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1.4 s when tilted 28° away. T_1 measurement at the 45° orientation was not feasible, the long relaxation time and broad line shapes combining to make acquisition of single-crystal platinum spectra prohibitive. In Figure 5, the narrow resonance at 93° required 2.3 min acquisition time; the broad resonance at 133°, 1.7 h. For practical reasons, then, we have used platinum chemical shift data clustered about specific crystal orientations to define the phase and amplitude of the single-crystal rotation curves.

Solution. Potassium tetrachloroplatinate(II) provides an important test case for ^{195}Pt solution NMR spectra. In dilute solution, K_2PtCl_4 exists as K^+ and $(PtCl_4)^{2-}$ ions. Hydration of the tetrachloro–platinum anion does not appreciably disturb the platinum–chloride bonds or their symmetry. In this special case, the shielding elements lying in the platinum–chloride plane will be little affected by weak solvation. The solution state CSA can therefore be calculated from the known shielding elements lying in the platinum–chloride plane, −5270 ppm, and the solution isotropic resonance. In 0.01 and 0.004 molar aqueous solution, the solution peak appears at −1735 ± 39 ppm, shifted only 64 ppm from its value in the solid. The unique shielding element is calculated to be +5255 ppm and the anisotropy 10485 ppm.

Such a large anisotropy allows the CSA relaxation mechanism to dominate many platinum NMR characteristics. In 0.01 M solution and at 4.7 T, the platinum relaxation rate is 3 s^{-1}. Reorientation of the chloroplatinum anion, to a very good approximation, may be considered isotropic. Simple calculation shows that correlation times of 2–3 ps completely account for observed relaxation.

Conclusion. Shielding tensor elements and anisotropies have been determined for potassium tetrachloroplatinate(II) in both solid and solution and for potassium hexachloroplatinate(IV) in the solid state. These measurements constitute the first direct evidence of 10000-ppm anisotropies in solid- and solution-state platinum compounds. This has important implications in platinum NMR studies.

In the solid state, K_2PtCl_4 and K_2PtCl_6 possess simplified shielding tensors due to crystal symmetry. It is generally not the case that all platinum nuclei will have a single shielding tensor or degenerate tensors. As a rule, static and MAS platinum spectra will consist of superimposed line shapes spanning several thousand ppm. Single-crystal rotation experiments, particularly in conjunction with known X-ray crystal structures, are shown to circumvent the difficulty of extracting reliable information.

In single-crystal chloroplatinum compounds, strong dipolar coupling to quadrupolar chlorine dominates platinum line widths. While this results in some difficulty in measurement, the angular dependence of the broadening provides information on shielding tensor orientation independent of X-ray studies or symmetry arguments. In K_2PtCl_4, line broadening alone allows complete determination of the orientation of the shielding tensor. In compounds of lower symmetry, this information will allow assignment of shielding tensors to nonequivalent platinum nuclei.

In solution, parts per thousand and part per hundred anisotropies cause relaxation to be dominated by the CSA mechanism for all reasonable values of correlation times at even moderate field strengths. In the dinucleoside monophosphate platinate(II) model systems of platinum antitumor drugs, slow correlation times make CSA relaxation much more effective. The broadening of platinum resonances and the decoupling of platinum from other spin $^1/_2$ nuclei observed in these model systems arises from platinum(II) chemical shift anisotropy.

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Elucidation of the Mechanism and Kinetics of the Si, Al Ordering Process in Synthetic Magnesium Cordierite by ^{29}Si Magic Angle Spinning NMR Spectroscopy

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Abstract: The course of Si, Al ordering in synthetic magnesium cordierite was determined from the high-field (9.4 T) ^{29}Si MAS NMR spectra of samples annealed from the glass precursor at 1185 °C for various periods of time. The results indicate that the driving force of the ordering process is the establishment of Loewenstein's aluminum avoidance principle in the structure of orthorhombic cordierite and that the hexagonal-orthorhombic ordering transformation takes place by an apparently continuous mechanism via a sequence of intermediate structural states. The Si, Al ordering process was found to be approximately linear with log time, consistent with the continuous transformation mechanism proposed previously, and involves a net migration of silicon from rings to chains within the structure and rearrangements within the rings via a series of $Si^{T_2} \rightleftharpoons Al^{T_1}$ and $Si^{T_2} \rightleftharpoons Al^{T_2}$ exchanges.

Magnesium cordierite, $Mg_2Al_4Si_5O_{18}$, occurs in two polymorphic forms. In the high-temperature hexagonal structure, space group *P6/mcc*, stable above ~1450 °C.[1,2] the Al and Si atoms are distributed over two sets of tetrahedral sites—three T_1 and six T_2 sites per formula unit, with Mg in octahedral coordination. In a structure refinement of indialite, the naturally occurring hexagonal polymorph of magnesium cordierite, it was suggested[3] that the Al, Si distribution involved 2.2 Al and 0.8 Si atoms disordered over the T_1 sites and 1.8 Al and 4.2 Si disordered over the T_2 sites. In the slightly distorted, low-temperature (<1450 °C) orthorhombic polymorph, space group *Cccm*, the T_1 sites are

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Table I. Tetrahedral Sites in Cordierites 3–5 (Nine Tetrahedral Sites per $Mg_2Al_4Si_5O_{18}$ Formula Unit)

sites		linkages per tetrahedron	
hexagonal	orthorhombic	orthorhombic	hexagonal
$3T_1$ sites chain	$2T_11$ sites	$2T_21 + 2T_23$	$4T_2$
	$1T_16$ site	$4T_26$	
$6T_2$ sites (ring)	$2T_21$ sites	$2T_11 + T_23 + T_26$	$2T_1 + 2T_2$
	$2T_23$ sites	$2T_11 + T_21 + T_26$	
	$2T_26$ sites	$2T_26 + T_21 + T_23$	

Table II. Tetrahedral Site Occupancies in Orthorhombic (Ordered) Cordierite

	site	contents	Si environment
chain	$2T_11$	2Al	
	$1T_16$	1Si	Si(4Al)
ring	$2T_21$	2Si	Si(3Al)
	$2T_23$	2Si	Si(3Al)
	$2T_26$	2Al	

split into two nonequivalent sites, T_11 and T_16, while the T_2 sites are split into three nonequivalent sites, T_21, T_23, and T_26.[3] Within this orthorhombic phase, the Al, Si atoms form a completely ordered distribution, with four Al in the $2T_11$ and $2T_26$ tetrahedra and five Si occupying the $1T_16$, $2T_21$, and $2T_23$ tetrahedra, as suggested by X-ray and neutron diffraction studies[4,5] (Figure 1 and Tables I and II).

Crystallization of stoichiometric magnesium cordierite glass at temperatures between 1050 and 1450 °C yields metastable hexagonal disordered cordierite, which on annealing transforms in an apparently continuous sequence to the ordered orthorhombic form. Experiments carried out on the mechanism and kinetics of the hexagonal-orthorhombic transition confirm that the polymorphism is associated with Al, Si ordering: it has been generally accepted that the aluminum and silicon atoms are disordered in hexagonal cordierite, ordered in orthorhombic cordierite, and intermediate ordered in intermediate states,[4] although their absolute degree of Al, Si order is not known. The characterization of the degree of Al, Si order attained in these synthetic cordierite samples annealed isothermally for various periods of time has been the subject of considerable recent research.

Miyashiro[6,7] generally characterized the polymorphism on the basis of a distortion index Δ, which related the separation of three peaks in the powder diffraction pattern recorded with Cu K_α radiation to the deviation from the hexagonal geometry of the disordered end member. In the hexagonal form, Δ is zero, while in the fully ordered orthorhombic form of anhydrous magnesium cordierite Δ is approximately 0.25°. The symmetry change associated with the onset of long-range order leads to splitting of X-ray powder peaks, but the use of such "splitting indexes" to characterize structural states has serious shortcomings.[2,8] In an isothermal annealing sequence of cordierite at 1200 °C, the first splitting of X-ray diffraction peaks due to deviation from overall hexagonal symmetry is observed only after 100 h of heating. It was concluded that this was not a very good technique to monitor the ordering transformation, since by the time the transition was observable by X-ray diffraction, most of the ordering was thought to have already occurred on a microscale. Optical techniques are more sensitive and departures from uniaxial symmetry have been noted in the optic axial angle before any X-ray splitting is evident.[9] Transmission electron microscopy reveals the existence of short-range ordered domains well before diffraction or optical techniques can detect any ordering:[2] on initial crystallization and early annealing at 1200 °C, the cordierite appears homogeneous and possesses hexagonal symmetry according to electron microscopy. After 3 h, two orthogonal order modulations appear, producing a "tweed" microstructure. These modulations initially have a wavelength of about 100 Å, and with continued annealing, they coarsen to finally develop into optically visible lamellar twins after approximately 100 h at 1200 °C. Infrared[10] and Raman[11] spectroscopies of the same materials have also made qualitative distinctions between various stages of short-range order. Infrared spectra of the disordered hexagonal phase showed fewer bands, which were considerably broader than those for the ordered orthorhombic cordierite. A smooth development of bands in infrared spectra with initial annealing time was noted, but no major changes occur after 5 h of annealing. It was concluded that the infrared technique was sensitive to structural change on a smaller scale than detected by electron microscopy, i.e., less than around 100 Å, but insensitive to longer-range modifications. The Raman spectra of a series of cordierites annealed from the glass of 1200 °C display major changes for annealing times of about 4 h to at least 64 h. Initial modifications appear in the Raman spectra when the ordered domains are around 100 Å across and, perhaps before this, also are consistent with the infrared study. Heat of solution calorimetry has been used quantitatively to measure enthalpy effects associated with changes in Al, Si ordering in synthetic cordierites annealed isothermally.[12] The progress of ordering can be partially characterized in this way by determining both the magnitude and variation of the enthalpy effect with time. A continuous change of ΔH_{soln} with annealing time was observed, supporting the suggestion of a continuous hexagonal → orthorhombic transformation in cordierite under metastable conditions.

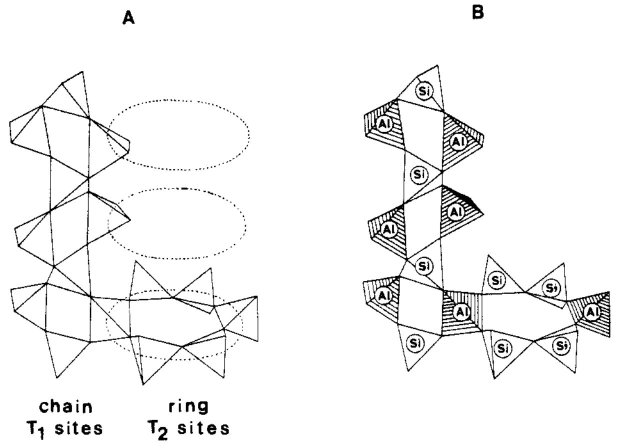

Figure 1. (A) Elevation view of the cordierite structure depicting the arrangement of tetrahedra. Each ring tetrahedron (T_2 site) is joined via a chain tetrahedron (T_1 site) to the ring above and the ring below, such that all tetrahedra are corner sharing. The dashed lines show the position of similar rings of T_2 tetrahedra forming channels, only one of which is shown in detail, along the *C* axis. (B) Structure proposed for the completely ordered form showing the location of the Si and Al atoms.

Obviously, for materials that lack long-range order, X-ray diffraction techniques are generally of little value in determing the character and occupancy of structural sites. A further complication, in the case of cordierite, is the fact that Al and Si have similar X-ray scattering factors, making it difficult to distinguish between them. Magic angle spinning (MAS) NMR, on the other hand, is capable of probing the short-range local environment of certain atoms and is, therefore, a potentially viable technique for investigating this unique transformation. High-resolution solid-state ^{29}Si MAS NMR is capable of detecting the relative amounts of the five possible Si(*n*Al) structural groups in framework aluminosilicates, Si(*n*Al), where n = 0–4 is the number of tetrahedral Al atoms joined, by oxygen bridges, to the central Si atom.[13-15]

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Table III. ^{29}Si MAS NMR Peak Intensities Determined by Computer Simulation (Corrected for Spinning Sidebands and Normalized Together with the Si/Al Ratios):[Si/Al] NMR, and the Number of Al–O–Al Linkages per Al_4Si_5 Formula Unit Determined from the Spectra of Synthetic Magnesium Cordierites Annealed at 1185 °C for Various Periods of Time

annealing time at 1185 °C	chain (T_1 sites)				ring (T_2 sites)					
	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	$[Si/Al]_{NMR}$[a]	N_{Al-Al} per Al_4Si_5 unit
2 min	0.020	0.0532	0.0417	0.0062	0.075	0.408	0.347	0.0489	1.54	1.51
6.5 min	0.033	0.0529	0.0317	~0	0.077	0.397	0.343	0.0649	1.54	1.49
20 min	0.037	0.0581	0.0379	~0	0.079	0.428	0.308	0.0520	1.50	1.33
6 h	0.080	0.0434	0.0217	0.0111	0.108	0.513	0.203	0.0202	1.38	0.74
23.5 h	0.098	0.0393	0.0124	0.0131	0.069	0.568	0.177	0.0221	1.38	0.74
48.5 h	0.114	0.0232	0.0103	0.0030	0.061	0.625	0.143	0.0202	1.34	0.56
96 h	0.117	0.0293	0.0145	0.0081	0.062	0.645	0.111	0.0132	1.33	0.47
408 h	0.131	0.0182	0.0156	0.0081	0.084	0.672	0.056	0.0142	1.29	0.26
~2000 h	0.144	0.0274	0.0135	~0	0.058	0.698	0.059	~0	1.28	0.18
fully ordered	0.200	0.0000	0.0000	0.0000	0.000	0.800	0.000	0.0000	1.25	0.00

[a] Rounded to two decimals.

For aluminosilicate structures, it has also been shown that a Si/Al ratio may be derived for the lattice using eq 1 where $I_{Si(nAl)}$ is the intensity of the ^{29}Si resonance due to silicons surrounded by nAl atoms. If there are no Al–O–Al units present, this formula accurately reflects the Si/Al ratio of the lattice.

$$\left[\frac{Si}{Al}\right]_{NMR} = \frac{\sum\limits_{n=0-4} I_{Si(nAl)}}{0.25 \sum\limits_{n=1-4} nI_{Si(nAl)}} \qquad (1)$$

The technique is thus potentially extremely useful in studying the early stages of Al, Si ordering before any long-range order is established. This paper further details the changes in the local Si environments for progressively annealed synthetic cordierites, reported in a preliminary communication,[16] and shows how the kinetics of the ordering can be described quantitatively and a mechanism for the ordering process deduced. This is the first time that such a detailed description of the ordering process at the atomic level in a geological material has been obtained, and the general procedures used will form an appropriate basis for other investigations of this type.

Experimental Section

The starting material for the experimental runs was stoichiometric $Mg_2Al_4Si_5O_{18}$ cordierite glass. The method of preparation of the glass and its chemical analysis have been described elsewhere.[2] The glass was annealed isothermally in air at 1185 °C for periods ranging from 2 min (after 1.5 min for the sample to thermally equilibrate) to approximately 2000 h, and each product was examined by X-ray powder diffractometry and transmission electron microscopy.

High-resolution ^{29}Si NMR spectra were recorded at 79.5 MHz on a Bruker WH-400 multinuclear spectrometer equipped with a narrow-bore Bruker Spectrospin/Oxford Instrument superconducting magnet and a homemade MAS NMR probe which has been described in detail elsewhere.[17] The spinner assembly was of the Andrew-Beams type with rotors machined from Delrin and having internal volumes of approximately 0.5 cm^3. Rotors containing finely powdered samples were spun at the magic angle (54.7°) at speeds of approximately 3.6 kHz with compressed air as the driving gas. All ^{29}Si chemical shifts are given from tetramethylsilane (TMS) with high-field shifts being negative. Calculated deconvolutions of the experimental spectra were based on Gaussian peak profiles and corrected for the intensities of small spinning sidebands.

Results and Discussion

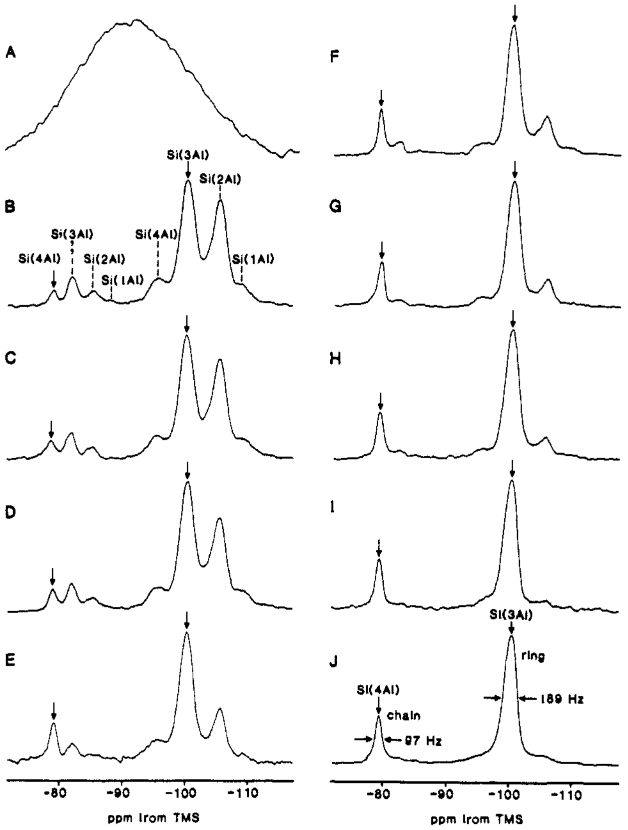

Figure 2. ^{29}Si (79.5 MHz) MAS NMR spectra of synthetic cordierite, $Mg_2Al_4Si_5O_{18}$. The crystalline cordierites were prepared from glass of the same composition (shown in (A)), by annealing at 1185 °C for (B) 2 min, (C) 6.5 min, (D) 20 min, (E) 6 h, (F) 23.5, (G) 48.5 h, (H) 96 h, (I) 408 h, and (J) ca. 2000 h.

On heating cordierite glass at 1185 °C, crystallization (but not ordering) is complete within less than 1 min, and X-ray diffractograms reveal the formation of hexagonal cordierite. Figure 2 shows ^{29}Si MAS NMR spectra obtained for the glass (starting material) and the nine other experimental samples in Table III: the ^{29}Si spectrum of the amorphous cordierite glass, shown in Figure 2A, predictably consists of a single, very broad resonance due to the combined effects of disordering due to different silicon environments and geometries combined with different distributions of Al in the first coordination sphere (see on), while the peaks of the newly formed crystals are relatively narrow, indicating the presence of local, short-range Si, Al ordering. Although these changes in the NMR spectra clearly indicate the occurrence of an ordering process, the X-ray powder diffraction patterns remain essentially unchanged, even after 100 h, when long-range Si, Al order becomes established. This is entirely due to the two techniques being sensitive to quite different ranges of ordering, giving complementary information on the structures, and is of quite general occurrence.

After prolonged annealing (approximately 2000 h) at 1185 °C, the ^{29}Si spectra reach the limiting spectrum of the thermodynamically stable orthorhombic form shown in Figure 2J, which consists of two major peaks at −79.3 and −100.2 ppm (from TMS) with intensities of 0.144 and 0.698, respectively. The assignment of these peaks may be made with reference to the structure and the tetrahedral site occupancies (Table II), as determined by

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neutron diffraction techniques.[5] Table II reveals that ordered orthorhombic cordierite has one Si with an environment Si(4Al) in the chains (T_16 site) and four Si with environments Si(3Al) in the six-membered rings ($2T_21$ and $2T_23$ sites) as shown in Figure 1B. Thus, the two main peaks in Figure 2J are assigned to Si(4Al) for the chains and Si(3Al) for the rings, as indicated in the figure. The ratio of the number of ring silicon atoms to chain silicon atoms for this sample is 4.41, as compared to the value of 4.00 for a fully ordered orthorhombic cordierite. This suggests that further annealing would be required in order to obtain the final equilibrium distribution, and a close inspection of Figure 2J (and Table III) reveals that there are small contributions to the spectrum from other minor peaks. Using the spectrum in Figure 2J as a "bench mark" reference, it is possible to identify Si(4Al) for chain sites and Si(3Al) for ring sites in the preceding spectra in the figure as indicated by the vertical arrows. This in turn leads to a self-consistent assignment of the local silicon environments of the remaining peaks, as indicated in Figure 2B using the information well established from the spectra of zeolites that the effect of Al in the first coordination sphere of a silicon-centered SiO_4 unit is to shift the ^{29}Si resonance by approximately 5 ppm *per aluminum.* Thus, each spectrum (Figure 2B–J) displays two distinct sets of peaks in the chemical shift ranges −79 to −88 and −95 to −109 ppm which are assigned to tetrahedral silicon atoms in the chains (T_1 sites) and the rings (T_2 sites), respectively, with the different chemical shift ranges for the chain and ring silicon tetrahedra probably arising from differences in bonding angles (for instance, the average T–O–T angles for chain and ring sites are ca. 130° and ca. 150°, respectively). For orthorhombic cordierite, the T_21 and T_23 ring sites are crystallographically nonequivalent, with average T–O–T angles of 153.0° and 149.7°, respectively. Qualitatively, one would expect the ^{29}Si chemical shifts of the T_21 and T_23 ring sites to be quite similar, and they are not resolved after ca. 2000 h of annealing (Figure 2J) although the line width of the peak at −100.2 ppm (189 Hz) is larger than that of the peak at −79.3 ppm (97 Hz). If this sample is annealed further (i.e., perfect ordering is achieved), the line widths should decrease slightly,[18,19] possibly splitting the peak at −100.2 ppm into a doublet and thus distinguishing T_21 from T_23 ring sites.

For each of the two types of sites [chain (T_1) and ring (T_2)], a maximum of five ^{29}Si peaks are theoretically possible, namely, Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si(0Al). It should be noted that within a few minutes of crystallization from the glass (Figure 2B and Table III), 8 of these 10 possible peaks are observed. No Si(0Al) [which is equivalent to Si(4Si)] groupings are observed, which is not unreasonable since for a highly aluminous material such as cordierite with a Si/Al ratio of 1.25, the probability of such groupings is quite low. The decrease in the number of ^{29}Si peaks in proceeding from the hexagonal to the orthorhombic form is consistent with the silicon and aluminum atoms being ordered in the latter and relatively disordered in the former. It has been suggested that the main kinetic control of the transformation is Al, Si exchange between neighboring cation sites. If it is assumed, as a first approximation, that the enthalpy change associated with a single Al, Si exchange, leading from a "wrong" to a "right" configuration during ordering, is independent of the degree of order already attained, then

$$\frac{-dN}{dt} \propto \frac{1}{t} \tag{2}$$

and

$$-N \propto \log t \tag{3}$$

where N is the number of Al–Si pairs in "wrong" sites and t represents the time.[12]

It is possible, using the ^{29}Si NMR data shown in Figure 1, to describe quantitatively the kinetics of the population and depopulation of all the individual sites and local environments during the ordering process in terms of the individual local silicon environments, information clearly not attainable by other techniques. The normalized populations of the different sites are presented in Table III. The nature of the disordered structures can be deduced from an examination of the $(Si/Al)_{NMR}$ ratios calculated for the various samples using eq 1 as presented in Table III. The actual Si/Al ratio is 1.25 for *all* the samples since the framework composition is $Al_4Si_5O_{18}$, but each of the $(Si/Al)_{NMR}$ ratios are greater than 1.25, which points strongly to the existence of Al–O–Al linkages, in violation of Loewenstein's rule[20] which forbids them. These linkages are, however, progressively eliminated as the annealing process continues (the degree of ordering increases), and in the final, orthorhombic form of cordierite (the thermodynamically stable state), there are no adjacent AlO_4 tetrahedra (Table III). These results clearly indicate that the impetus of the ordering process is the establishment of Loewenstein's aluminum avoidance principle in the final ordered structure of orthorhombic cordierite. The number of Al–O–Al linkages per Al_4Si_5 formula unit can be calcuated exactly from the ^{29}Si MAS NMR data as follows (in formulating the equations, the oxygen atoms in the T–O–T bonds have been omitted for the sake of simplicity):

$$\left[\frac{Si}{Al}\right]_{NMR} = \frac{N_{Si}}{N_{Si\text{-}Al\ bonds}/4} \tag{4}$$

The term $[Si/Al]_{NMR}$ is derived experimentally from the ^{29}Si MAS NMR spectrum as defined in eq 1, but no assumptions are made regarding the presence of Al–Al bonds.

Since $N_{Si\text{-}Al\ bonds}$(each Al is tetrahedrally bonded) $= 4N_{Al} - 2N_{Al\text{-}Al}$ (for each pair, there are 2 Al's with Al neighbors), eq 4 can be rewritten as (5).

$$\left[\frac{Si}{Al}\right]_{NMR} = \frac{N_{Si}}{(4N_{Al} - 2N_{Al\text{-}Al})/4} \tag{5}$$

This can be re-expressed as (6).

$$\left[\frac{Si}{Al}\right]_{NMR} = \frac{N_{Si}}{N_{Al} - \dfrac{N_{Al\text{-}Al}}{2}} = \frac{\dfrac{N_{Si}}{N_{Al}}}{1 - \dfrac{N_{Al\text{-}Al}}{2N_{Al}}} = \frac{\left[\dfrac{Si}{Al}\right]_{actual}}{1 - \dfrac{N_{Al\text{-}Al}}{2N_{Al}}} \tag{6}$$

Note that

$$\left[\frac{Si}{Al}\right]_{NMR} = \frac{\left[\dfrac{Si}{Al}\right]_{actual}}{1 - x}$$

where $x = N_{Al\text{-}Al}/2N_{Al}$ is the fraction of Al not affecting the ^{29}Si NMR peaks from the existence of Al–Al units. For each Al–Al pair, $^1/_4$Al is being "missed out" for each Al in the pair for a total of $^1/_2$Al. Therefore, the *fraction* of Al, x, which is being "missed out" is given by (7).

$$x = \frac{N_{Al\text{-}Al}/2}{N_{Al}} \tag{7}$$

The number of Al–Al bonds may now be expressed as in (8).

$$N_{Al\text{-}Al} \text{ per Al} = \frac{N_{Al\text{-}Al}}{N_{Al}} = 2 - \frac{2\left[\dfrac{Si}{Al}\right]_{actual}}{\left[\dfrac{Si}{Al}\right]_{NMR}} \tag{8}$$

The above equation is completely general, in the sense that it can be applied to any aluminosilicate framework structure and will form a valuable framework for the investigation of disordering

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Table IV. Partitioning of Al and Si between Chain (T_1) and Ring (T_2) Sites in Cordierite Annealed at 1185 °C, as Determined from ^{29}Si MAS NMR Data

annealing time at 1185 °C	$\sum_n I_{Si(nAl)^{T_1}}$	$\sum n I_{Si(nAl)^{T_2}}$	for Al_4Si_5 unit ($3T_1$ and $6T_2$ sites) $N_{Si^{T_1}}$	$N_{Si^{T_2}}$	$N_{Al^{T_1}}$	$N_{Al^{T_2}}$
2 min	0.121	0.879	0.605	4.395	2.395	1.605
6.5 min	0.118	0.882	0.590	4.410	2.410	1.590
20 min	0.133	0.867	0.665	4.335	2.335	1.665
6 h	0.156	0.844	0.780	4.220	2.220	1.780
23.5 h	0.162	0.838	0.810	4.190	2.190	1.810
48.5 h	0.151	0.849	0.755	4.245	2.245	1.755
96 h	0.168	0.832	0.840	4.160	2.160	1.840
408 h	0.173	0.827	0.865	4.135	2.135	1.865
~2000 h	0.185	0.815	0.925	4.075	2.075	1.925
fully ordered	0.200	0.800	1.000	4.000	2.000	2.000

Table V. Comparison of the Si(nAl) Peak Intensities and N_{Al-Al} Obtained from the ^{29}Si NMR Data with Those Calculated from a Statistically Random Ordering Model for the Sample Annealed at 1185 °C for 2 min

	chain (T_1 sites)					ring (T_2 sites)					
	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)	N_{Al-Al}
^{29}Si NMR data	0.020	0.0532	0.0417	0.0062		0.075	0.408	0.347	0.0489		1.51
random model	0.0010	0.0112	0.0461	0.0841	0.0576	0.0365	0.2182	0.3768	0.1510	0.0175	2.99

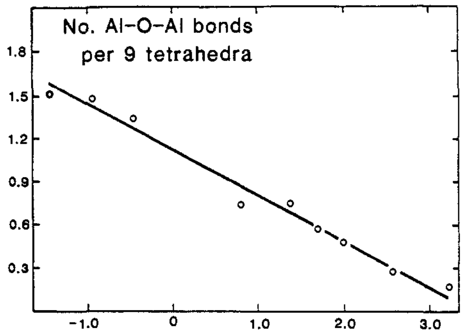

Figure 3. Number of Al–O–Al bonds per Al_4Si_5 structural unit of cordierite plotted as a function of the logarithm of the annealing time at 1185 °C.

processes in other mineral systems.

For the particular case of cordierite, $[Si/Al]_{actual} = {}^5/_4$ (from chemical analysis and the required stoichiometry of the structure). Therefore, N_{Al-Al} per Al $= 2 - {}^5/_2/[Si/Al]_{NMR}$. For the basic Al_4Si_5 unit of the cordierite structure,

$$N_{Al-Al} = 8 - \frac{10}{\left[\frac{Si}{Al}\right]_{NMR}} \tag{9}$$

where $[Si/Al]_{NMR} = \sum_{n=0-4} I_{Si(nAl)}/[0.25\sum_{n=1-4} nI_{Si(nAl)}]$ as introduced previously (eq 1). Further simplifications of the expression for N_{Al-Al} linkages per Al_4Si_5 unit are given in the Appendix section.

Equation 9 may now be used together with the data of Table III to determine the number of Al–Al units for each of the samples investigated and to probe the validity of the time dependence proposed in eq 3.

Figure 3 shows that the plot of the average number of Al–O–Al bonds per Al_4Si_5 formula unit (i.e., N(Al–Al)), evaluated by using eq 9 and the experimental NMR data, varies linearly with the logarithm of the annealing time for the nine experimental samples investigated by NMR. The correlation of N(Al–Al) with annealing time is good, and its general effectiveness as an order parameter lies in the fact that it is independent of the degree of long-range Si, Al order. As expected, the cordierite formed by annealing the glass at 1185 °C for 2 min is the most "disordered" of the experimental samples, based on the number of Al–O–Al linkages which are 1.51 per Al_4Si_5 formula unit (Table III). For a statistically random (non-Loewensteinian) ordered sample in which the partitioning of Si and Al between the $3T_1$ and $6T_2$ sites is chosen to be identical with that found experimentally (i.e., 0.605 Si and 2.395 Al in $3T_1$ sites and 4.395 Si and 1.605 Al in $6T_2$ sites (Table IV)), the calculated number of Al–O–Al bonds is 2.99 per formula unit (Table V), indicating that the initial sample is clearly not randomly disordered although obviously not well ordered. Furthermore, the relative intensities of the various chain and ring Si(nAl) peaks can be calculated for this random model and compared to the ^{29}Si NMR results (Table V). From a comparison of the tabulated data, it is clear that the order (disorder) is neither totally random nor totally Loewensteinian but intermediate between these two extremes. In fact, within the hexagonal space group of cordierite, a fully ordered configuration of Al and Si is not possible.[10] Also, if Si and Al were randomly partitioned over the $3T_1$, and $6T_2$ sites, one would expect the ratio of Si in the chain sites to Si in the ring sites to be 0.330:0.667. For the 2-min sample, this ratio is 0.121:0.879, indicating a preference of Si for ring sites (or, conversely, Al for chain sites) at this stage of crystallization from the glass. As can be seen from Table IV, the partitioning of Si (and Al) between chain and ring sites shows no regular variation with annealing time. This can be rationalized intuitively by realizing that no one partitioning guarantees Loewensteinian behavior, the system equilibrating by a path which involves a systematic reduction of metastable Al–O–Al linkages.

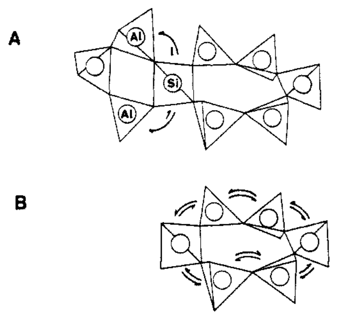

Figure 4. Schematic representation of atoms of the site exchanges thought to play major roles in the ordering process. (A) $Si^{T_2} \rightleftharpoons Al^{T_1}$ process which involves a net movement of silicon from ring to chain positions. (B) $Si^{T_2} \rightleftharpoons Al^{T_2}$ process which successively rearranges the ring atoms to produce a para distribution of aluminum atoms.

Figure 2 shows that during the annealing process, most of the Si(nAl) environmental changes involve the decrease of Si(2Al) units and increase of Si(3Al) units in the rings. Similarly, for the chain atoms, the change involves an increase in Si(4Al) units accompanied by decreases in Si(3Al) and Si(2Al) units (Figure 2, Table III).[21] The presence of Si(4Al) spectral peaks for T_2

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[21] Putnis, A.; Fyfe, C. A.; Gobbi, G. C. *Phys. Chem. Miner.*, in press.

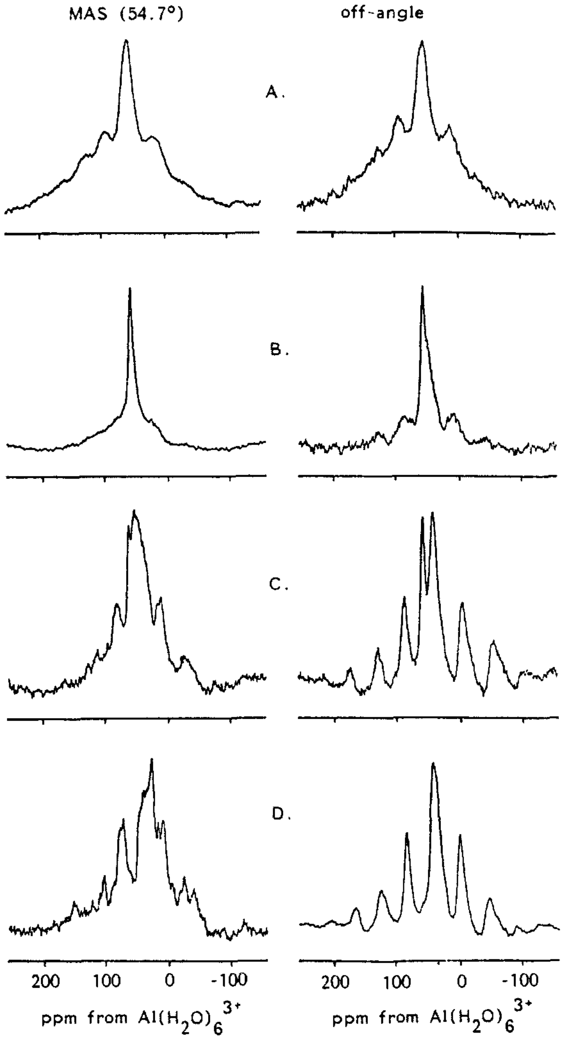

Figure 5. ^{27}Al (104.2 MHz) MAS (54.7°, left) and "off angle" (right) NMR spectra of synthetic cordierite samples: (A) glass starting material (before annealing); (B) 2 min after crystallization from the melt at 1185 °C; (C) after 23.5 h at 1185 °C; (D) after ~2000 h at 1185 °C.

sites indicates meta substitution of Al within some rings. From this observation and an inspection of the Si, Al partitioning between chain and ring sites, it is suggested that the ordering process involves a progression of $Si^{T_2} \rightleftharpoons Al^{T_1}$ and $Si^{T_2} \rightleftharpoons Al^{T_2}$ exchanges (Figure 4) until the fully ordered orthorhombic cordierite structure is achieved (Tables III and IV).

The ^{27}Al MAS NMR spectra (Figure 5) exhibit very distorted and ill-defined peak profiles due to incompletely averaged second-order quadrupole interactions even at the very high fields used in the present work. The chemical shift values do, however, confirm that all the aluminum in the samples is in tetrahedral coordination. Spectra were also obtained with the samples spun at an angle off of the magic angle (54.7°) to more efficiently average the second-order quadrupolar interactions,[23] the optimum angle being chosen experimentally. The quality of the spectra improves in most cases, but limited additional information is gained. However, a very small sharp peak of yet undetermined origin is resolved and the main resonance exhibits a small and gradual shift in position which mirrors the progress of the ordering process. In all cases, the relatively large residual quadrupolar interaction indicated by the substantial number of spinning sidebands at this high-field strength indicates that the Al sites are distorted from tetrahedral symmetry, in agreement with the diffraction determined structure.

In conclusion, MAS NMR has shown itself to be a valuable technique for elucidating the course and nature of local environment changes during the solid-state transformation of cordierite to its ordered form, while other complementary techniques, such as X-ray diffraction, are largely insensitive to such local changes. The overall progress of the reaction can be monitored quantitatively via the number of Al–O–Al bonds per formula unit present at various stages of annealing, and the timescale over which NMR reveals changes is quite large. Since ordering processes of the type outlined above are not easily detected by diffraction techniques, they may be much more widespread than expected in many mineral systems. This is the very first example of a quantitative treatment of a local ordering process of this type, and the general experimental protocol outlined here will form a basis for future investigations of ordering processes in other systems. Further work in this area is currently in progress.

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Appendix

Equations 1 and 9 were derived earlier in the text, so from 1

$$\left[\frac{\mathrm{Si}}{\mathrm{Al}}\right]_{\mathrm{NMR}} = \frac{4}{\sum_n n(I_{\mathrm{Si}(n\mathrm{Al})^{T_1}} + I_{\mathrm{Si}(n\mathrm{Al})^{T_2}})} \tag{10}$$

Since for the specific case of cordierite, (1) $I_{\mathrm{Si}(n\mathrm{Al})} = I_{\mathrm{Si}(n\mathrm{Al})}T_1 + I_{\mathrm{Si}(n\mathrm{Al})}T_2$ (T_1 and T_2 denote chain and ring sites, respectively, and (2) $\sum_n I_{\mathrm{Si}(n\mathrm{Al})} = 1.0$ (since the total peak area is normalized to unity).

Therefore, for each Al_4Si_5 unit, from eq 9,

$$N_{\mathrm{Al-Al}} = 8 - \tfrac{5}{2}[\sum_n n(I_{\mathrm{Si}(n\mathrm{Al})^{T_1}} + I_{\mathrm{Si}(n\mathrm{Al})^{T_2}})]^{-1} \tag{11}$$

Equation 11 is now in the form described by Putnis et al.[21,22] from an alternate and independent derivation.

Registry No. $Mg_2Al_2Si_5O_{18}$, 12026-18-5.

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[22] Putnis, A.; Angel, R. J. *Phys. Chem. Miner.*, in press.

[23] Ganapathy, S.; Schramm, S.; Oldfield, E. *J. Chem. Phys.* **1983**, *77*, 4360.