

Investigation of the Structure of Zeolites by Solid-State High-Resolution ^{29}Si NMR Spectroscopy

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Abstract: The high-resolution magic angle spinning ^{29}Si NMR spectra of a number of synthetic and natural zeolites have been studied. A regular dependence of the ^{29}Si chemical shifts upon the number of AlO_4 tetrahedra linked to the SiO_4 tetrahedron under study allows us to establish the structures of various zeolites and to get information about the Si/Al ordering. It is likely that the Loewenstein rule is violated in NaA and in some other zeolites.

Crystal structures and the related adsorption, ion-exchange, catalytic, and other properties of zeolites have been extensively investigated during recent years. The ordering of Si and Al atoms in the zeolite framework, although of importance for the spatial distribution of nonframework cations and the chemical properties of zeolites, has not been studied as extensively. In many cases several Si/Al distributions fit the X-ray data equally well, and the final assignment has been rather arbitrary. Imperfections of zeolite structure and structural changes during cation exchange, although very important in determining the physical and chemical properties of zeolites, could not be efficiently studied by existing methods, except by the very recent high-resolution electron microscopy studies.²

In two recent papers^{3,4} we have shown that solid-state high-resolution ^{29}Si NMR spectroscopy of the framework silicon atoms is a very useful tool for structural studies of solid silicates and aluminosilicates. The ^{29}Si chemical shifts of all the common silicate anions are generally the same in the solid state and in solution.⁴ The differences are comparable to the usual solvent shifts and amount to 1 or 2 ppm at most. In the solid insoluble aluminosilicates with tectosilicate framework the ^{29}Si chemical shifts depend primarily on the degree of silicon substitution by aluminum in the lattice. Five distinct ^{29}Si chemical shift ranges are thus created, depending on the number of AlO_4 tetrahedra connected to the SiO_4 tetrahedron under consideration.⁴ In contrast to the X-ray data, information gained from the ^{29}Si NMR spectra thus related primarily to the type and regularity of Si/Al distribution in the lattice and describes the aluminosilicate structure through structural units, similar to those used for the description of the structure of siloxanes⁵ and silicates.⁴

It was of interest to check the validity of the ^{29}Si shift/structure relationships in the case of the aluminosilicate frameworks of zeolites and to study the possibilities of the new method for the structural investigation of various synthetic and natural zeolites in general. In this paper we present the results of high-resolution ^{29}Si NMR studies of synthetic zeolites A, X, Y⁶ and sodalites and of a series of natural zeolite minerals with different structures and Si/Al ratios.

Experimental Section

a. Samples. The synthetic zeolites NaA, NaX, NaY and sodalites were prepared by standard procedures and were used as fine powders of

the hydrated forms. The natural zeolite minerals were donated by the Mineralogical Museum of the Humboldt-University, Berlin, and were studied as fine powders, prepared manually in an agate mortar.

b. NMR Measurements. All ^{29}Si NMR spectra were recorded in a 47-kG field at 39.75 MHz on a Bruker-Physik CXP-200/300 solid-state high-resolution NMR spectrometer, equipped with a wide-bore superconducting magnet and an Aspect-2000 data system. High-power ^1H spin decoupling and rapid (about 3 kHz) sample spinning at the magic angle to the external magnetic field were used. The samples were filled in conical Andrew-type hollow rotors, manufactured from Delrin. In most cases conventional FT-NMR was the best method to achieve good signal to noise ratios, but cross-polarization was used as well wherever applicable (particularly with minerals containing immobilized water or SiOH protons). The cross-polarization (CP) ^{29}Si NMR spectra can be very different from the conventional FT-NMR ^{29}Si spectra with the lines corresponding to hydroxylated silicon atoms strongly enhanced due to nuclear polarization transfer from the abundant protons. The ^{29}Si radio frequency $\pi/2$ pulse amplitude was 7–10 μs , but 4–5- μs radio frequency pulses were actually used in the direct FT-NMR experiments and ^1H radio frequency $\pi/2$ pulses of 7–10 μs in CP experiments. Time intervals between the radio frequency pulses were typically 2–6 s and in some cases up to 30 s in the direct FT-NMR experiments and 1 or 2 s between the CP pulse sequences. The ^1H - ^{29}Si spin contact time with the Hartmann-Hahn condition fulfilled in the doubly rotating frame was typically about 10 ms. The total measuring times varied from a few minutes to overnight runs. All measurements were carried out at 35 °C temperature with solid Q_3M_8 (trimethylsilyl ester of the double four-ring silicate) used as a secondary standard. The ^{29}Si chemical shift of the trimethylsilyl M group in Q_3M_8 was taken to equal +11.5 ppm in the low field from liquid Me_4Si . This cubic compound is just as useful for solid-state ^{29}Si NMR spectroscopy as hexamethylbenzene has proved to be for ^{13}C NMR. Slight distortion of the cube in the crystal leads to a splitting of the Q resonance with four lines at -108.5, -108.8, -109.5 and -109.8 ppm. The 0.15-ppm line widths provide a very good check for the magic angle setting of the probe. The ^{29}Si line widths are broader in minerals and usually of the order of 0.5–3 ppm in samples with a regular lattice structure and nearly perfect Si/Al ordering. The mean error of the measured isotropic ^{29}Si chemical shifts amounts to ± 0.5 ppm.

Results and Discussion

a. Assignment of the NMR Spectra. In the previous paper⁴ it was shown that the ^{29}Si chemical shifts of natural aluminosilicates depend mainly on the number of Al atoms in the second coordination sphere of Si atoms. The silicon atoms in zeolites belong to a three-dimensional framework and carry the designation Q^4 in the silicate nomenclature (Q^3 in layers, Q^2 in chains, Q^1 for end groups, Q^0 for monosilicates). Since the degree of silicon substitution by aluminum in the second coordination sphere must also be shown, the correct designation for a fully aluminum-substituted framework silicon atom would be $\text{Q}^4(4\text{Al})$. In order to simplify nomenclature, we use $\text{Si}(4\text{Al})$ instead in this paper. We indicate in brackets the number of aluminum tetrahedra sharing oxygens with the SiO_4 tetrahedron under consideration and define five different structural units in the aluminosilicate framework, namely, $\text{Si}(0\text{Al})$, $\text{Si}(1\text{Al})$, $\text{Si}(2\text{Al})$, $\text{Si}(3\text{Al})$, and $\text{Si}(4\text{Al})$ for which characteristic ^{29}Si shift ranges with about 5-ppm low-field shifts for each additional aluminum substituent have been

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Table I. ^{29}Si NMR Isotropic Chemical Shifts of Hydrated Synthetic and Natural Zeolites

zeolite	typical unit-cell contents	Si/Al ratio	$\delta^{29}\text{Si}$ from Me_4Si				
			Si(4Al) ^a	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
NaX	$\text{Na}_{88}[(\text{AlO}_2)_{88}(\text{SiO}_2)_{104}] \cdot 264\text{H}_2\text{O}$	1.18	-84.6 ^b	-89.0	-94.2 ^c	-98.8 ^c	-103.1 ^c
NaY	$\text{Na}_{55}[(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}] \cdot 250\text{H}_2\text{O}$	2.5	-83.8 ^c	-89.2	-94.5 ^b	-100.0	-105.5
NaA	$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$	1	-85.0 ^c	-89.6 ^b	-94.5 ^c		
hydrated sodalite	$\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6] \cdot 7.5\text{H}_2\text{O}$	1	-83.5				
sodalite	$\text{Na}_8[(\text{AlO}_2)_8(\text{SiO}_2)_8] \cdot \text{Cl}_2 \cdot x\text{H}_2\text{O}$	1	-84.8				
thomsonite	$\text{Na}_4\text{Ca}_8[(\text{AlO}_2)_{20}(\text{SiO}_2)_{20}] \cdot 24\text{H}_2\text{O}$	1	-83.5				
natrolite	$\text{Na}_{16}[(\text{AlO}_2)_{16}(\text{SiO}_2)_{24}] \cdot 16\text{H}_2\text{O}$	1.5		-87.7 ^b	-95.4		
gmelinite	$\text{Na}_8[(\text{AlO}_2)_8(\text{SiO}_2)_{16}] \cdot 24\text{H}_2\text{O}$	2		-92.0 ^c	-97.2 ^b	-102.5	
chabazite	$\text{Ca}_2[(\text{AlO}_2)_4(\text{SiO}_2)_8] \cdot 13\text{H}_2\text{O}$	2		-94.0 ^c	-99.4 ^b	-104.8	-110 ^c
analcime	$\text{Na}_{16}[(\text{AlO}_2)_{16}(\text{SiO}_2)_{32}] \cdot 16\text{H}_2\text{O}$	2		-92 ^c	-96.3 ^b	-101.3	-108 ^c
stilbite	$\text{Na}_2\text{Ca}_4[(\text{AlO}_2)_{10}(\text{SiO}_2)_{26}] \cdot 28\text{H}_2\text{O}$	2.6			-98	-101.5 ^b	-108
harmotome	$\text{Ba}_2[(\text{AlO}_2)_4(\text{SiO}_2)_{12}] \cdot 12\text{H}_2\text{O}$	3			-95	-103.6 ^d	-108 ^c
heulandite	$\text{Ca}_4[(\text{AlO}_2)_8(\text{SiO}_2)_{28}] \cdot 24\text{H}_2\text{O}$	3.5			-95	-99.0 ^b	-108
clinoptilolite	$\text{Na}_3\text{K}_3[(\text{AlO}_2)_6(\text{SiO}_2)_{30}] \cdot 24\text{H}_2\text{O}$	5				-105.3 ^d	-106.9 ^{b,d}
						-100.6	-112.8

^a Si(*n*Al) designates the SiO_4 tetrahedron connected through shared oxygen atoms with *n* AlO_4 tetrahedra in the zeolite framework. ^b Signal of highest intensity. ^c Signal of low intensity. ^d Tentative assignment.

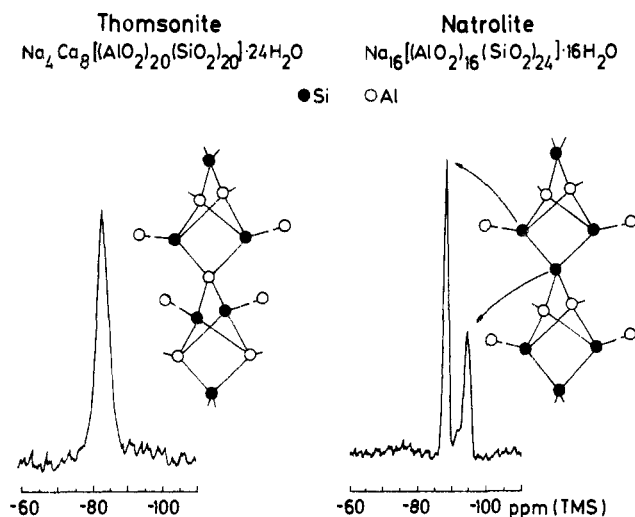


Figure 1. High-resolution solid-state ^{29}Si NMR spectra of thomsonite and natrolite. Only the central atoms of the tetrahedra are shown.

found. Si(4Al) resonates at about -85 ppm and Si(0Al) in aluminum-free quartz at -107.4 ppm.⁴

The ^{29}Si chemical shifts of the aluminosilicates investigated are given in Table I. It is immediately obvious that the five distinct ranges of silicon chemical shifts, corresponding to five different Si(*n*Al) units, appear again. Si(4Al) is unambiguously represented by sodalites and thomsonite, both with a perfect alternating ordering of the Si and Al tetrahedra. In accordance with this structure, only one sharp signal (60–120 Hz) is observed from all three samples with shift values about -84 ppm, in excellent agreement with those found for nepheline and anorthite.⁴ The structure of natrolite is similar to that of thomsonite,⁷ but it consists of Si(3Al) and Si(2Al) units in a 2:1 ratio, in accordance with the increased silicon content (Si/Al = 1.5). The ^{29}Si spectrum of natrolite consists of two lines at -87.7 ppm and -95.4 ppm in a 2:1 intensity ratio and thus serves for an unequivocal assignment of these two units (Figure 1). Si(1Al) is found in many zeolites with low aluminum content, together with other Si(*n*Al) units.

The ^{29}Si spectra of the NaX and NaY zeolites consist of 5 lines each, three of which can be assigned to the Si(4Al), Si(3Al), and Si(2Al) units in accordance with the chemical shifts in thomsonite (sodalites) and natrolite. The signals at the highest field are close to that of quartz and should correspond to the unsubstituted

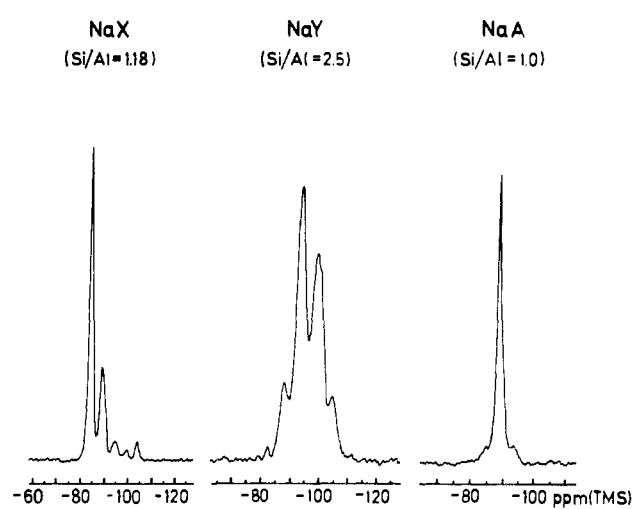


Figure 2. ^{29}Si NMR spectra of NaX, NaY, and NaA zeolites.

Si(0Al) units. The lines at -98.8 ppm for NaX and -100.0 ppm for NaY can be assigned to the Si(1Al) units. This assignment is confirmed by the very similar shifts found for this structural unit in feldspars.⁴ Intensity distribution of the ^{29}Si NMR lines changes in accordance with the Si/Al ratio. In NaX with a high aluminum content (Si/Al = 1.18) the Si(4Al) line has the highest intensity while the NaY with Si/Al = 2.5 the Si(3Al) and Si(2Al) lines are dominant (see Figure 2). This agrees well with the expected distribution of the silicon units at different Si/Al ratios. Obviously, the same trend holds for the whole set of data shown in Table I. Increasing Si/Al ratio leads to increasing intensities of ^{29}Si lines corresponding to units with lower degree of substitution by aluminum. For Si/Al = 1 only the single Si(4Al) line is present in several zeolites, while for Si/Al = 1.5–2 the Si(3Al) and Si(2Al) lines have the highest intensities and for Si/Al = 3–5 the Si(1Al) and Si(0Al) lines are predominant. This general trend can be regarded as a further indirect proof for the assignment of the ^{29}Si NMR spectra of aluminosilicates. In summary, ^{29}Si chemical shifts of all aluminosilicates investigated in this study and in ref 4 are presented on a single chart (Figure 3), containing five partly overlapping shift ranges for the Si(*n*Al) units.

b. Synthetic Zeolites. The aluminosilicate framework of the synthetic zeolites investigated in this study can be described in terms of cubooctahedra (truncated octahedra of 24 SiO_4 and AlO_4 tetrahedra) which are connected in different ways.⁷ In sodalite these polyhedra are closely packed to fill space so that each face is shared between two cubooctahedra. The structure of zeolite NaA consists of the same cubooctahedra, connected octahedrally

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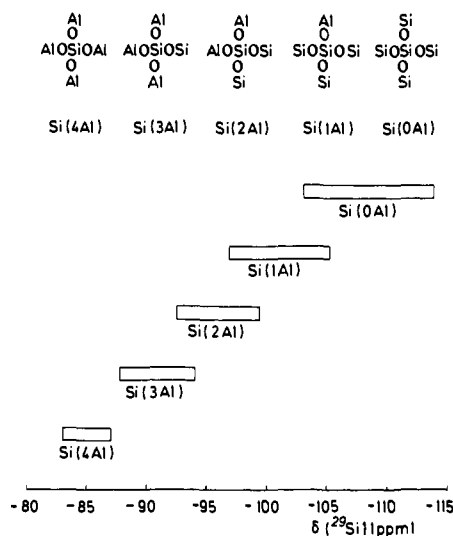


Figure 3. ^{29}Si chemical shift ranges of aluminosilicates. $\text{Si}(n\text{Al})$ designates the SiO_4 tetrahedron connected through shared oxygen atoms with $n\text{AlO}_4$ tetrahedra in the aluminosilicate framework.

through double four-rings. The NaX and NaY zeolites have identical lattice arrangements (faujasite-type structure), where the cubooctahedra are linked tetrahedrally through double six-rings just like the carbon atoms in diamond. The difference between NaX and NaY zeolites is caused by the different Si/Al ratios which lead to different Si/Al distributions in the framework.

Zeolite NaX (Si/Al = 1.18). The ^{29}Si NMR spectrum of zeolite NaX is shown in Figure 2. The Si/Al = 1.18 ratio leads to a spectrum consisting predominantly of signals of Si(4Al) and Si(3Al) units in a 2.5:1 ratio. The other three structural units are also present, but in small amounts only, about 20 times less than that of Si(4Al). A detailed investigation of structural models shows that in the case of an idealized regular distribution of AlO_4 and SiO_4 tetrahedra in the zeolite framework with a Si/Al = 1.18 ratio (every cubooctahedron contains 13 Si and 11 Al tetrahedra) only the Si(4Al), Si(3Al), and Si(0Al) units in the ratio 8:4:1 can be present,⁸ while all other types of Si(n Al) units must be absent. Consequently, this ^{29}Si spectrum of zeolite NaX (line widths about 70 Hz) reveals a mainly regular zeolite framework with some irregularities in the Si/Al ordering in some parts of the lattice. The latter give rise to small amounts of Si(2Al) and Si(1Al) units and lead to deviations from the calculated 8:4:1 intensity ratio.

Zeolite NaY (Si/Al = 2.5). The ^{29}Si NMR spectrum of zeolite NaY (Figure 2) with a Si/Al = 2.5 ratio shows that the sample consists of SiO_4 tetrahedra, connected to three, two, one, or zero AlO_4 tetrahedra. From the signal intensities an approximate ratio Si(3Al):Si(2Al):Si(1Al):Si(0Al) equal to 1.3:5.4:5.0:1.0 can be estimated. The signal of very low intensity at -83.8 ppm shows the presence of a small number of Si(4Al) units as well. The signal of Si(1Al) units at -100 ppm is markedly broadened, which indicates the presence of Si-OH groups in $\text{Q}^3(0\text{Al})$ units. The presence of Si-OH groups leads to a significant rise of the intensity of this signal in CP experiments. The chemical shift of such Q^3 units in silicic acid solutions lies at -100 ppm.⁹ Because of the relatively high Si/Al ratio and the presence of at least four different Si(n Al) units, it is very difficult to draw reliable conclusions about the Si/Al ordering in the zeolite Y framework. The number of possible regular repeating patterns of aluminum distribution in this zeolite framework is very large in this case. It should be noted, however, that the Si/Al ordering following from the rules of Dempsey¹⁰ leads to a distribution of Si(4Al):Si(3Al):Si(2Al):Si(1Al):Si(0Al) equal to 0:2:8:6:1 for the NaY zeolite with

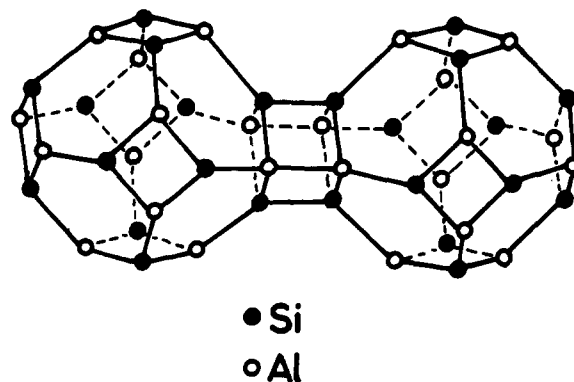


Figure 4. Si/Al distribution in the proposed model structure of the NaA zeolite consisting of Si(3Al) units. Only the central atoms of the tetrahedra in two interconnected cubooctahedra of the three-dimensional framework are shown.

the Si/Al ratio of 2.43. This distribution is very similar to the intensity ratios found in the NaY spectrum shown in Figure 2. First results on other faujasite-type zeolites with Si/Al ratios varying from 1.18 to 23 confirm in general the reliability of Dempsey's predictions of the Si/Al distribution in the faujasite lattice.¹¹

Zeolite NaA. The ^{29}Si NMR spectrum of NaA zeolite (Figure 2) consists of a single sharp line (70 Hz) at -89.6 ppm, i.e., in the range of typical Si(3Al) shifts instead of the expected -84 ppm which would correspond to the Si(4Al) groups and to a regular alternating ordering of the SiO_4 and AlO_4 tetrahedra. The spectra are practically identical ($\Delta\delta = \pm 0.5$ ppm) for all the samples of this type of zeolite, some of which were carefully prepared in several laboratories while the others were industrial products. The same shift (-89.6 ± 1 ppm) is observed partially in (10–90%) cation-exchanged NaCaA, NaMgA, and NaLaA zeolites.

The unusually diamagnetic ^{29}Si shielding in NaA zeolite could be caused by some unusual structural effect, peculiar to A-type zeolites only, and leading to a partial overlap of the otherwise quite distinct Si(4Al) and Si(3Al) chemical shift ranges in zeolites. However, comparison of the Si(4Al) and Si(3Al) shifts found in other aluminosilicates of very different structures (ref 4 and Table I) makes the assignment of the -89.6 ppm signal to Si(4Al) rather unlikely. A more likely explanation of the -89.6-ppm shift would be to assume that the NaA zeolite consists of Si(3Al) units. In this case there is a regular distribution of SiO_4 tetrahedra, each connected to three AlO_4 and one SiO_4 tetrahedron, and symmetrically distributed SiOSi and AlOAl pairing in the double four-rings connecting the cubooctahedra (Figure 4). It should be noted that in this model the Si/Al distribution is perfectly alternating within the sodalite units (the cubooctahedra). The existence of AlOAl bridges of course violates the Loewenstein rule¹² which forbids sharing of an oxygen atom by two four-coordinated aluminum atoms. After an overnight run with about 12-h accumulation time very weak signals appeared at -94.5 ppm and, in some samples, also at -85.0 ppm (Figure 2). If these signals arise from the lattice silicon atoms, they may reflect the dominant share of the Si(3Al) units as shown in Figure 4 and the presence of a small admixture of Si(4Al) and Si(2Al) units in the less ordered regions of the NaA lattice.

In the refinement of the X-ray structure of the hydrated¹³ and dehydrated¹⁴ NaA zeolite the space group $Fm\bar{3}c$ was used but some weak diffractions do not obey this group.¹⁴ The space group $Fm\bar{3}c$ for NaA zeolite assumes a perfectly alternating order of the SiO_4 and AlO_4 tetrahedra in accordance with the Loewenstein

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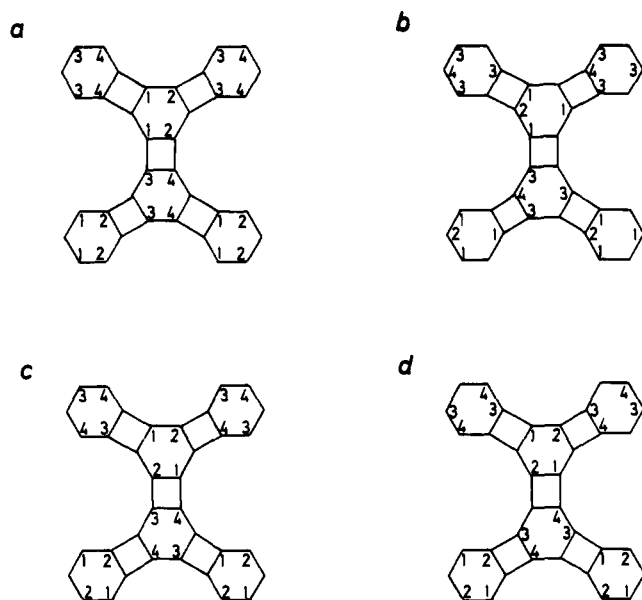


Figure 5. The possible ordered arrangements of Si and Al atoms in the double six-rings of gmelinite: (a and b) with Al atoms in the meta positions of the six rings; (c and d) with Al atoms in the para positions of the six-rings. The Si and Al atoms lie at the intersection of the lines; the heights of the intersections are expressed by the numbers from 1 to 4 that also indicate the positions of Al atoms.

rule and is in contradiction with the model shown in Figure 4.¹⁵ On the other hand, electron diffraction studies of Lodge, Bursill, and Thomas¹⁶ contradict the space group $Fm\bar{3}c$, and the space group $Pm\bar{3}$ (or $Fm\bar{3}$) is considered. This result matches the model given in Figure 4, when the Si/Al ratio is unity. It is obvious that further careful studies of the NaA structure are necessary.

c. Natural Zeolites. Gmelinite and Chabazite. The aluminosilicate frameworks of gmelinite and chabazite with the theoretical components ratio Si/Al = 2 consist of double six-ring (D6R) units linked by tilted four-rings.⁷ There are three principally different possibilities for a regular Si/Al distribution in the D6R units with Al atoms occupying meta or para positions in the six-rings¹⁷ (see Figure 5 for gmelinite structure, a-c). In the latter case (Figure 5c) the tilted four-rings contain besides the SiOAl bridges AlOAl bridges as well; i.e., the Loewenstein rule is violated. Investigation of these three model structures which fit both gmelinite and chabazite leads to two different ratios of the Si(*n*Al) units in the lattice—Si(3Al):Si(2Al):Si(0Al) equal to 2:1:1 in the two cases of meta-substituted rings (Figure 5a,b) and Si(2Al):Si(1Al) equal to 3:1 in the case of para-substituted rings (Figure 5c). Only the latter ratio is in close agreement with the relative signal intensities in the sharp-line ^{29}Si NMR spectrum of gmelinite (from Patterson, NJ, see Figure 6). The models with meta-substituted rings that predict the presence of the strongest line in the range of Si(3Al) shifts are in agreement with the Loewenstein rule but in a sharp contrast with the experimental spectrum, where only a weak signal is present at -92 ppm and no signal in the range of Si(0Al) units. This means that the Loewenstein rule may be violated in gmelinite as well. The presence of a small admixture of Si(3Al) units can be caused by crystal structures where para-substituted rings are linked together as shown in Figure 5d. The same is most likely valid for chabazite (from Aussig, Bohemia) too, because only a weak signal of the Si(3Al) units appears in the spectrum. The ^{29}Si lines of chabazite are broadened in comparison to those of gmelinite (Figure 6), and consequently the Si/Al ordering is less perfect in this natural zeolite. In connection with chabazite it

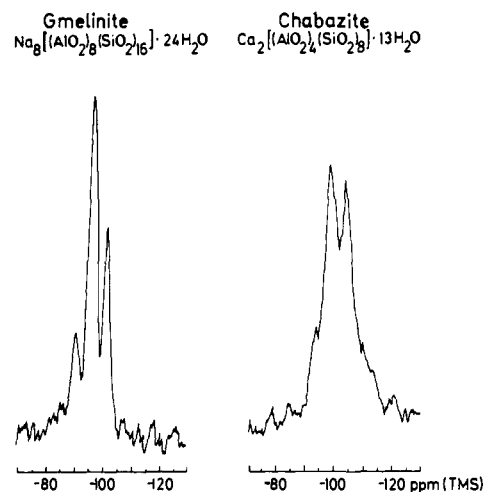


Figure 6. ^{29}Si NMR spectra of gmelinite and chabazite.

must be pointed out that the Si(1Al) signal is relatively strong and there is an additional weak signal in the range of Si(0Al) shifts. Furthermore, all signals are shifted by about 2 ppm to high field relative to the lines of gmelinite and other Na zeolites. These features may be caused by a higher Si/Al > 2 ratio in chabazite minerals, as has been frequently observed,⁷ and the influence of Ca^{2+} ions. The high-field shifts of about 2 ppm have also been observed in CaX zeolite (relative to NaX) and in heulandite (see below).

Analcime and Harmotome. The aluminosilicate framework of analcime (Si/Al \approx 2) and harmotome (Si/Al \approx 3) consists of single four-rings (S4R).⁷ The structure of analcime has been described by silicon-containing four-rings which are connected through aluminum atoms,¹⁸ i.e., there must be only Si(2Al) groups in the perfectly ordered lattice. ^{29}Si NMR spectra of the analcime sample used in the present study (from Patterson, NJ) are not in complete agreement with this structure. The signal in the range of Si(2Al) units shows the highest intensity but is accompanied by a signal of relatively high intensity in the range of Si(1Al) units at -102 ppm, and the Si(3Al) and Si(0Al) units are also present, although in low concentration. It is also remarkable that the line of the Si(2Al) units at -97 ppm is strongly enhanced in the cross-polarization experiments. The corresponding silicon atoms must have in close proximity relatively fixed hydrogen atoms in hydroxyl groups or in water molecules.

The four-rings in harmotome framework are linked together in cross-linked chains as in feldspars, but in harmotome such linking has led to a more flexible framework which contains larger internal cavities.⁷ The ^{29}Si spectrum of harmotome consists of three main lines as does that of albite,⁴ a typical feldspar with ordered Si/Al distribution.¹⁹ The three signals can be assigned in full analogy to albite to Si(2Al) at -95 ppm and two different Si(1Al) units at -98.6 and -102.6 ppm. The unequal line intensities and considerable line broadening show that the Si/Al ordering in harmotome (from Andreasberg, Harz, East Germany) is less perfect than in albite.

Heulandite and Stilbite. The crystal structure of heulandite and stilbite (Si/Al = 3-3.5) is based on the $\text{T}_{10}\text{O}_{20}$ units, which consist of four- and five-rings.⁷ Both zeolites (heulandite from Berufjord, Norway, stilbite from Faeroe Islands), especially stilbite, have ^{29}Si spectra with strongly broadened lines; i.e., the Si/Al distribution is not very regular. The signals of greatest intensity correspond to the Si(1Al) units. The other strong lines at -103.6 ppm in stilbite and at -105.3 ppm in heulandite are tentatively assigned to Si(1Al) units as well. An investigation of possible Si/Al distributions in model structures makes a high concentration of Si(0Al) units unlikely but allows for the presence of two different kinds of Si(1Al) units. The relative high-field shift of one type of these Si(1Al) units is probably caused by the influence

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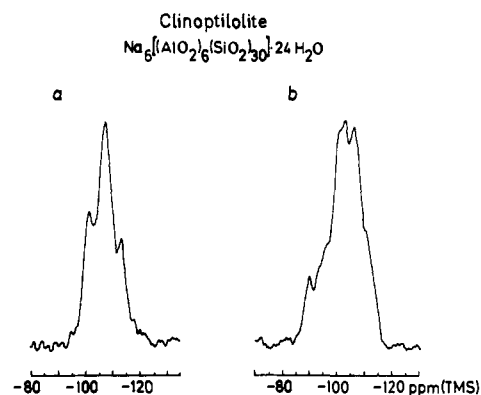


Figure 7. ^{29}Si NMR spectra of clinoptilolite: (a) without and (b) with cross-polarization. Polarization transfer from the ^1H nuclei in hydroxyl groups leads to significant enhancement of the $\text{Si}(\text{OH})_2$ and SiOH lines.

of Ca^{2+} ions as was the case in chabazite.

Clinoptilolite. The crystal structure of clinoptilolite $\text{T}_{10}\text{Q}_{20}$ Dzegvi, GA, $\text{Si}/\text{Al} = 5$) has not been unequivocally determined to our knowledge, although similarity with the structure of heulandite has been proposed.⁷ Investigation of model structures with $\text{T}_{10}\text{Q}_{20}$ as the main unit predict the highest concentration for $\text{Si}(\text{Al})$ units in spite of the high Si/Al ratio. The ^{29}Si chemical shift of the most intense line (-106.9 ppm) in the clinoptilolite spectrum lies in the shift range of $\text{Si}(\text{OAl})$ units. It is therefore possible that the structure of clinoptilolite is not based on the $\text{T}_{10}\text{O}_{20}$ units. The intensity in the region of the signal at -100

ppm is substantially increased in CP experiments and a shoulder appears at about -90 ppm (Figure 7). In these ranges lie the ^{29}Si NMR signals of SiOH and $\text{Si}(\text{OH})_2$ groups.⁹

Concluding Remarks

The overall results of the ^{29}Si NMR study of the structure of zeolites lead to the following conclusions.

(1) ^{29}Si NMR spectra provide qualitative and semiquantitative information about the zeolite structure and especially about Si/Al ordering in the aluminosilicate framework. The ^{29}Si chemical shifts display a regular dependence upon the number of AlO_4 tetrahedra connected to the SiO_4 tetrahedron under study.

(2) The regularities in ^{29}Si chemical shifts were used to establish the presence in zeolites of silicon tetrahedra of various degree on aluminum substitution and the type and regularity of distribution of the Si and Al atoms in the lattice.

(3) Independent information about the Si/Al ordering can be used to supplement X-ray structure studies of zeolites. Possible examples of anti-Loewenstein AlOAl bridging were found in synthetic and natural zeolites.

(4) Cross-polarization techniques can be used to establish the presence of SiOH and $\text{Si}(\text{OH})_2$ groups in the samples studied.

(5) All the NMR methods used in this study are applicable to the investigation of microcrystalline or amorphous powder samples as well. The line widths correlate with the long-range regularity of the lattice.

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1,2-Dilithioethane. A Molecular Orbital Study

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Abstract: The potential energy surface of $\text{LiCH}_2\text{CH}_2\text{Li}$ was examined at several levels of ab initio theory, e.g., 3-21G (geometries) and MP2/6-31G*///3-21G (energies). The global energy minimum was found to be **1**, C_{2h} , with a trans conformation (dihedral angle, $\phi_{\text{LiCCLi}} = 180^\circ$) but an unusual partially bridged geometry ($\angle\text{LiCC} = 73.2^\circ$). However, the symmetrically trans doubly bridged structure (**2**, D_{2h}), a transition state for dyotropic rearrangement, is only 1.9 kcal/mol higher in energy. The rotational potential energy surface is characterized by a gauche minimum (**3**, C_2 , $\angle\text{LiCC} = 66.4^\circ$) at $\phi_{\text{LiCCLi}} = 84.0^\circ$, 8.0 kcal/mol less stable than **1**. Only a small rotational barrier separates **3** and **1** when the dihedral angle is increased from 84° to 180° , but the $\phi_{\text{LiCCLi}} = 0^\circ$ barrier (corresponding to the eclipsed structure, **4**) is much higher in energy, 28.9 kcal/mol above **1**. A cis dyotropic transition state, **3'** (C_{2v}), is 2.4 kcal/mol less stable than **3** and 10.4 kcal/mol less stable than **1**. Although **1** is indicated to be marginally unstable thermodynamically toward dissociation into ethylene and Li_2 , the lithium substituents interact in a mutually stabilizing manner. The similarities of $\text{C}_2\text{H}_4\text{Li}_2$ geometries **1** and **2** with known X-ray structures of more highly substituted 1,2-dilithium compounds and with the geometries of ethane derivatives substituted vicinally by other metals are emphasized. For comparison, C_2H_6 in doubly bridged (**7**, D_{2h}) diborane-like and in quadruply bridged (**8**, D_{4h}) geometries were examined. These are very unstable, lying 149 and 437 kcal/mol (MP2/6-31G*///6-31G*), respectively, above D_{3d} ethane (**5**).

Although 1,2-dilithioethane has been claimed only as a poorly characterized pyrophoric gray powder,^{2a} and as a possible reaction intermediate,^{2b} this species is inherently interesting as the simplest possible ethane vicinally substituted by two metals. 1,2-Dilithioethane also serves as a model for several dilithio derivatives

for which X-ray structures are available: 9,9'-bifluorenyl-bis-(lithium tetramethylethylenediamine),³ stilbene-bis(lithium tetramethylethylenediamine),⁴ and acenaphthylene-bis(lithium

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