

## **$^{29}\text{Si}$ Spin-Lattice Relaxation in Aluminosilicates**

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$^{29}\text{Si}$  N.m.r. spin-lattice relaxation times have been measured in some layer aluminosilicates and found to vary over three orders of magnitude, demonstrating that, in contrast to results reported to date,  $^{29}\text{Si}$   $T_1$ 's may be extremely long in aluminosilicates.

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Since the possibility of obtaining high resolution  $^{29}\text{Si}$  n.m.r. spectra of solids was first described by Lippmaa and co-workers,<sup>1</sup> the value of the technique has been demonstrated

by the applications published to date.<sup>2-4</sup> The generally small chemical shift anisotropy of  $^{29}\text{Si}$  allows easy removal of this contribution to solid state linewidths by magic angle spinning

(m.a.s.) without spinning sideband problems, even at high field. The presence of hydrogen in the form of hydroxy groups or bound water enables use of  $^{29}\text{Si}$ - $^1\text{H}$  cross-polarization (c.p.) to enhance sensitivity and overcome the possible problem of long  $^{29}\text{Si}$  spin-lattice relaxation times. However, it has generally been found that  $^{29}\text{Si}$   $T_1$ 's in aluminosilicates are not prohibitively long like  $^{13}\text{C}$   $T_1$ 's generally observed in rigid solids. Hence spectra have readily been obtained on hydrogen deficient species using a single  $^{29}\text{Si}$  pulse, and relatively short recycle delays (*i.e.*  $<30$  s).<sup>2-4</sup> Furthermore, spectra which are quantitatively interpretable as regards types of silicon environments can be obtained without the problems and uncertainties associated with  $^{13}\text{C}$  c.p./m.a.s. spectra. For example,  $^{29}\text{Si}$   $T_1$ 's have been found to be sufficiently short in synthetic zeolites to allow quantitative spectra to be obtained with recycle delays of 5 s.<sup>3</sup> In fact the quantitative interpretation of  $^{29}\text{Si}$  c.p./m.a.s. spectra, when obtainable, is likely to be far more difficult than for  $^{13}\text{C}$  owing to the absence in most silicates of directly bonded hydrogen and wide variation in  $^{29}\text{Si}$ - $^1\text{H}$  internuclear separation. No attempt has been made to explain why  $^{29}\text{Si}$   $T_1$ 's in aluminosilicates are so much more favourable than  $^{13}\text{C}$   $T_1$ 's in rigid solids nor has any work been performed to determine whether this is a general phenomenon. It is likely that most workers in the area assume that rapid  $^{29}\text{Si}$  spin-lattice relaxation is due to spin-diffusion from paramagnetic centres.<sup>5</sup> However, confirmation of this would require first the demonstration that  $^{29}\text{Si}$  spin-lattice relaxation in aluminosilicates can be inefficient and, secondly that a relationship exists between efficiency of relaxation and concentration of paramagnetic centres.

We report that we have found in naturally occurring layer aluminosilicates  $^{29}\text{Si}$   $T_1$ 's which vary over three orders of magnitude with an upper limit of *ca.* 5000 s in one case. These

results confirm that  $^{29}\text{Si}$   $T_1$ 's in aluminosilicates can be extremely long and, in conjunction with preliminary e.s.r. studies, provide evidence of the dependence of relaxation rate on paramagnetic centre concentration consistent with relaxation *via* spin-diffusion.

In a recent study, we reported the  $^{29}\text{Si}$  spectra of samples of the three types of kaolin (kaolinite, dickite, and nacrite) and pyrophyllite.<sup>4</sup> Kaolins  $\{\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8\}$  have a  $Q^3(\text{OAl})$ , dioctahedral repeat '1:1' layer structure consisting of an octahedral aluminium hydroxide sheet (gibbsite sheet) and a tetrahedral silica sheet. A rigid three-dimensional structure is obtained *via* hydrogen bonding between layers of paired sheets. The three chemically equivalent forms differ in the stacking of layers in different regular sequences. Pyrophyllite, whilst also being a  $Q^3(\text{OAl})$  aluminosilicate, differs in that it has a '2:1' dioctahedral structure with a silica tetrahedral sheet on either side of the gibbsite sheet.

As part of this study, the cross-polarization characteristics were examined. In order to determine the c.p. enhancements obtainable it was necessary to obtain fully relaxed  $^{29}\text{Si}$  spectra without c.p., and hence, to determine  $^{29}\text{Si}$  spin-lattice relaxation times. The determined  $^{29}\text{Si}$   $T_1$ 's are given in Table 1 along with details of instrument conditions and method of measurement. The values range from *ca.* 4 s in the kaolinite sample to *ca.* 5000 s in the nacrite sample. Figure 1 shows a  $T_1$  experiment for the nacrite sample.  $^1\text{H}$   $T_1$ 's and cross-polarization enhancements are also given in Table 1. The  $^1\text{H}$   $T_1$ 's also vary widely with that for the kaolinite sample being *ca.* 0.1 s and for the nacrite sample, *ca.* 6 s. In contrast, the carefully determined linewidths range only from *ca.* 60 to 80 Hz.<sup>4</sup>

The only obvious reason for this wide variation in relaxation times given the close structural relationship of the materials examined, is the presence of paramagnetic impurities causing

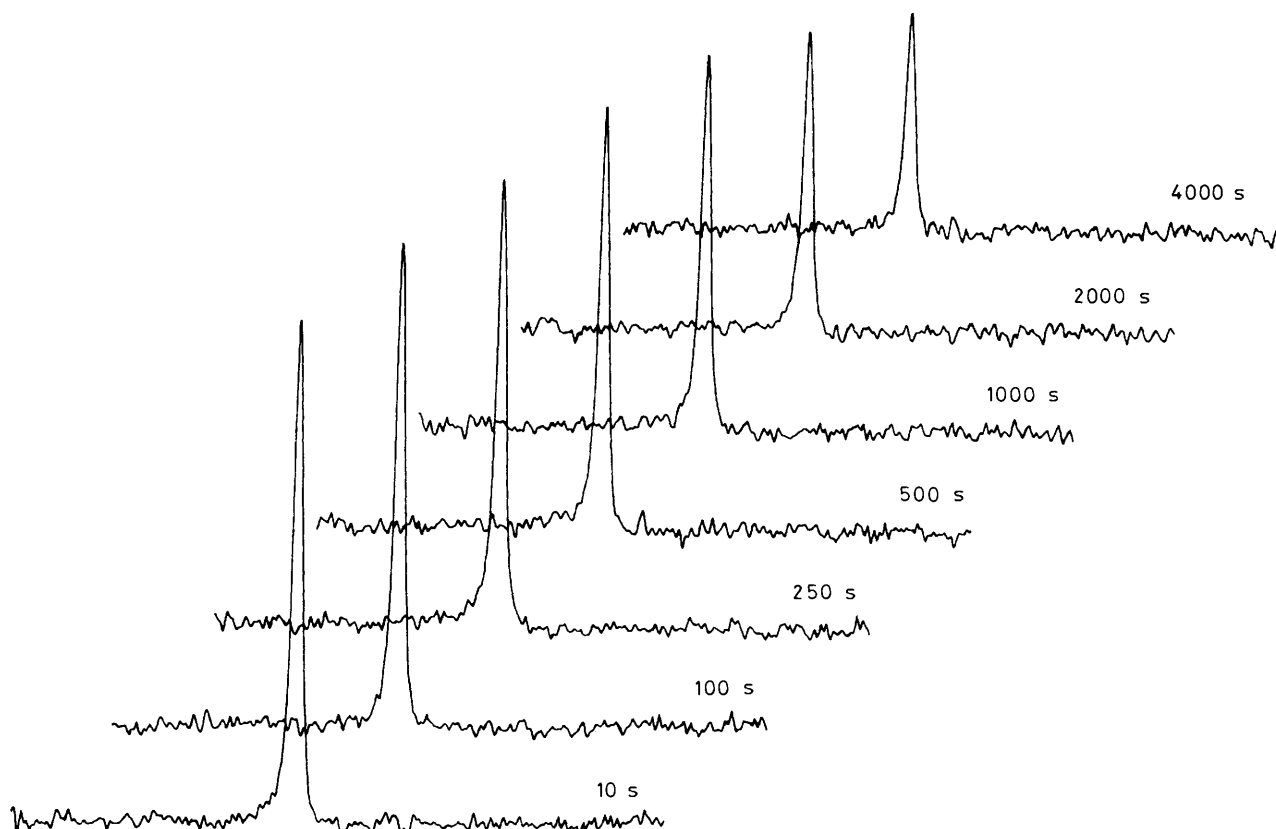


Figure 1.  $^{29}\text{Si}$  C.p./m.a.s.  $T_1$  experiment for Nacrite sample. A recycle delay of 30 s was used. Other parameters are given in notes to Table 1.

**Table 1.** N.m.r.<sup>a</sup> parameters for layer aluminosilicates.

	<sup>29</sup> Si T <sub>1</sub> <sup>b</sup> /s	<sup>1</sup> H T <sub>1</sub> <sup>c</sup> /s	C.p. enhancement <sup>d</sup>	%Fe <sub>2</sub> O <sub>3</sub>
Kaolinite	4.0	0.1	2.3	0.23
Dickite	924 <sup>e</sup>	0.5	2.7	0.13
Nacrite	ca. 5000	6.0	—	0.14
Pyrophyllite	46 <sup>e</sup>	0.8	2.7	0.05

<sup>a</sup> All measurements made on a Bruker CXP-300 spectrometer at 59.61 MHz using <sup>1</sup>H and <sup>29</sup>Si H<sub>1</sub> fields of 10 and 50 G, respectively. Samples were packed in delrin rotors and spun at 3–4 kHz.

<sup>b</sup> Measured using a spin-temperature alternated cross-polarization pulse sequence followed by 90° phase shifted  $\pi/2-\tau-\pi/2$  <sup>29</sup>Si pulse sequence prior to acquisition with <sup>1</sup>H dipolar decoupling. Recycle delays of greater than five times the <sup>1</sup>H T<sub>1</sub> were used.

<sup>c</sup> Measured using a cross-polarization pulse sequence preceded by a  $\pi-\tau$  <sup>1</sup>H pulse with a recycle delay of greater than five times the T<sub>1</sub>. <sup>d</sup> Determined via a cross-polarization experiment using contact time resulting in maximum enhancement and single  $\pi/2$  <sup>29</sup>Si pulse experiment with a delay of greater than five times the measured <sup>29</sup>Si T<sub>1</sub>. <sup>e</sup> Larger component of two component decay.

relaxation via spin-diffusion.<sup>5</sup> Kaolins are found to vary in iron content up to a few percent with the major portion of the iron present as Fe<sup>3+</sup> substituted for aluminium in the octahedral layer.<sup>6</sup> Table 1 shows clearly that there is little relationship between the total Fe<sup>3+</sup> contents of the four samples and their respective <sup>29</sup>Si and <sup>1</sup>H T<sub>1</sub>'s. It is not certain, however, that all of this iron is present in the kaolin and pyrophyllite phases and may, to some extent, be concentrated in a separate phase. If this were the case, the variation of <sup>29</sup>Si spin-lattice relaxation may reflect the extent to which substitution of this iron occurs in the crystal lattice, i.e. substitution for aluminium. Preliminary e.s.r. studies, to be reported in detail elsewhere, provide further support for this theory. Meads and Malden<sup>6</sup> have carried out an extensive e.s.r. study of a wide variety of kaolins and observed, as well as the expected Fe<sup>3+</sup> signals, the presence of Mn<sup>2+</sup>, (VO)<sup>2+</sup>, and hole/trap defects. Whilst the only significant feature of the nacrite e.s.r. spectrum is the presence of minor amounts of Mn<sup>2+</sup>, the kaolinite spectrum exhibits very strong signals from Fe<sup>3+</sup> substituted for Al<sup>3+</sup> and from trapped holes. The only significant signal in the pyrophyllite e.s.r. spectrum is due to trapped holes which, given the relatively short <sup>29</sup>Si T<sub>1</sub> of 46 s, suggests that trapped holes can provide rapid spin-diffusion.

In conclusion, it is clear that <sup>29</sup>Si spin-lattice relaxation times may vary widely and be extremely long. Hence great care should be exercised when obtaining <sup>29</sup>Si spectra of solids without cross-polarization, especially where it is desired to detect all silicon environments in a quantitative manner. The performance of variable recycle time experiments within wide limits, as carried out in many of the studies cited, is obviously essential.

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