

## A multinuclear NMR study of clinochlore

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### ABSTRACT

Tetrahedral and octahedral ordering in synthetic clinochlore with compositions  $(\text{Mg}_5\text{Al})[\text{Si}_3\text{Al}]\text{O}_{10}(\text{OH})_8$  and  $(\text{Mg}_{4.56}\text{Al}_{1.44})[\text{Si}_{2.58}\text{Al}_{1.42}]\text{O}_{10}(\text{OH})_8$  have been studied by  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ , and  $^1\text{H}$  MAS NMR spectroscopy. The  $^{29}\text{Si}$  spectra indicate that Al-O-Al avoidance occurs on tetrahedral sites with considerable short-range order in accordance with the Homogeneous Dispersion of Charges (HDC) model of Herrero et al. (1985a), in which charge imbalance within the tetrahedral sheets is minimized. The  $^1\text{H}$  MAS NMR spectra indicate that every  $^{61}\text{Al}$  is surrounded by six Mg octahedra.

### INTRODUCTION

Studies of chlorites with general stoichiometry  $\text{Mg}_{(5-x)}\text{Al}_{(1+x)}\text{Si}_{(3-x)}\text{Al}_{(1+x)}\text{O}_{10}(\text{OH})_8$  are relevant to the petrology of ultramafic and calc-silicate rocks. Knowledge of the ordering of tetrahedral and octahedral cations is important in quantifying the thermodynamic properties and, hence, the stabilities of these minerals. Solid solution extends from clinochlore ( $x = 0$ ) to  $x \sim 0.5$  (e.g., Shirozu and Momoi, 1972) and involves the Tschermak's coupled substitution  $^{61}\text{Mg} + ^{44}\text{Si} = ^{61}\text{Al} + ^{44}\text{Al}$ . The distinctive feature of the chlorite structure is the alternation of talc-like 2:1 layers and brucite-like interlayers, in which two different types of octahedral sheet sandwich a tetrahedral aluminosilicate sheet. There are four crystallographically distinct octahedral sites: M1 and M2 are in the 2:1 layer, M3 and M4 are in the interlayer sheet. In the 2:1 layer, each M1 site (trans-bonded to OH) is surrounded by six M2 sites (cis-bonded to OH). In the interlayer sheet, each M4 site is surrounded by six M3 sites. The octahedral site ratio M1:M2:M3:M4 is 1:2:2:1.

Refinements of X-ray and neutron diffraction data for natural chlorites indicate that tetrahedral cations are highly disordered (Rule and Bailey, 1987; Zheng and Bailey, 1989; Joswig et al., 1989). In contrast,  $^{29}\text{Si}$  magic-angle-spinning (MAS) NMR studies of other 2:1 phyllosilicates indicate Al-O-Al avoidance with considerable short-range order (Sanz and Serratos, 1984; Herrero et al., 1985a, 1985b, 1987; Kinsey et al., 1985; Circone et al., 1991). In his review of ordering in micas Bailey (1984) stated that ordering of tetrahedral cations is rare. Helgeson et al. (1978) and Clemens et al. (1987) found that the results of phase-equilibrium studies of phlogopite imply considerable tetrahedral Al-Si disorder. The Homogeneous Dispersion of Charges (HDC) model of Herrero et al. (1985a) has been successfully applied to micas (Herrero et al., 1985b, 1987; Circone et al., 1991) and indicates that usually there is considerable short-range Al-Si order, with

the formation of ordered domains in which Al-O-Al avoidance operates and Al is distributed as evenly as possible to minimize the concentration of excess charge. It is important to appreciate that considerable short-range order could be present that may be missed in the average picture given by diffraction methods. Diffraction studies mentioned above also show that  $^{61}\text{Al}$  is partially or highly ordered onto M4 octahedral sites. Rule and Bailey (1987) suggested various structural effects favoring the occupancy of M4 by trivalent cations. These include the reduction of cation-cation repulsion between interlayer and tetrahedral sheets. Using electrostatic energy minimization methods, Bish and Giese (1981) showed that ordering of trivalent cations at M4 can increase the stability of the chlorite structure.

An important objective of the present study was to determine the nature of tetrahedral Al-Si ordering in magnesium chlorites. We report the results of a multinuclear MAS NMR study of ordering in synthetic clinochlores with  $x = 0$  and 0.43, referred to hereafter as Ccl and Ccl<sub>ss</sub>, respectively.

### EXPERIMENTAL DETAILS

#### Sample preparation and characterization

The chlorites studied were synthesized from stoichiometric gels having  $x = 0$  (Ccl) and  $x = 0.50$ , prepared by the method of Hamilton and Henderson (1968), in a piston-cylinder device at 15 kbar and 690–720 °C using a NaCl pressure cell 0.75 in. in diameter. The Ccl<sub>ss</sub> sample was kindly provided by J. Baker (Department of Earth Sciences, Cambridge). Products were examined by optical microscopy, SEM, HRTEM, powder X-ray diffraction, and electron microprobe. Care must be taken in syntheses to avoid metastable growth and persistence of lizardite, which occurs below 650 °C. Standards for electron microprobe analysis were periclase, corundum, and wollastonite. A beam current of 10 nA and accelerating voltage

**TABLE 1.** Electron microprobe data for Ccl and Ccl<sub>ss</sub>

Wt% oxide	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Total
Ccl	32.63	15.58	28.73	76.95
Theoretical	36.27	18.35	32.43	87.05
Normalized	36.91(85)	17.62(46)	32.50(67)	87.03
Ccl <sub>ss</sub>	30.18	23.88	25.39	79.45
Theoretical	32.59	27.48	26.99	87.06
Normalized	33.17(98)	26.17(73)	27.82(75)	87.16
Atoms (pfu)	Mg	Al	Si	Total
Ccl	5.11	1.93	3.00	10.04
Theoretical	5.00	2.00	3.00	10.00
Ccl <sub>ss</sub>	4.56	2.85	2.58	9.99
Theoretical	4.50	3.00	2.50	10.00

Note:  $n = 12$  for Ccl and  $n = 17$  for Ccl<sub>ss</sub>. Atoms per formula unit based on 14 O. Numbers in parentheses are 2 sd for  $n$  analyses.

of 15 kV were used. Microprobe specimens were prepared as grain mounts in epoxy. Unit cell data were obtained by Guinier photography with Ni-filtered CuK $\alpha$  radiation and elemental Si as internal standard.

### MAS NMR spectroscopy

NMR spectra were acquired using a Chemagnetics CXP-400 multinuclear spectrometer. MAS rotors were spun in N<sub>2</sub> at 4.5 kHz. The <sup>27</sup>Al MAS NMR spectra were recorded at 104.26 MHz using very short 0.32  $\mu$ s (equivalent to  $\pi/18$ ) radiofrequency pulses, 0.5 s recycle delays, and 5000 acquisitions. The <sup>1</sup>H-<sup>27</sup>Al CP/MAS spectra were measured with a single contact, optimized contact time of 500  $\mu$ s, <sup>1</sup>H  $\pi/2$  pulse of 3  $\mu$ s and 14000 acquisitions. The Hartmann-Hahn condition was established in one scan on a sample of high-quality kaolinite under the same conditions. Because only the central ( $+1/2 \leftrightarrow -1/2$ ) transition is observed, excitation in the <sup>1</sup>H-<sup>27</sup>Al CP/MAS experiment is selective, and thus the Hartmann-Hahn condition is  $3\gamma_{Al}B_{Al} = \gamma_H B_H$  (Samson and Lippmaa, 1983). Chemical shifts are given in parts per million from external aqueous Al(NO<sub>3</sub>)<sub>3</sub>. The <sup>29</sup>Si MAS NMR spectra were recorded at 79.45 MHz using 2.5  $\mu$ s (equivalent to  $\pi/6$ ) radiofrequency pulses, 120 s recycle delays, and 600 acquisitions. The <sup>1</sup>H MAS NMR spectra were measured at 399.91 MHz using 3.8  $\mu$ s ( $\pi/2$ ) pulses, 10 s recycle delays, and 16 acquisitions. The <sup>29</sup>Si and <sup>1</sup>H spectra chemical shifts are given in parts per million from external TMS. Sample sizes were 0.18 (Ccl) and 0.17 g (Ccl<sub>ss</sub>). The very long spin-lattice relaxation times ( $t_1$ ) of <sup>29</sup>Si nuclei in chain and phyllosilicates can result in noisy spectra or lengthy experiments. To avoid this, we added 0.2 wt% Gd<sub>2</sub>O<sub>3</sub> (Specpure) to the gels in order to decrease spin-lattice relaxation times (Stebbins and Kanzaki, 1990).

### Infrared spectroscopy

Infrared spectra were collected using a Nicolet spectrometer in a sample chamber purged with N<sub>2</sub>. The powder (0.02 g) was added to crushed KBr (0.2 g), pressed into a disk, dried in an oven at 120 °C, and then stored in an evacuated desiccator until analyzed.

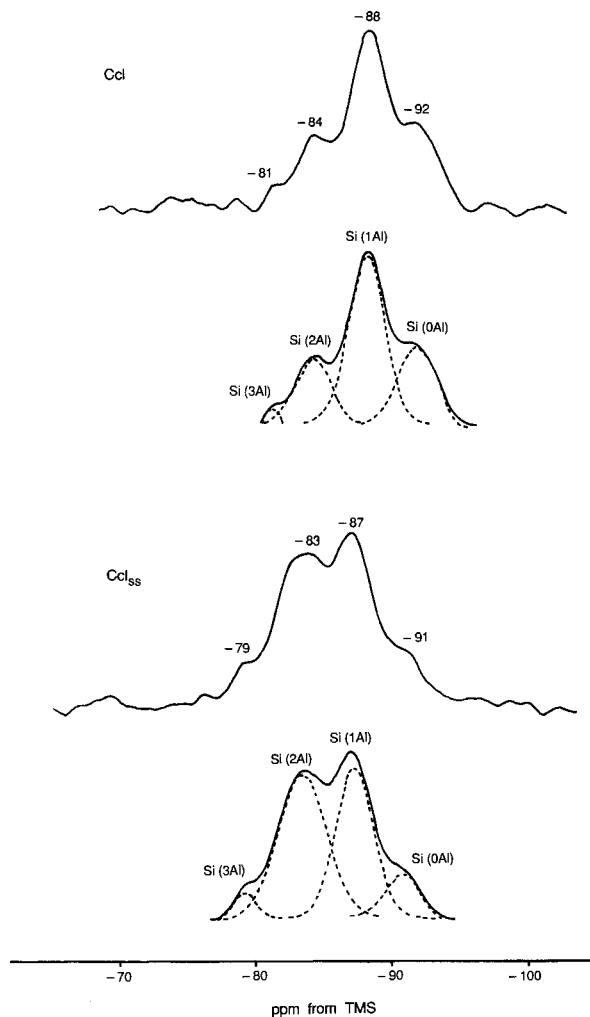


Fig. 1. The <sup>29</sup>Si MAS NMR spectra of Ccl and Ccl<sub>ss</sub>.

## RESULTS

Ccl products were monophasic chlorite; Ccl<sub>ss</sub> products were chlorite with trace amounts (<5% total) of spinel and corundum. In both samples, chlorite formed polycrystalline aggregates of small grains (<5  $\mu$ m) and occasional larger equant subhedral grains up to ~15  $\mu$ m in diameter. Electron microprobe analyses (Table 1) indicate a close approach to the ideal formulae, with Ccl<sub>ss</sub> having  $x = 0.43$ . The oxide totals for both samples are much lower than theoretical values owing to small grain size and the porous nature of the aggregates, resulting in only part of the electron beam exciting a crystal or group of crystallites. Typically, oxide weight percent totals ranged from 70 to 83%. However, the derived chemical formulae are independent of oxide totals. This strongly suggests that the analyses are reliable and that the low totals do not imply differential loss of Mg, Al, or Si. In Table 1 we have included values for weight percent oxides that are normalized to their theoretical anhydrous totals. Cell parameter refinements from the powder X-ray diffraction data are as follows: for Ccl,  $a = 5.320(0)$ ,  $b = 9.215(1)$ ,  $c$

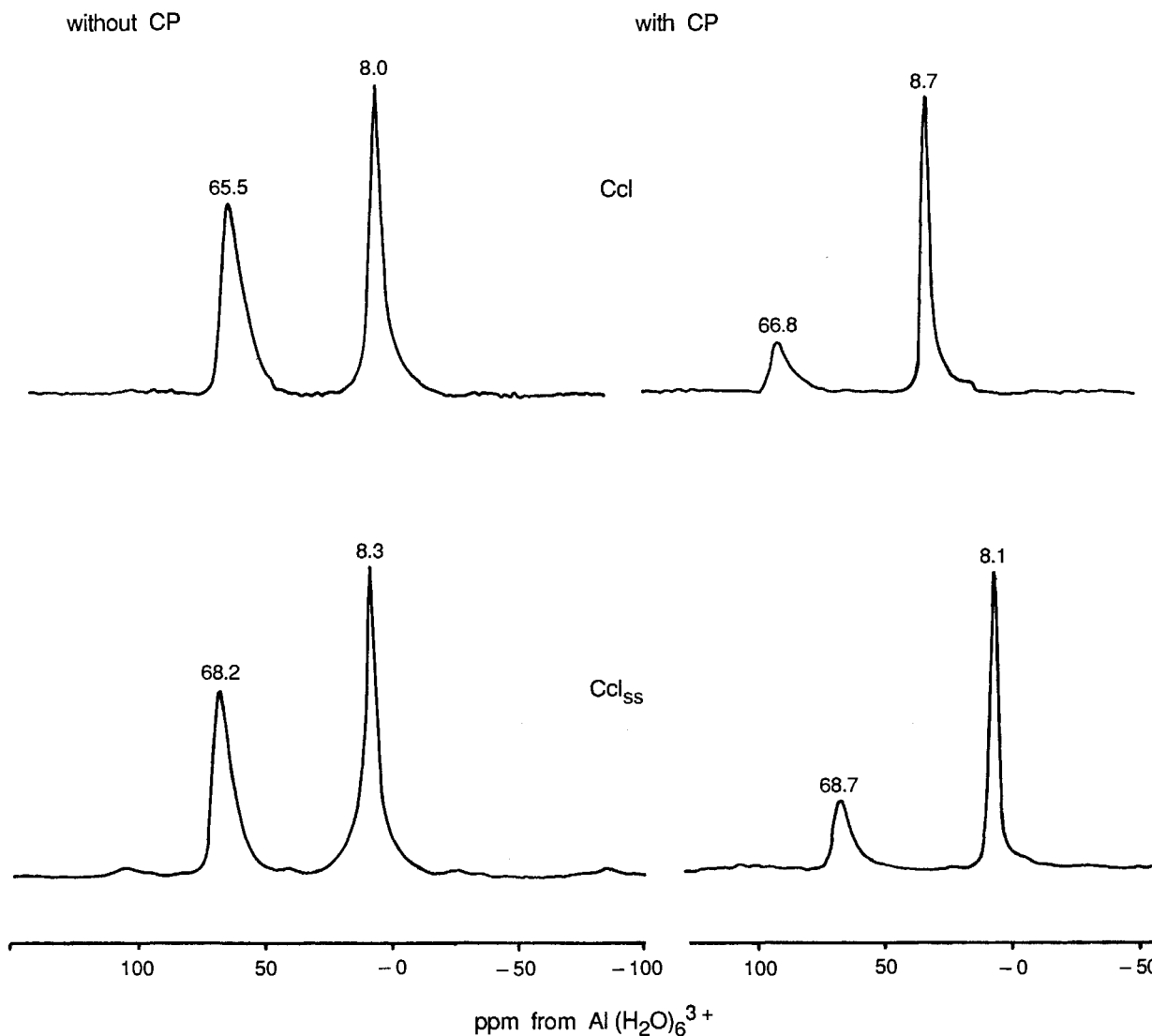
$^{27}\text{Al}$  MAS NMR

Fig. 2. The  $^{27}\text{Al}$  MAS NMR spectra of Ccl and Ccl<sub>ss</sub> with and without cross-polarization.

= 14.393(2) Å,  $\beta = 97.09^\circ$ , and  $V = 700.2(1)$  Å<sup>3</sup>; for Ccl<sub>ss</sub>,  $a = 5.292(4)$ ,  $b = 9.210(5)$ ,  $c = 14.359(7)$  Å,  $\beta = 96.01(2)^\circ$ , and  $V = 696.0(6)$  Å<sup>3</sup>. Numbers in parentheses are two standard deviations and refer to the last digit. These cell parameters agree well with those obtained by Nelson and Roy (1958), Jenkins and Chernosky (1986), and Roots (1994) for Ccl and chlorites with  $x = 0.45$ – $0.55$ .

#### The $^{29}\text{Si}$ MAS NMR spectra

The  $^{29}\text{Si}$  MAS NMR spectra of Ccl and Ccl<sub>ss</sub> are shown in Figure 1. In both cases the spectra can be simulated accurately by four Gaussian peaks. The chemical shifts

of these peaks correspond between samples. The downfield peak assignments follow the conventional sequence for phyllosilicates and are Q<sup>3</sup>(0Al), Q<sup>3</sup>(1Al), Q<sup>3</sup>(2Al), and Q<sup>3</sup>(3Al). For Ccl their relative intensities are 25, 52, 20, and 3%, respectively. For Ccl<sub>ss</sub> these are 2, 49, 42, and 7%, respectively. From the simulations, we estimate that the uncertainties in peak intensities are about 2% absolute.

#### The $^{27}\text{Al}$ MAS NMR spectra

The  $^{27}\text{Al}$  MAS NMR spectra of Ccl and Ccl<sub>ss</sub> are shown in Figure 2. In both there are two strong resonances at

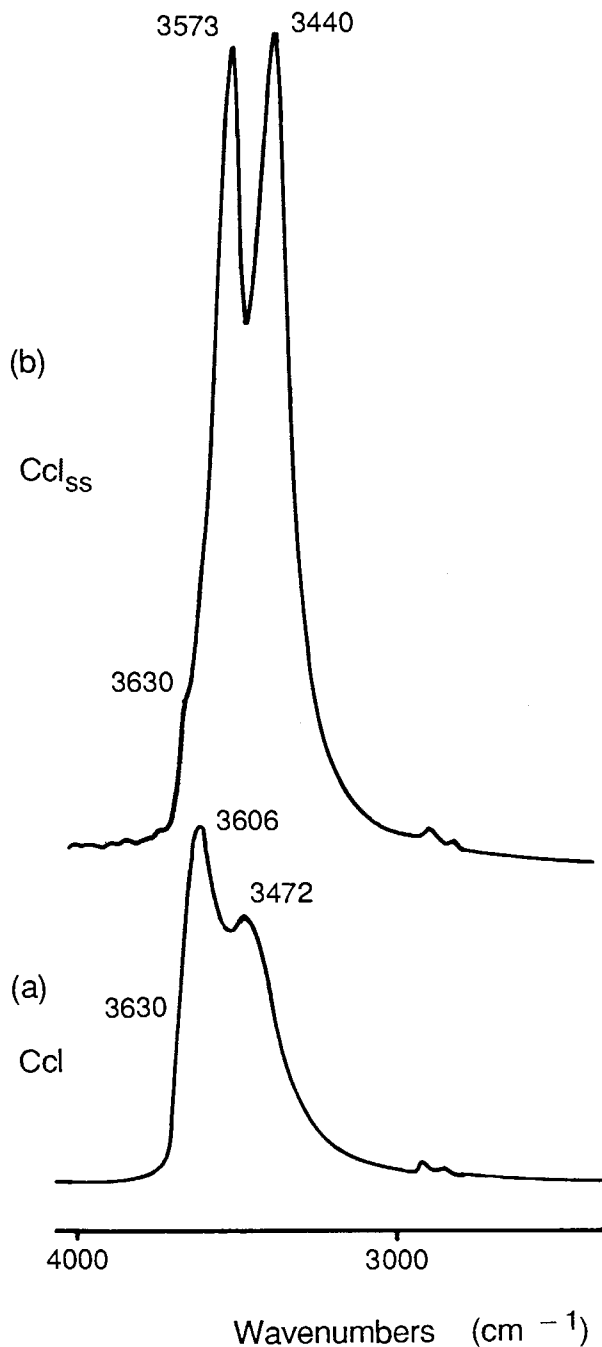


Fig. 3. Infrared spectra in the OH stretching region for (a) Ccl and (b) Ccl<sub>ss</sub>.

8–9 and 66–68 ppm, which are due to <sup>16</sup>Al and <sup>14</sup>Al, respectively, with <sup>14</sup>Al:<sup>16</sup>Al = 1:1, as expected from Table 1. The sharp <sup>16</sup>Al peak strongly cross polarizes and appears to be a single resonance, although there is some minor quadrupolar broadening at the baseline. The <sup>14</sup>Al resonance is a single peak.

### Infrared and <sup>1</sup>H MAS NMR spectra

The infrared spectra in the OH stretching region at 3000–3800 cm<sup>-1</sup> of Ccl and Ccl<sub>ss</sub> are shown in Figure 3. Both spectra have two strong absorptions at around 3440–3472 and 3573–3606 cm<sup>-1</sup>. A third much weaker peak is present at 3630 cm<sup>-1</sup> in both spectra. The difference in relative peak height of the two strong peaks for Ccl and Ccl<sub>ss</sub> is due to the different tetrahedral Si-Al ratios. Hence, the peak at lower frequency in each spectrum may be due to a H-bonded interaction with <sup>14</sup>Al, and the higher frequency peak may be due to <sup>14</sup>Si (Shirozu and Momoi, 1972).

The <sup>1</sup>H MAS NMR spectra of Ccl and Ccl<sub>ss</sub> are shown in Figure 4. Both contain two strong resonances at around 1 and 4 ppm with spinning sidebands at ca. δ ± 20 ppm. The sidebands contribute 20–25% of the total intensity of each peak, and each main peak is flanked by highly asymmetric sidebands. Simulations indicate that the intensity ratio for the peaks at 1 and 4 ppm is about 45:55 for both samples.

### DISCUSSION

#### Tetrahedral sites

The <sup>29</sup>Si MAS NMR spectra may be interpreted by considering well established models for Al-Si ordering on tetrahedral sites in phyllosilicates, all summarized in Table 2. For comprehensive discussions see Sanz and Serratos (1984) and Herrero et al. (1985, 1987).

**Random mixing on tetrahedral sites.** The relative intensities of Q<sup>3</sup>(0Al), Q<sup>3</sup>(1Al), Q<sup>3</sup>(2Al), and Q<sup>3</sup>(3Al) peaks for a random distribution of Al and Si are given statistically by the binomial distribution (1 - x)<sup>3</sup>, x(1 - x)<sup>2</sup>, x<sup>2</sup>(1 - x), and x<sup>3</sup>, respectively, where x is the atomic fraction of <sup>14</sup>Al.

**Al avoidance: Short-range and long-range order.** A test for the operation of Al-O-Al avoidance is given by the following formula (Sanz and Serratos, 1984):

$$\frac{^{14}\text{Al}}{^{14}\text{Si}} = \frac{1}{3} \frac{\sum_{n=0}^3 nI_n}{\sum_{n=0}^3 I_n}$$

Theoretical values for Al/Si are 0.33 for Ccl and 0.56 for Ccl<sub>ss</sub>. Measured values for Ccl and Ccl<sub>ss</sub> are 0.34 and 0.51, respectively. Thus, avoidance of Al-O-Al linkages is clearly indicated.

**Homogeneous Dispersion of Charges (HDC) model.** Various simple Al-O-Al avoidance (AA) schemes can be conceived that may be used to interpret the <sup>29</sup>Si MAS NMR spectra of 2:1 phyllosilicates. The simplest predicts peak intensity ratios that would result from a purely statistical (binomial) distribution. Here, the intensities for Q<sup>3</sup>(0Al), Q<sup>3</sup>(1Al), Q<sup>3</sup>(2Al), and Q<sup>3</sup>(3Al) peaks are given by s<sup>3</sup>, 3s<sup>2</sup>a, 3sa<sup>2</sup>, and a<sup>3</sup>, where a = x/(1 - x) and s = 1 - a (Herrero et al., 1985a).

Alternatively, taking an extreme case, increasing de-

**TABLE 2.** Tetrahedral distribution schemes relevant to the interpretation of  $^{29}\text{Si}$  MAS NMR spectra of Ccl and  $\text{Ccl}_{\text{ss}}$ 

$^{1}\text{Al}$ scheme	0Al	1Al	2Al	3Al	R
<b>Ccl: tetrahedral with Si/Al = 3</b>					
RD*	0.42	0.42	0.14	0.02	0.42
AA**	0.30	0.44	0.22	0.04	0.24
LRO†	0.33	0.33	0.33	0.00	0.51
HDC‡	0.22	0.57	0.21	0.01	0.19
Observed	0.25	0.52	0.20	0.03	—
<b><math>\text{Ccl}_{\text{ss}}</math>: tetrahedral with Si/Al = 1.8</b>					
RD	0.26	0.44	0.25	0.05	0.56
AA	0.09	0.33	0.41	0.17	0.42
LRO	0.24	0.14	0.35	0.27	0.92
HDC	0.09	0.34	0.42	0.16	0.39
Observed	0.02	0.49	0.42	0.07	—

Note: calculated R-factor for Ccl is the maximum deviation allowed for the 2% uncertainty in peak area (see text). R-factor, LRO, and HDC for  $\text{Ccl}_{\text{ss}}$  calculated by Circone et al. (1991) for a phlogopite-eastonite mica with  $X_{\text{eastonite}} = 0.45$ .

\* Random distribution (statistical).

\*\* Simple Al-O-Al avoidance (statistical).

† Long-range order (see text).

‡ Determined by Herrero et al. (1985a) for Si/Al = 3.

gress of Al-O-Al avoidance would be achieved by having domains of only  $\text{Q}^3(0\text{Al})$  and  $\text{Q}^3(3\text{Al})$  groups. If a two-dimensional domain structure is assumed, we calculate that  $\text{Q}^3(n\text{Al})$  groupings at domain junctions will be undetectable by  $^{29}\text{Si}$  MAS NMR for a domain radius  $> 800$  Å. For a tetrahedral ratio  $\text{Si}/\text{Al} = 3$ , such an ordering scheme and minimum domain size would produce two strong peaks with an intensity ratio  $\text{Q}^3(0\text{Al}):\text{Q}^3(3\text{Al}) = 2:1$  [ $3\text{Si}_3\text{Al} = 2\text{Si}(\text{Si}_3) + \text{Si}(\text{Al}_3)$ ]. In contrast, the spectra obtained for a range of 2:1 phyllosilicates with tetrahedral  $\text{Si}/\text{Al} \sim 3$  have no  $\text{Q}^3(3\text{Al})$  (Sanz and Serratos, 1984). Ccl appears to be exceptional in this respect.

Such observations led Herrero et al. (1985a) to explore less extreme ordering schemes in phyllosilicates in which Al-O-Al avoidance is obeyed but  $\text{Q}^3(0\text{Al})$  and  $\text{Q}^3(3\text{Al})$  are minimized. The crystal-chemical principle involves minimizing the local concentration of excess charge in the tetrahedral sheets. Herrero et al. (1987) called this the Homogeneous Dispersion of Charges model (HDC). It is a short-range order concept involving domains within which a particular ordering pattern prevails. The tetrahedral sheet of phyllosilicates can be considered to be composed of hexagonal six-membered rings of tetrahedral sites. Rings with 0, 1, or 3 Al are not symmetrically unique and are interchangeable. However, rings with 2 Al can have a meta configuration in which the Al sites are separated by 1 and 3 Si sites, or alternatively a para configuration in which Al sites are separated by 2 Si sites. The HDC model considers the variation in the meta:para ratio with bulk Al/Si. A computer program may be used to generate an Al-Si array for a large number (e.g., 10000) of tetrahedra. The proportions of  $\text{Q}^3(0\text{Al})$ ,  $\text{Q}^3(1\text{Al})$ ,  $\text{Q}^3(2\text{Al})$ , and  $\text{Q}^3(3\text{Al})$  sites are then determined. The reader is referred to Circone et al. (1991, p. 1497) for an illustration.

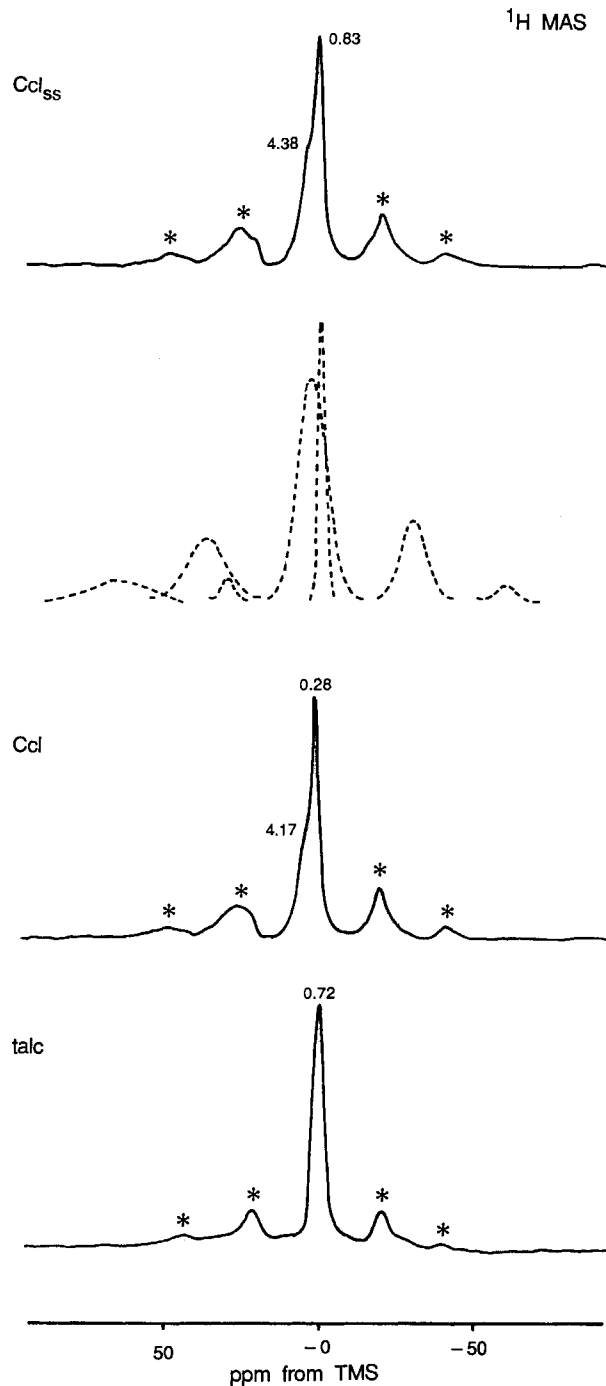


Fig. 4. The  $^1\text{H}$  MAS NMR spectra of Ccl,  $\text{Ccl}_{\text{ss}}$  (with deconvolution, not to scale), and synthetic talc. The asterisks denote the spinning sidebands.

**Long-range order.** Finally, a long-range order model is considered in which alternating sites are filled by only Si, and then the remaining sites are filled randomly by Al or Si, with the probability  $2x$  that Al will occupy the site.

Long-range order is produced, which complies with Al-O-Al avoidance and involves only the meta configuration.

In evaluating the different Al-Si distribution schemes for Ccl and Ccl<sub>ss</sub>, we use a residual error (R) defined by Herrero et al. (1987):

$$R = \sum_{n=0}^3 |I_{n,obs} - I_{n,calc}|.$$

The R values shown in Table 2 are the largest deviations allowed by the estimated uncertainties in peak intensities ( $\pm 2\%$  absolute). For Ccl, the observed relative peak intensities agree very well with the HDC model. Statistically random Al-Si distributions do not occur. For Ccl<sub>ss</sub>, the HDC model is indicated by the dominance of Q<sup>3</sup>(1Al) and Q<sup>3</sup>(2Al) groupings. A comparison of the <sup>29</sup>Si MAS NMR spectrum of Ccl<sub>ss</sub> with that of a synthetic phlogopite-eastonite mica having almost the same Si/Al value,  $X_{eastonite} = 0.45$  (Circone et al., 1991), is instructive. For Ccl<sub>ss</sub>, the intensities of the Q<sup>3</sup>(1Al) and Q<sup>3</sup>(2Al) are higher and those of Q<sup>3</sup>(0Al) and Q<sup>3</sup>(3Al) lower than those of the mica, possibly suggesting a significantly higher degree of short-range order than is implied by the HDC model.

### Octahedral sites

Four chemically different groupings of three octahedra (M1 + 2M2; M4 + 2M3) around each OH are possible in these chlorites: Mg<sub>3</sub>-OH, Mg<sub>2</sub>Al-OH, MgAl<sub>2</sub>-OH, and Al<sub>3</sub>-OH, henceforth designated as 3Mg, 2Mg, 1Mg, and 0Mg, respectively. Analogous octahedral groupings occur in amphiboles and micas, for which the correlations between octahedral site occupancies and OH stretching frequencies are well known (e.g., Robert, 1976; Raudsepp et al., 1987; Welch et al., 1994). These correlations suggest that peaks due to other possible octahedral groupings of the 2:1 layer, such as 2Mg and 1Mg, could occur at lower frequencies than those of 3Mg. Our infrared spectra are comparable to those obtained for compositionally similar chlorites by Shirozu and Momoi (1972). These workers attributed the intense peaks to H-bonded interactions between protons of the interlayer and the <sup>161</sup>Al and <sup>141</sup>Si of the 2:1 layer and the relatively weak peak at 3630 cm<sup>-1</sup> to 3Mg. Farmer (1974) observed that, when heated, chlorites dehydrate by selectively losing H<sub>2</sub>O from the interlayer first and then, more slowly, from the 2:1 layer. In his infrared spectra this was seen as retention of the peak(s) assigned to the 2:1 layer OH (3610–3676 cm<sup>-1</sup>) and loss of the intense peaks (H bonding) of the interlayer. The observation of only one non-H-bonded talc-like peak that has the highest frequency in the spectra suggests that it is due to 3Mg. Peaks from other groupings, if present, are presumably swamped by the adjacent intense ones associated with H bonding.

Bond-valence arguments suggest that 1Mg and 0Mg groupings are very unlikely to occur because of the excessively high bond valences incident at the O atom of the OH group (2.33 and 2.5 vu for 1Mg and 0Mg, re-

spectively). This is certainly the case for amphiboles (Raudsepp et al., 1987; Welch et al., 1994) and eastonitic micas (Robert, 1976). While only the 3Mg grouping is resolved in the infrared spectra of chlorite, there are two peaks in the <sup>1</sup>H MAS NMR spectra, suggesting two different octahedral groupings. Hence, it is probable that these are 3Mg and 2Mg. However, it is unclear which peak corresponds to which grouping. Very few <sup>1</sup>H MAS NMR spectra of minerals are available for comparison. In synthetic pargasite 3Mg and 2Mg have chemical shifts of 0 and 1.3 ppm, respectively (Welch et al., 1994). The <sup>1</sup>H MAS NMR spectrum of synthetic end-member talc (synthesized at 2 kbar and 750 °C) has a single main peak at 0.7 ppm, suggesting that the chlorite peak at 0.3–0.8 ppm may be due to 3Mg. If this were so, then the 3Mg:2Mg peak ratio for the Ccl studied should be 56:44, which is not the case (43:57). A puzzling feature of the <sup>1</sup>H MAS NMR spectra of chlorite is the similar peak intensity ratio for the two samples. On compositional grounds, the 2Mg peak should be noticeably more intense than the 3Mg peak. The highly asymmetric intensity distributions in the spinning sidebands may also complicate the interpretation of these spectra (in contrast, the talc spectrum has symmetric intensity in the sidebands). In view of these ambiguities, we do not feel justified in attempting a detailed interpretation. However, the <sup>1</sup>H MAS NMR spectra do indicate that every <sup>161</sup>Al is surrounded by six <sup>161</sup>Mg. Such an array is consistent with ordering of <sup>161</sup>Al at M1, M4, or both, but does not exclude other short-range order domain schemes involving other sites.

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