

FURTHER CONSIDERATION OF THE ^{29}Si NUCLEAR MAGNETIC RESONANCE SPECTRUM OF KAOLINITE

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Abstract—The introduction of artificial $\pm b/3$ stacking faults into well-crystallized kaolinite by intercalating and removing hydrazine had no observable effect on the solid-state ^{29}Si nuclear magnetic resonance spectrum of kaolinite. Also, the introduction of such stacking faults did not alter the hydroxyl-stretching region of the infrared spectrum, implying no change in the hydrogen bonding between the displaced layers. Calculations of Si...H distances and Si-O...H angles from reported structures for kaolinite indicated that the resolution of the two Si chemical environments was due to differences in hydrogen-bonding at the surface of the silicate sheet.

Key Words—Hydrazine, Hydrogen bond, Kaolinite, Nuclear magnetic resonance, Stacking fault.

INTRODUCTION

Solid-state ^{29}Si nuclear magnetic resonance (NMR) has proved to be a useful tool in studying the distribution of Al and Si in synthetic zeolites (Lippmaa *et al.*, 1980; Klinowski *et al.*, 1981) and clay minerals (Thompson, 1984b; Lipsicas *et al.*, 1984; Sanz and Serratos, 1984; Alma *et al.*, 1984). Moreover, ^{29}Si NMR of clay minerals is sensitive to the nature of the octahedral cation and to interlayer effects (Sanz and Serratos, 1984; Thompson, 1984b; Thompson, 1985). In particular, Barron *et al.* (1983) observed two resolved ^{29}Si signals for kaolin-group minerals. Thompson (1984a) subsequently demonstrated that this resolution was due to interlayer effects: overlap of tetrahedral sites in one layer with occupied or unoccupied octahedral sites in the adjacent layer, or hydrogen-bonding effects at the silicate surface. Barron *et al.* (1983) also noted different levels of signal splitting for different kaolinite polymorphs, and Watanabe *et al.* (1983) observed a correlation between the kaolinite signal width and the Fe content of the sample.

Based on the conclusions of Thompson (1984a), a series of well-characterized kaolinites was examined to delineate the effects of artificially induced stacking disorders on the ^{29}Si spectra. If signal resolution is solely due to Si-Al overlap between kaolinite layers, the introduction of a high proportion of $\pm b/3$ stacking defects should affect the relative signal intensities. On the other hand, if hydrogen-bonding effects are the cause of signal resolution, such a change in relative signal intensities should not be found. Thus, by careful deconvolution of the ^{29}Si spectra for each of these kaolinites and their corresponding artificially disordered equivalents (Barrios *et al.*, 1977), the effect of stacking disorder on the ^{29}Si NMR spectra should be observed

and the uncertainty as to the cause of signal resolution in kaolinite group minerals resolved.

EXPERIMENTAL

The five kaolinites used in this investigation all had relatively low iron content, yet different degrees of crystallinity (Figure 1). Their descriptions are listed in Table 1.

Each of the kaolinites was artificially disordered by hydrazine treatment using a modified version of the method described by Barrios *et al.* (1977). Several grams of kaolinite was suspended in excess laboratory-grade hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) at room temperature for 3 days. The samples were spread into thin films and left to stand in air for 2–3 days, until the intercalate had completely collapsed. The samples were then dried at 110°C for 24 hr to ensure the removal of free water. The formation and subsequent collapse of the kaolinite:hydrazine intercalate was monitored by X-ray powder diffraction (XRD), on a Rigaku horizontal-goniometer diffractometer (Model No. CN2155D5), using graphite monochromated $\text{CuK}\alpha$ radiation.

^{29}Si magic-angle spinning (MAS) NMR spectra were collected at 59.61 MHz using a Bruker CXP-300 NMR spectrometer at the Brisbane NMR Centre, Griffith University, Queensland. Cross-polarized (CP) MAS experiments were conducted on all the kaolinites and their artificially disordered equivalents using ^1H and ^{29}Si H_1 fields of 10 and 50 G, respectively, with single 5-ms contacts and a recycle time of 3 s.

Particular care was taken to monitor the effect of Fe content on the ^{29}Si NMR spectra in view of the findings of Oldfield *et al.* (1983), Watanabe *et al.* (1983), and Fyfe *et al.* (1984). Compositions were determined by atomic absorption spectrometry (AAS) analysis. The

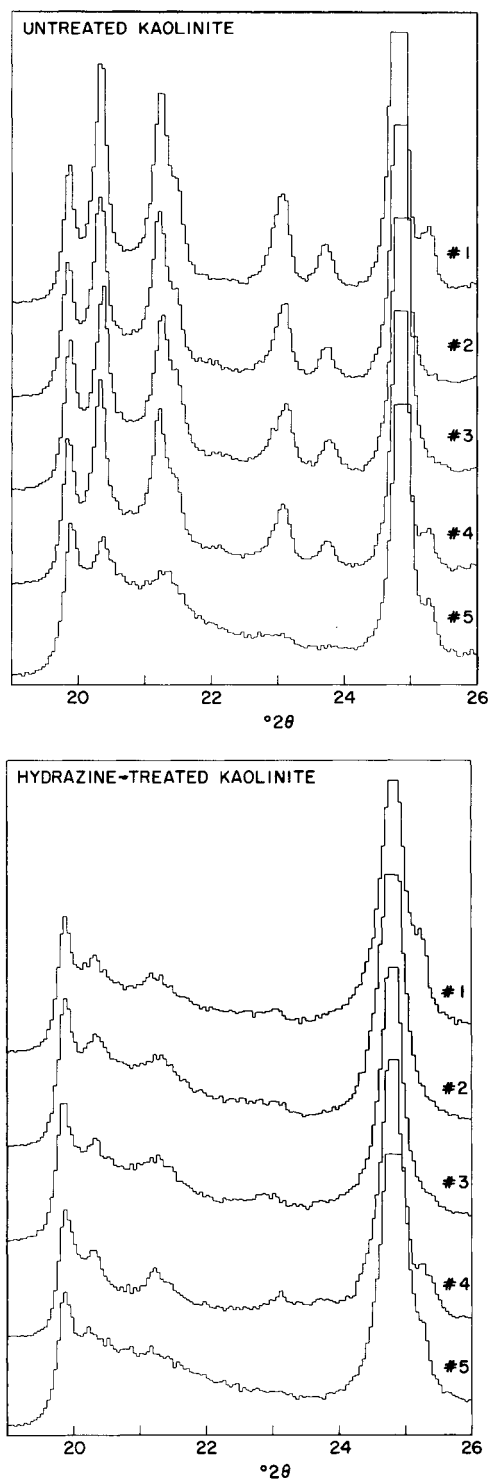


Figure 1. X-ray powder diffraction (XRD) patterns displaying the (02,11) band profile of the five kaolinites before (upper) and after (lower) hydrazine treatment. XRD diffraction patterns were collected using monochromated $\text{CuK}\alpha$ radiation with steps of $0.05^\circ 2\theta$ and a counting time of 100 s.

Table 1. Composition and other details of the five kaolinites used in this investigation.

Sample	Origin	Source	Composition (wt. %)								Particle size <4 μm	²⁹ Si signal Hinckley half width (Hz)	Index			
			SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O				LOI		
Kaolinite 1	Macon, Georgia	Georgia Kaolin Research	45.4	39.1	2.03	0.25	0.02	0.04	0.03	0.02	0.02	0.02	13.9	94%	1.40	93
Kaolinite 2	Blackpool pit, St. Austell	English China Clays, RL O2936	46.2	39.2	0.09	0.23	0.07	0.06	0.09	0.21	0.21	0.21	13.8	98%	1.27	92
Kaolinite 3	Blackpool pit, St. Austell	English China Clays, RL O2891	46.1	39.0	0.18	0.39	0.08	0.07	0.05	0.47	0.47	0.47	13.7	93%	1.24	100
Kaolinite 4	Jordan, Georgia	English China Clays, RL O2890	44.8	38.9	1.20	0.17	0.08	0.06	0.03	0.02	0.02	0.02	14.0	97%	1.08	92
Kaolinite 5	Macon, Georgia	Wards Nat. Sci. Est., Rochester, New York	45.7	38.7	1.81	0.35	0.30	0.14	0.10	0.05	0.05	0.05	14.2	56%	0.43	94

results are listed in Table 1. As a further check on the nature of the Fe content, electron spin resonance (ESR) spectra were collected using a Bruker ER200D ESR spectrometer at the Chemistry Department, University of Queensland.

RESULTS

The five untreated kaolinites gave similar ^{29}Si spectra. The reproducibility of these observed NMR spectra was tested by repeating the experiments on independent samples of kaolinite 1 and kaolinite 5. For both samples, the overall peak profiles were almost identical, and the signal widths were reproducible to within 2 Hz. Fitting two signals, using a Lorentzian profile with signal widths constrained to be equal, resulted in very low residuals for each sample. The same applied to the fitting of two peaks to the corresponding hydrazine-treated samples; however, a strong correlation between the phase correction of the Fourier-transformed overall spectrum and the resultant proportions of the two resolved signals was noted. As a result of this correlation and the uncertainty in chemical shift (~ 0.1 ppm), we concluded that observation of meaningful variation in relative intensities of resolved signals, between the untreated kaolinites and their hydrazine-treated equivalents, was not possible. For this reason pairs of spectra were compared directly to try to observe trends in the change of peak shape. The difference plots (Figure 2) provided the clearest illustration of any change in ^{29}Si spectra compared with overall signal-to-noise. No significant trend in resolution vs. crystallinity index (Hinckley, 1963) was observed, however, the overall peak width did appear to depend on the sample Fe content (Table 1), in agreement with Watanabe *et al.* (1983). ESR spectra of the five kaolinites were very similar and consistent with a majority of the Fe being present as Fe^{3+} substituting for Al^{3+} in the octahedral sites of kaolinite.

DISCUSSION

The absence of a significant change in the ^{29}Si spectra of well-ordered kaolinites (kaolinites 1 and 2) after inducing as much as $30\% \pm b/3$ translational defects between the layers via hydrazine intercalation (Barrios *et al.*, 1977), apart from an apparent broadening of the overall signal, indicated that the overlap of Si in one kaolinite layer over the $2/3$ -filled octahedral sites in the adjacent layer was not a valid explanation. This conclusion was supported by the similarity between the ^{29}Si spectra of untreated kaolinites ranging from well-ordered to poorly ordered. If Si-Al overlap was the primary explanation of the signal resolution, two resolved signals of unequal relative intensities (57.5% for Si overlapping Al, and 42.5% for Si overlapping vacant site) should have been observed. The predicted ^{29}Si spectrum, based on this explanation, is compared to the observed spectra for kaolinite 1 in Figure 3. Al-

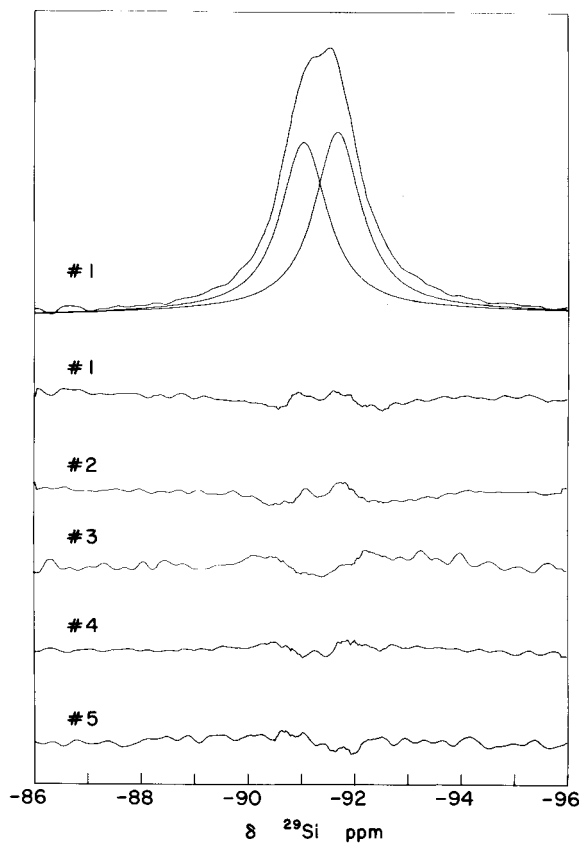


Figure 2. Difference ^{29}Si cross-polarized magic-angle spinning nuclear magnetic resonance spectra for the five kaolinites (untreated kaolinite minus hydrazine-treated kaolinite). The ^{29}Si spectrum of kaolinite 1 (same scale) is shown for reference. Well-crystallized kaolinites 1 and 2 displayed little change after inducing as much as $30\% \pm b/3$ translational defects via hydrazine intercalation apart from minor broadening of the signals.

though the predicted spectrum for $30\% \pm b/3$ disordered kaolinite may not be totally justified, some overall change in peak shape, consistent with one component signal intensifying relative to the other, should have been expected after hydrazine treatment. No such change was detected for any of the kaolinites (Figure 2).

Having ruled out the interpretation of signal resolution based on Si-Al overlap, the alternative explanation, based on differences in hydrogen-bonding interactions, needed closer examination. Barrios *et al.* (1977) observed that inducing artificial stacking faults in a well-crystallized kaolinite, by intercalation with hydrazine and subsequent collapse, resulted in no detectable change in the hydroxyl-stretching region of the infrared (IR) spectrum. This result was reproduced in the present study. Because these bands are sensitive to changes in hydrogen bond length, and thus bond strength, the introduction of $\pm b/3$ stacking faults did

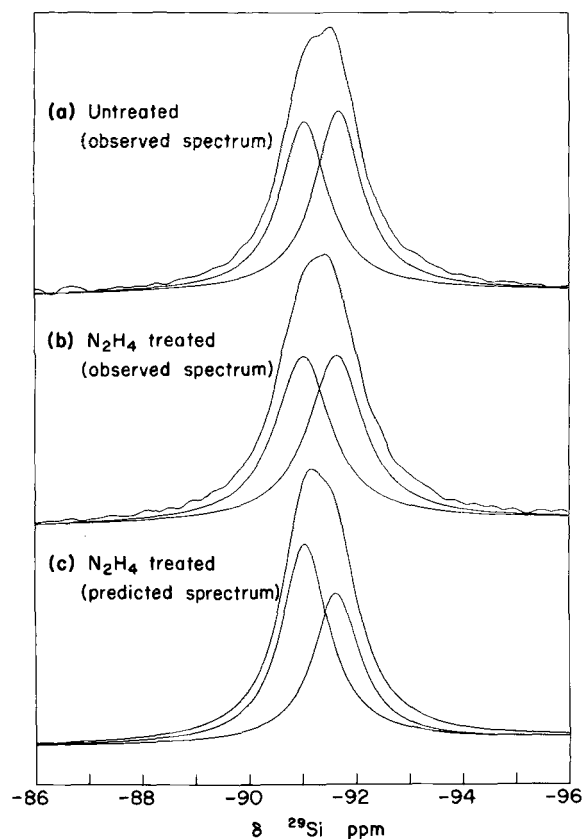


Figure 3. The ^{29}Si cross-polarized magic-angle spinning nuclear magnetic resonance spectra of (a) untreated kaolinite 1 and (b) hydrazine treated kaolinite 1, together with their two resolved signals, fitted as two Lorentzian profiles with signal widths constrained to be equal. The predicted ^{29}Si spectrum for hydrazine-treated kaolinite 1 (c), based on Si-Al overlap being the primary explanation of signal resolution, is displayed for comparison.

not appear to affect interlayer hydrogen-bonding interactions greatly. Therefore, the IR data concurred with the observation of no significant change in relative intensities of ^{29}Si signals upon the introduction of $\pm b/3$ disordering.

The success of recent workers (Smith and Blackwell, 1983; Smith *et al.*, 1983; Magi *et al.*, 1984; Grimmer and Radeaglia, 1984; Radeaglia and Engelhardt, 1985) in empirically correlating ^{29}Si chemical shift with various distance and angle parameters, inspired similar calculations for Si in kaolinite using the more recently determined structures. From such calculations it was hoped that the appearance of two resolved ^{29}Si signals might be rationalized. Structural models for kaolinite have been determined by several authors using texture electron diffraction (Zvyagin, 1960), XRD (Brindley and Robinson, 1946; Suitch and Young, 1983), and neutron powder diffraction (Adams, 1983; Suitch and Young, 1983). The model proposed by Zvyagin (1960) is acknowledged to be somewhat inaccurate, but has

Table 2. Selected mean bond lengths and bond angles in kaolinite.

		Model	Si1	Si2
Mean Si-O distance (Å)	BRR average ¹		1.63 (9)	1.60 (9)
	ZRT average ¹		1.62 (9)	1.61 (8)
	ZVY ²		1.67 (4)	1.61 (4)
Mean Si...H distance (Å)	AHR average ¹		3.16 (10)	2.96 (10)
	GDR average ¹		3.11 (10)	2.88 (10)
	Adams ³		3.17 (20)	2.94 (20)
Mean Si-O...H angle (°)	AHR average		117 (5)	106 (5)
	GDR average		118 (5)	105 (5)
	Adams		118 (13)	106 (12)

¹ Suitch and Young (1983); atoms placed in averaged C-face centered positions.

² Zvyagin (1960); labels reversed.

³ Adams (1983) and Zvyagin (1960); labels reversed.

been included as it forms the basis of Adams (1983) neutron powder profile refinement of the hydrogen atom positions. Atomic positions in the structural models of Suitch and Young (1983) have been averaged to their C-face centered positions, as recent electron diffraction evidence suggests that all atoms in kaolinite are related by C-face centering (Thompson and Withers, 1986). The reported standard deviations for the non-C-face centered structural models of Suitch and Young (1983) have been applied to the "averaged" C-face centered models as a good approximation, given that halving the number of atomic parameters should improve the reliability of those parameters.

Of the parameters used by Smith and Blackwell (1983) in their calculations on framework silicates, only mean Si-O bond length can differ for the two silicon sites, Si1 and Si2, in the C-face centered kaolinite structure. These values are listed in Table 2. The lack of any significant difference between mean Si1-O and Si2-O bond lengths indicates that the resolution of ^{29}Si signals does not have its cause within the kaolinite layer. This observation agrees with the initial interpretation of Thompson (1984a) that signal resolution is an interlayer effect.

Calculation of analogous values involving Si and H from the adjacent layer, namely, the mean Si...H distance and the mean Si-O...H angle, was performed to test whether difference in hydrogen-bonding interactions is a plausible explanation. The results of these calculations are also listed in Table 2. These latter calculations indicate that the perturbation of the magnetic environment of silicon by hydrogen-bonding is possibly less for Si1 than Si2. Whereas uncertainty in the atomic positions for the reported structures does not allow an unequivocal interpretation of these results, the general agreement between the different models does add some weight to our argument. Thompson (1985) demonstrated that ^{29}Si chemical shift in kaolinite intercalates was sensitive to hydrogen-bonding

interactions at the silicate surface. It follows that the differences in hydrogen-bonding experienced by Si1 and Si2 accounts for the ^{29}Si signal splitting of 40 Hz observed in all of the ordered and disordered kaolinite samples studied here.

CONCLUSIONS

One of the explanations of ^{29}Si NMR signal splitting for kaolinite put forward by Barron *et al.* (1983) was the presence of two slightly different Si environments due to distortion within the layer. Grimmer and Rade-glia (1984) recently proposed that, based on their correlation between ^{29}Si chemical shifts and mean Si bond length, this was a valid interpretation. The evidence presented by Thompson (1984a), and in the present work, suggests that interlayer effects, specifically inter-layer hydrogen-bonding effects resulting in two differently shielded environments, are the most probable cause of signal resolution in kaolinite. The same explanation is expected to apply to the other kaolinite polymorphs, nacrite and dickite.

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