature. This splitting obviously hints to non-equivalent positions of four Q4 silicon atoms in the ilerite framework at low temperature, indicating that the structure of the ilerite is deformed at low temperatures with respect to its structure at room temperature.

Vortmann et al. [12] proposed an ideal cell content of Na{Si4O8(OH)}·4H2O. This composition is close to the values of our as-synthesized material, which were determined by chemical analysis (ICP). Vortmann et al. [12] found a weight loss of 20% by thermal analysis (TGA) in the temperature range from 373 to 473 K and a water amount of 19.95% by Karl Fischer titration. This corresponds to 3.9 water molecules per cell. The TGA analysis of the Na ilerite synthesized in this work shows by heating to 1473 K a weight loss, which corresponds to a loss of 4.8 water molecules.

Fig. 4. $^{29}$Si MAS NMR spectra at a spinning frequency of 10 kHz. The spectra were acquired at room temperature with a repetition delay of 150 s (A) and 30 s (B), respectively. On top, the $^{29}$Si CP MAS NMR spectra at 130 K (C).
from the starting material Na\{Si\sub{4}O\sub{8}(OH)\} \cdot 4\text{H}_{2}\text{O}, which is probably transformed to tridymite (SiO\sub{2}) and Na\sub{2}O above 1000 K. The experimental value of 4.8 is in good agreement with the expected water loss of 4.5 molecules per cell. The difference could be due to a slight exchange of the sodium by protons during the washing procedure with de-ionized water, which is always slightly acidic. Therefore, the ICP of the Na ilerite gives an enhanced ratio Si/Na \approx 4.08 with respect to the ratio 4 for the proposed structure [12].

\(^1\text{H} \text{MAS NMR spectra, which were measured from room temperature down to 200 K, consists of two signals, cf. Fig. 5. Wolf et al. [21] assigned the stronger signal, which we found with 88 \pm 1\% of the total intensity (intensities of the spinning sidebands must be added to the intensity of the corresponding center bands) at a chemical shift of 3.8 ppm, to the ilerite water molecules and the weaker signal, which we found with 12 \pm 1\% of the total intensity at a chemical shift of 16.3 ppm, to the silanol groups, which are part of the ilerite structure. The ratio 1:7.7–9.1 for the proton concentration in silanol groups with respect to that in the water molecules is in good agreement with the ratio 1:8 that corresponds to the cell content Na\{Si\sub{4}O\sub{8}(OH)\} \cdot 4\text{H}_{2}\text{O proposed by Vortmann et al. [12]. Another important argument of Wolf et al. [21] for assigning the 16 ppm signal to the silanol groups is a \(^1\text{H}–^{29}\text{Si} \text{cross-polarization experiment, which affects only this signal. Also, our studies about the influence of the sample pretreatment supports this assignment; vacuum treatment of the ilerite at 423 K halves the total intensity of the} \(^1\text{H} \text{NMR signal, whereas the loss of intensity of the 16 ppm signal is only 20\%. It is most likely that the structural silanol group is more stable against dehydration than the water molecules of the ilerite.\)

The temperature dependence of the spectra in Fig. 5 shows a broadening of the signals with decreasing temperature. Hydrogen exchange rates between water molecules and silanol groups are lower than 0.2 \text{s}^{-1} at 200 K [21] and cannot give rise to this broadening. It is more likely that jump frequencies of a hindered rotation of the water molecules around the Na–O axes are not much larger than the MAS rotation frequency at the low temperature. This could cause a broadening of the MAS spectra.

The chemical shift of an isolated water molecule is 0.31 ppm [25] and that for water molecules hydrogen bonded to other water molecules in bulk water is 4.78 ppm [26]. This means that hydrogen-bonding shifts the proton resonance in bulk water by ca. 4.5 ppm and in the ilerite by 3.5 ppm. The narrow signal at 3.5 ppm cannot be explained by a uniform hydrogen bonding. Various O–O distances for the hydrogen bridges in the range of 2.8–3.6 Å could be determined by XRD [12]. Therefore, several lines with chemical shifts in the range of 1–6 ppm should be expected, cf. Ref. [27] for immobile hydrogen atoms in the water molecules. A single signal with an averaged chemical shift occurs, if a fast exchange of the hydrogen atoms (exchange frequency much greater than 2.5 kHz) between all possible bridging positions takes place. From the observation of the single narrow signal of the ilerite water molecules, it follows that at temperatures above 200 K a fast exchange in the order of magnitude of 10 kHz or even more takes place.
Isolated silanol groups at the surface of silicates or at defects of porous silicates give rise to a $^1$H MAS NMR signal in the range of 1.2–2.2 ppm, cf. Ref. [28]. OH–O bonds with a chemical shift of about 16 ppm occur in inorganic materials. For instance, the hydrogen bonded anions in CaHPO$_4$ have a bridging hydrogen with a H–O distance of 1.23 A, which gives rise to a signal at 16.2 ppm [29]. This value of 1.23 A or the value of 1.38 A, which can be taken for 16.3 ppm from a plot of a variety of chemical shifts in solids as a function of the H–O distance [27], can be compared with some O–O distances of hydrogen bonds in the ilerite [12], which should be equal to or smaller than the sum of the O–H distance (about 1 A) and the H–O distance. It turns out that all distances between the silanol oxygen atom (O4) and oxygen atoms of the water molecules (O5, O6, O7) are too large to explain a chemical shift of about 16 ppm. Only the shorter one of the two O4–O4 distances, which amounts to 2.3 A [12], is short enough. This explains why there exists only one silanol group for two O4 atoms: The proton is on a bridging position on the short O4–O4 distance in a double minimum potential.

$^2$H MAS NMR spectra show the typical quadrupole powder pattern in addition to the two signals at 4 and 16 ppm. Fig. 6 shows the room temperature spectrum. The fit by means of the program WINFIT gives two sets of the quadrupole coupling constants $C_{\text{qcc}}$ and the asymmetry parameters $\eta$, $C_{\text{qcc}} = 100$ kHz with $\eta = 0.2$ for the 4 and 16 ppm signal, respectively. Static $^2$H NMR measurements (without MAS) shows a decrease ($C_{\text{qcc}} = 40$ kHz) for the 4 ppm signal going from room temperature to 360 K and an increase ($C_{\text{qcc}} = 52$ kHz) going down to 240 K.

The static quadrupole coupling constant of immobile water molecules decreases from about 240 kHz for weak hydrogen bonding between the water molecules to about 180 kHz for strong hydrogen bonding between the water molecules [30]. Molecular motions can reduce this value. A rotation of the molecule around the axis of symmetry of the water molecule reduces the coupling constant by the factor $(3 \cos^2 \beta - 1)/2$, if $\beta$ is the half bonding angle. Free water has a bonding angle of 105° ($\beta = 52.5°$) and the obtained factor is 0.06. The chemical shift of the ilerite water signal is 3.8 ppm. This value is not far from the bulk water chemical shift of 4.8 ppm. Therefore, we assume that the static coupling constant of ilerite water is not far from the value for solid water, which amounts to about 215 kHz [30]. Then, the experimentally obtained value of 42 kHz (room temperature) corresponds to a value $\beta = 47.1°$ or a bond angle of 94.2°. This value slightly increases with increasing temperature. The quadrupole coupling constant $C_{\text{qcc}}$ of the 16 ppm signal can be explained by very strong hydrogen bonding without local mobility. This agrees with a $C_{\text{qcc}} = 119.6$ kHz and a chemical shift of $\delta = 14.8$ ppm for the strongly hydrogen bonded hydrogen atom in ammonium dihydrogen phosphate, cf. [31].

In our $^{17}$O NMR experiments, three lines were resolved in the high field of 17.6 T. The different peaks (SiOH, SiOSi and H$_2$O) could be assigned via $^{17}$O $^1$H CP MAS NMR- and $^{17}$O $^1$H REDOR NMR experiments. Fig. 7 shows a cross-polarization effect for oxygen atoms, which are coupled to protons (peaks at $\delta = 60.8$ and $-29.2$ ppm), whereas there is no cross-polarization for the oxygen atoms, which are only coupled to silicon atoms (peak at $\delta = 42.6$ ppm). Fig. 7 also shows the $^{17}$O $^1$H REDOR NMR dephasing and reference experiment with six $\pi$ pulses applied to the $^1$H spins. The peak at $-29.2$ ppm vanishes due to the mobility of water, the intensity of the peak at 52.6 ppm is unaffected, since at this site the

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**Fig. 6.** $^2$H MAS NMR spectra of a deuterated ilerite at a spinning frequency of 8 kHz.
oxygen atoms are only coupled to silicon atoms and the intensity of the peak at 61.2 ppm is clearly decreased.

The $^{17}$O $\{^{1}$H\} REDOR NMR and $^{17}$O $\{^{1}$H\} CP MAS NMR experiments are used to assign the different sites, the line at 61.2 ppm to the silanol groups (SiOH), the line at 42.6 ppm to the bridging oxygen atoms (SiOSi) and the line at $-29.2$ ppm to water (H$_2$O). The XRD data of the sodium ilerite yield three different SiOSi-angles 161.3°, 145.6° and 141.2° that are not visible in the ordinary $^{17}$O MAS NMR spectra (cf. Figs. 7 and 8). Unfortunately, the application of 3QMAS does not improve the resolution. The simulation of the MAS spectra (Fig. 8) was performed by taking the quadrupole parameters of the two slices from the 3QMAS spectra. Results are shown in Table 1.

The range of bridging oxygen angles can be related to the value $\delta_{1/2}$ of the SiOSi line. One obtains a value of 9.3 ppm/20° = 0.46 ppm deg$^{-1}$ for the layer silicate Na-Ilerite. For the SiOSi resonance in the hydrated zeolite Na-ZSM-5 [32], a value of 5.7 ppm/13.4° = 0.43 ppm deg$^{-1}$ can be calculated. Supposed that with increasing bond angle, the isotropic chemical shift decreases. These data show the similarity of the framework structure between RUB-18 and MFI-type zeolites.

PFG NMR experiments, which were performed at room temperature and 330 K, gave diffusion coefficients of $D = 5 \times 10^{-13}$ and $1.6 \times 10^{-12}$ m$^2$s$^{-1}$ at 330 K, respectively. The values are much lower than the diffusion coefficient of bulk water at room temperature, which amounts to $2.3 \times 10^{-9}$ m$^2$s$^{-1}$. Unfortunately, the accuracy of the PFG NMR measurements of the ilerite water is limited by the short relaxation times of 300 μs and 3 ms for $T_2$ and $T_1$, respectively. It cannot be excluded that PFG NMR is monitoring only a small mobile portion of water in the sample. But the experiments undoubtedly show that the diffusion of ilerite water is very slow compared to that of bulk water.

The diffusion of water in the ilerite was also monitored by an NMR tracer exchange experiment [24]. For this purpose, D$_2$O has been introduced into the sample in such an amount that the concentration of D$_2$O notably exceeded the concentration of intercalated H$_2$O molecules. 20s, after this loading procedure, the acquisition of the $^1$H NMR signal was started. Immediately after loading there exist two distinct phases: intercalated H$_2$O and D$_2$O in the intercrystalline space between the ilerite particles. The $^1$H NMR signal shows that already after 20 s, a weak exchange with intercalated water has taken place. The establishment of the $^1$H NMR signal in the water phase in the intercrystalline space is found to follow an exchange curve that may be represented by a superposition of two exponentials. One exponential

Table 1

<table>
<thead>
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<th>Site</th>
<th>$C_{eq}$ (MHz)</th>
<th>$\eta$</th>
<th>$T_{2\text{Hahn,MAS}}$ (ms)</th>
<th>$\delta_{CS \text{ iso}}$ (ppm)</th>
<th>Intensity (%)</th>
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<tr>
<td>1 (Si$^{17}$OH)</td>
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<td>0</td>
<td>6</td>
<td>61.2</td>
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<tr>
<td>2 (Si$^{17}$OSi)</td>
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<td>0</td>
<td>19</td>
<td>42.6</td>
<td>75.2</td>
</tr>
<tr>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>29.2</td>
<td>16.5</td>
</tr>
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with a relative intensity of 66% and a time constant of $\tau_{\text{short}} = 74 \pm 5$ s and a second one with a relative intensity of 34% and a time constant of $\tau_{\text{long}} = 790 \pm 380$ s.

Barrer's relation [33], $D = d^2/32\tau$, allows the determination of the coefficient of the intracrystalline diffusivity $D$ from the exchange time constant $\tau$ for the diffusion of molecules in a disc (diameter $d$) with impenetrable faces. It is assumed that the rate of the molecular migration in the phase of the bulk water in the intercrystalline space is much larger than in the intercalated water layers. Using the value $D = 5 \times 10^{-13}$ m$^2$ s$^{-1}$ from the PFG NMR experiment and the time constants $\tau_{\text{short}} = 74 \pm 5$ s and $\tau_{\text{long}} = 790 \pm 380$ s from the tracer exchange experiment, we would obtain the diameters $d_{\text{small}} \approx 34 \mu$m and $d_{\text{large}} \approx 112 \mu$m by means of Barrer's equation. From the REM picture (Fig. 3), we can see that crystallites of such a large size do not exist and the estimated distribution of the crystallite size is rather in the range of 1.5–5 $\mu$m. With $d_{\text{small}} = 1.5 \mu$m, $d_{\text{large}} = 5 \mu$m and the time constants from the tracer exchange experiment, we obtain $D \approx 10^{-15}$ m$^2$ s$^{-1}$ by means of Barrer's equation. Thus, the intracrystalline diffusion coefficient that is estimated from the tracer exchange NMR experiment by using crystallite sizes from the REM picture is lower than the diffusion coefficient determined by the PFG NMR experiment by more than two orders of magnitude. With this result of NMR tracer exchange, it is proven that PFG NMR is in fact monitoring only a small mobile portion of water in the sample, which is probably located on the external surface of the crystallites.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft in connection with the projects Ka 429/9-3 and Schw 478/1-3, the Sonderforschungsbereich 294 and the Graduiertenkolleg Physikalische Chemie der Grenzflächen.

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