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TWO POSSIBLE INTERPRETATIONS OF ^{29}Si NUCLEAR MAGNETIC RESONANCE SPECTRA OF KAOLIN-GROUP MINERALS

Key Words—Crystal structure, Dickite, Hydroxyl, Kaolinite, Nacrite, Nuclear magnetic resonance.

The recent paper by Barron *et al.* (1983) reopened the question regarding the crystal structure of kaolin-group minerals. They proposed that the most likely explanation for the nuclear magnetic resonance (NMR) signal splitting was that two slightly different but equally populated silicon sites existed in the kaolinite structure, this difference being due to distortion within the layer. I propose that the two silicon environments can be explained by either differences in hydrogen-bond interactions or by differences in Si–Al distances.

Giese (1982) confirmed the existence of an interlayer hydrogen-bonding mechanism in kaolin-group minerals. Giese's earlier work (Giese and Datta, 1973) proposed the orientations of inner surface hydroxyls in kaolinite using electrostatic calculations based on the Zvyagin structure (Zvyagin, 1967). The hydroxyl proton H(3) is angled toward Si(1) and away from Si(2), while H(1) and H(2) show no corresponding preference. If this orientation of hydroxyl protons is correct, Si(1) should generate the more deshielded component of the overlapping signals.

The comparison between the chemical shifts of pyrophyllite ($\delta = -95$, ppm relative to TMS) (Lippmaa *et al.*, 1980) and Polkville montmorillonite ($\delta = -93$) (Thompson, 1983) supports the idea that Si(1) could be deshielded relative to Si(2) by a magnitude of 27 Hz (Barron *et al.*, 1983), which is approximately equivalent to 0.5 ppm, by reason of differences in overall hydrogen bonding to the respective silicate tetrahedra. Both Polkville montmorillonite and pyrophyllite are 2:1 dioctahedral phyllosilicate minerals; however, in montmorillonite hydrogen-bonded water is present at the interlayer surface, whereas in pyrophyllite there are only relatively weak ionic and van der Waals interactions (Giese, 1975). The deshielding caused by hydrogen-bonded water in the montmorillonite is 2 ppm relative to pyrophyllite. The difference in resonance frequencies observed in kaolin-group minerals is consistent with this considering that only H(3)–Si distances differ significantly.

In nacrite and dickite, where resonance frequencies differ by less than 20 Hz (Barron *et al.*, 1983), the above rationale works for the former polymorph but not for the latter. In nacrite (Giese and Datta, 1973) the hydroxyl proton H(2) angles slightly toward Si(1) and away from Si(2), again producing different H–Si distances. The difference is not as great as in kaolinite and is consistent with the smaller resonance frequency difference. In dickite this explanation falters as the H–Si distances are approximately the same for Si(1) and Si(2).

Recently, Giese (1982) reviewed his earlier calculations for kaolinite as neutron diffraction data (Suitch and Young, 1983) tended to support the Brindley and Nakahira structure (Brindley and Nakahira, 1958). His reworked calculations resulted in orientations of inner surface hydroxyls such that both Si(1) and Si(2) had similar Si–H distances. Re-adoption of the Brindley and Nakahira structure, however, resulted in Si(2) being adjacent to Al(1) in the next layer while Si(1) was adjacent to a vacant octahedral site. Thus, Si(2) would be deshielded relative to Si(1). Similar observations have been made in framework silicates (Lippmaa *et al.*, 1980), though in framework silicates the magnitude of such chemical shifts was greater due to shorter interaction distances. Applying this rationale to nacrite and dickite the resonance frequency differences can be adequately explained for dickite but not nacrite (Giese and Datta, 1973).

The case for the two proposed explanations outlined

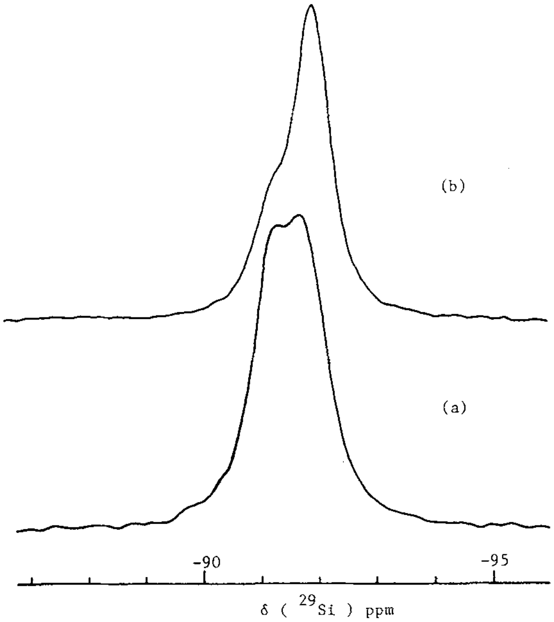

Figure 1. Comparison of the solid state CP/MASS ^{29}Si NMR spectra of (a) Georgia kaolinite, Oneal pit, Macon, Georgia, with (b) its formamide intercalate (90% expanded). The spectra were collected at 59.61 MHz. Complete experimental conditions are detailed elsewhere (Thompson, 1983). The two distinct silicon environments in the untreated kaolinite degenerate into one in the intercalate, confirming that interactions between the layers are the probable cause of the signal splitting.

above is enhanced by comparison of the ^{29}Si NMR spectra of a Georgia kaolinite and its formamide intercalate (Figure 1). In the kaolinite-formamide intercalate the two silicon environments are no longer resolved and its ^{29}Si resonance is shielded relative to that of the untreated mineral, suggesting a decrease in hydrogen-bond strength. While the full implications of this result will not be discussed here it does confirm that the difference in silicon environment cannot be due either to distortion within the layer, as postulated by Barron *et al.* (1983), or to the two different inner hydroxyl proton orientations observed by Suitch and Young (1983).

Consequently, the two silicon environments observed in kaolin-group minerals can be explained in terms of either Si-Al interactions between layers or hydrogen-bonding differences, both with reasonable justification. The two resonances in dickite are best understood in terms of the former, whereas for nacrite the latter provides a better explanation. For kaolinite, both approaches can explain the two resonances, and until an unambiguous neutron diffraction structure is resolved the question as to which approach is more correct will remain open. Either way, the final interpretation of the ^{29}Si NMR data will depend on accurate crystal-structure determination, and not the converse.

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REFERENCES

Barron, P. F., Frost, R. L., Skjemstad, J. O., and Koppi, A. J. (1983) Detection of two silicon environments in kaolins via solid state ^{29}Si NMR: *Nature* **302,** 49–50.

Brindley, G. W. and Nakahira, M. (1958) Further considerations of the crystal structure of kaolinite: *Mineral. Mag.* **31,** 781–786.

Giese, R. F., Jr. and Datta, P. (1973) Hydroxyl orientation in kaolinite, dickite, and nacrite: *Amer. Mineral.* **58,** 471–479.

Giese, R. F., Jr. (1975) Interlayer bonding in talc and pyrophyllite: *Clays & Clay Minerals* **23,** 165–166.

Giese, R. F., Jr. (1982) Theoretical studies of the kaolin minerals: Electrostatic calculations: *Bull. Soc. Fr. Mineral. Crystallogr.* **105,** 417–424.

Lippmaa, E., Mägi, M., Samoson, A., Englehardt, G. and Grimmer, A.-R. (1980) Structural studies of silicates by solid-state high-resolution ^{29}Si NMR: *J. Amer. Chem. Soc.* **102,** 4889–4893.

Suitch, P. R. and Young, R. A. (1983) Atom positions in highly ordered kaolinite: *Clays & Clay Minerals* **31,** 357–366.

Thompson, J. G. (1983) Clay mineral analysis using solid state ^{29}Si NMR: *Clay Miner.* (submitted).

Zvyagin, B. B. (1967) *Electron-diffraction analysis of Clay Mineral Structures*: Plenum Press, New York, 249–259.

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