

## <sup>39</sup>K SOLID-STATE NMR STUDIES OF POTASSIUM TECTO- AND PHYLLOSILICATES: THE *IN SITU* DETECTION OF HYDRATABLE K<sup>+</sup> IN SMECTITES

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**Abstract**—We report the first application of <sup>39</sup>K solid-state NMR to the study of tecto- and phyllosilicates. Under high field (11.7 Tesla) and with the application of a spin-echo sequence, informative <sup>39</sup>K spectra can be obtained for several compounds of interest to the geologist and the agronomist. Tectosilicates and phyllosilicates can be distinguished from the uncorrected frequency ( $\delta_{CG}$ ) of the observed NMR peak. A series of montmorillonites submitted to increasing numbers of wetting and drying cycles was studied in order to discriminate between mobile and “fixed” forms of K<sup>+</sup>: when the spectra are run on hydrated samples, two different signals are observed corresponding to K<sup>+</sup> in different hydration states, and NMR data can be correlated with the amount of exchangeable K<sup>+</sup> measured by ion exchange. Thus, it appears that NMR can provide useful information on K fixation complementary to classical chemical methods.

**Key Words**—Potassium, Solid-state NMR, Phyllosilicates, Vermiculite, Montmorillonite (potassium, wetting-drying of).

### INTRODUCTION

NMR studies of clays and clay minerals may be separated into three groups according to the particular component of the clay structure that comes under focus. The most common to date are studies of the organisation of the silicate sheets, especially the problem of Al ordering by <sup>29</sup>Si and <sup>27</sup>Al NMR (Alma *et al.*, 1984; Lipsicas *et al.*, 1984; Sanz and Serratos, 1984a, 1984b; Thompson, 1984; Barron *et al.*, 1985; Herrero *et al.*, 1985; Kinsey *et al.*, 1985; Weiss *et al.*, 1987; Woessner, 1989). Then, there are investigations aimed at determining the structure and state of motion of water in the interlayer space by proton or deuterium magnetic resonance (Hougardy *et al.*, 1976; Woessner, 1979; Kadi-Hanifi, 1980; Lipsicas *et al.*, 1985). Finally, the third constituent of clays, namely the compensating cations, could be used as probes to provide complementary information on interlayer organisation. Except for the case of Li (Conard, 1976) NMR has only recently begun to be applied to compensating cations due to the difficulties often associated with the observation of their resonance. For example, many of these nuclei are quadrupolar and, to enhance resolution,

require high magnetic fields that are only recently available. Since 1988, publications have appeared on Cd-hectorite (Bank *et al.*, 1989; Tinet *et al.*, 1991), Cs-hectorite (Kirkpatrick, 1988; Weiss *et al.*, 1990), Na-synthetic micas (Soma *et al.*, 1989), Na-montmorillonite (Luca *et al.*, 1989), and Cd, Na, and Cs-vermiculite (Laperche *et al.*, 1990).

It would be of particular interest to investigate the utility of potassium as a probe of its molecular environment, in view of the agronomical importance of the K<sup>+</sup> cation and of its relevance to many problems in geology.

One important problem that would benefit from such an approach is the distinction between “exchangeable” and “fixed” K in soils. It is well known empirically that K in soils is distributed among several pools, or compartments, with different accessibilities to chemical exchange, as well as different bioavailabilities: one would like to know if any significant correlations can be established between these and some of the physico-chemical parameters relating to K<sup>+</sup> ions.

Potassium would seem to present a particular challenge to the NMR spectroscopist. Its main isotope, <sup>39</sup>K, is a spin 3/2 quadrupolar nucleus. The low symmetry of K sites in many compounds results in high values of the electric field gradient, and therefore high QCC (quadrupole coupling constants). In addition, the low gyromagnetic ratio,  $\gamma$  ( $1.907 \cdot 10^6$  s<sup>-1</sup> T<sup>-1</sup>), induces a low value of  $\nu_L$ , and both factors contribute to an important quadrupolar effect increasing the line width for

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powder spectra. Another consequence of the low  $\nu_L$  is that acoustic ringing and other low frequency artefacts are often present, so that undistorted NMR powder lineshapes are difficult to obtain. Indeed, very few authors have reported  $^{39}\text{K}$  solid-state NMR results to date and these have mostly been on simple model compounds (Kunwar *et al.*, 1986; Bastow and Stuart, 1990 and references therein).

In spite of these difficulties, the preliminary results presented here establish that  $^{39}\text{K}$  solid-state NMR not only is feasible for important minerals naturally occurring in soils and geological formations, but can provide information of practical significance to the agronomist and mineralogist alike.

### EXPERIMENTAL

The present study was restricted to K tecto- and phyllosilicates since some of the most abundant mineral components in soils belong to these classes. In the hope of decreasing the broadening of the NMR signals, attempts were made to select single crystals. Samples of gem-quality orthoclase and muscovite (both from Madagascar) were cut to a  $7 \times 7 \times 10$  mm size in order to fit in the NMR coil; the muscovite sample was covered with liquid glue to prevent exfoliation.

A 230 mg "crystal" of Llano vermiculite was hand-picked, washed with dilute HCl, and submitted to 2 successive exchanges in 500 ml of 0.1 M KCl at 90°C. In fact, such a "crystal" consists of several domains with different orientations of the a and b axes, so that only the c axis orientation is preserved.

For powder studies, we used a series of  $\text{K}^+$  Wyoming montmorillonites that had been submitted to increasing numbers of wetting and drying cycles. These samples had been previously characterised by a variety of techniques including X-ray diffraction and chemical exchanges (Mamy and Gaultier, 1975, 1976; Plançon *et al.*, 1977; Gaultier, 1978). The  $<2 \mu\text{m}$  fraction had been saturated with  $\text{K}^+$ , then the following treatment had been repeated the desired number of times: wetting by suspension in water under stirring, followed by drying under air at 80°C overnight. This treatment constituted one wetting and drying (further abbreviated as W-D) cycle. The samples had been stored for 15 years prior to use. In addition, 7 days prior to running the NMR spectra, the 100 W-D sample was submitted to exchange with  $\text{Sr}^{++}$  ions to eliminate "exchangeable  $\text{K}^+$ ": 1 g of sample in the  $\text{K}^+$  form was suspended in 120 ml of 0.25 M  $\text{SrCl}_2$  and stirred at room temperature for 24 hr. This treatment was repeated 4 times for complete exchange and the clay was collected by centrifugation.  $\text{Sr}^{++}$  was used rather than  $\text{NH}_4^+$  in the hope that a divalent cation would be favored in the exchange reaction, resulting in the complete elimination of exchangeable  $\text{K}^+$ . The interest in such samples will be outlined in the discussion.

$^{39}\text{K}$  spectra were obtained using either a 10 mm (for

single crystals) or a 5 mm inner diameter horizontal solenoid coil on a Bruker MSL500 spectrometer operating at  $\nu_L = 23.336$  MHz. To avoid lineshape distortion through "baseline roll," we used a  $\pi/2 - \tau - \pi/2$  spin echo sequence similar to that described by Kunwar *et al.* (1986), with an interpulse spacing of 50 to 60  $\mu\text{s}$ . A recycle delay of 0.25 ms proved sufficient to prevent saturation for all samples. The spectra were smoothed by application of an exponential filter so as to improve the signal/noise ratio without significantly broadening the lineshape. All spectra are referenced to a 1 M KCl solution, with solid KCl used as a secondary standard (of  $\delta_{\text{CG}} = +42$  ppm). For this sample, which has a QCC  $\approx 0$ , the length of a  $\pi/2$  pulse was determined to be 8  $\mu\text{s}$ ; hence, a 90° pulse length of 4  $\mu\text{s}$  was used for all our samples, since the use of a  $\pi/2(I + 1/2)$  pulse allows the selective excitation of the central ( $-1/2 \leftrightarrow 1/2$ ) transition (Schmidt, 1971). It was verified that the background did not contribute significant intensity to the observed spectrum.

XRD spectra of the montmorillonite samples used for NMR investigations were subsequently recorded on a conventional Philips powder diffractometer. Surface areas were estimated for the same samples by application of the BET treatment to  $\text{N}_2$  physisorption isotherms measured volumetrically (7 points) after 2 hr evacuation at 200°C.

### RESULTS

Figure 1 shows the static NMR spectra of the three nominally single crystals; approximate peak widths ( $\nu_{1/2}$ ) and positions ( $\delta_{\text{CG}}$ ) of the line center of gravity are given in Table 1. The considerable width of the signals observed for orthoclase and muscovite was unexpected. In the case of muscovite, this might be due to a relatively high Fe content, inducing a fast relaxation and a high value of  $1/T_2$ . A microprobe analysis of selected areas of the muscovite crystal indeed revealed Fe contents of the order of 0.3 Fe per  $(\text{Si,Al})_4(\text{Al,M})_2\text{VI-O}_{10}(\text{OH})_2$  formula; the crystal had a greenish-brown colour. For the orthoclase sample, a different explanation must be used (see discussion).

In spite of the linewidth, the resonance position is significantly different for the tectosilicate (orthoclase:  $\delta_{\text{CG}} = +205$  ppm) than for the two phyllosilicates ( $\delta_{\text{CG}} < 40$  ppm).

Figure 2 illustrates the orientation dependency of the  $^{39}\text{K}$  resonance of K-vermiculite. The spectra were recorded with the c axis parallel and perpendicular to Bo. It is noteworthy that not only the peak position, but also the peak width change considerably; the half-height width decreases from 230 ppm ( $c \perp \text{Bo}$ ) to 80 ppm ( $c \parallel \text{Bo}$ ).

We have tried to use this orientational dependency to estimate the parameters  $\eta_Q$  and QCC, assuming that the main cause of line broadening was the quadrupolar interaction. For the central transition of a nucleus with

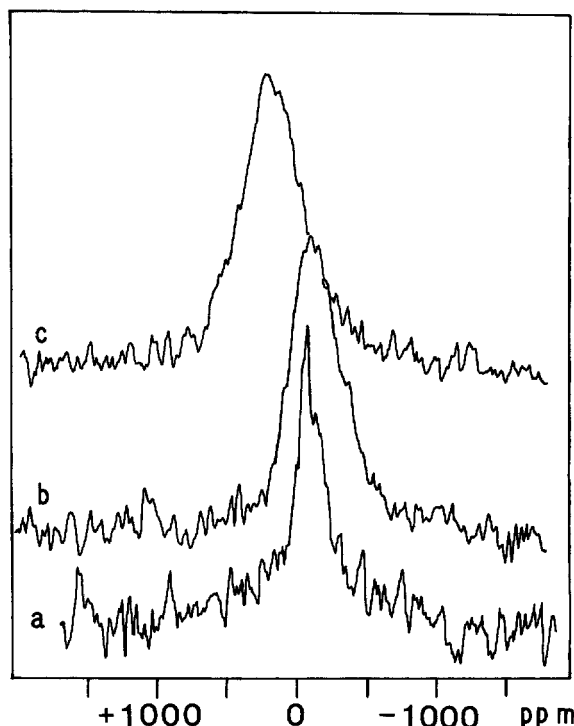


Figure 1.  $^{39}\text{K}$  solid state NMR spectra of (nominally) single crystals: a. vermiculite ( $c \parallel \text{Bo}$ ). b. muscovite ( $c \parallel \text{Bo}$ ). c. orthoclase.

$I = 3/2$ , the resonance position ( $\nu_{\text{CG}}$ ) for a static spectrum is given by (Taylor *et al.*, 1975):

$$\nu_{\text{CG}\perp} = \nu_{\text{CS}} + \frac{\nu_{\text{Q}}^2}{12\nu_{\text{L}}} \left\{ \frac{3}{2} \sin^2\theta(6 - 18 \cos^2\theta) + \eta_{\text{Q}} \cos 2\varphi \cdot \sin^2\theta(-6 - 18 \cos^2\theta) + \frac{\eta_{\text{Q}}}{16} [-12 + 36 \cos^2\theta + 18 \cos^2 2\varphi(\cos^2\theta - 1)] \right\}, \quad (1)$$

where  $\theta$  is the angle between Bo and the Z axis of the

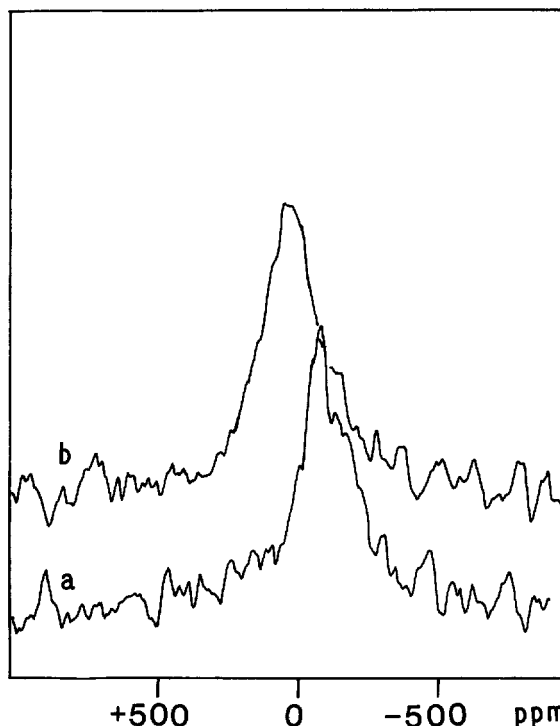


Figure 2.  $^{39}\text{K}$  solid state NMR spectra of a (nominally) single crystal of vermiculite as a function of crystal orientation: a.  $c \parallel \text{Bo}$ . b.  $c \perp \text{Bo}$ .

principal axes system (PAS), and  $\varphi$  one of the Euler angles defining the position of Bo in the PAS. Now the Z axis of the PAS most probably coincides with c; thus, for  $c \parallel \text{Bo}$  ( $\theta = 0$ ), we get:

$$\nu_{\text{CG}\parallel} = \nu_{\text{CS}} + \frac{\nu_{\text{Q}}^2 \eta_{\text{Q}}}{3\nu_{\text{L}}}, \quad (2)$$

while, for  $c \perp \text{Bo}$ , we have:

$$\nu_{\text{CG}\perp} = \nu_{\text{CS}} + \frac{\nu_{\text{Q}}^2}{12\nu_{\text{L}}} \{ 9 - 6\eta_{\text{Q}} \cos 2\varphi + \eta_{\text{Q}}^2 (3 \cos^2 2\varphi - 2) \}. \quad (3)$$

Here  $\varphi$  is unknown and varies between domains with

Table 1.  $^{39}\text{K}$  NMR peak positions ( $\delta_{\text{CG}}$ ) and peak widths ( $\nu_{1/2}$ ) of the silicate samples under study.

Sample	$\delta_{\text{CG}}$	$\nu_{1/2}$
Vermiculite, $c \parallel \text{Bo}$ (Figure 1a)	-60 ppm ( $\pm 10$ )	85 ppm
Vermiculite, $c \perp \text{Bo}$ (Figure 2b)	+40 ppm ( $\pm 10$ )	230 ppm
Muscovite, $c \parallel \text{Bo}$ (Figure 1b)	-125 ppm ( $\pm 25$ )	420 ppm
Orthoclase	+205 ppm ( $\pm 25$ )	230 ppm
Montmorillonite, 0 W-D cycles—dry (Figure 3a)	-40 ppm ( $\pm 25$ )	630 ppm
Montmorillonite, 11 W-D cycles—dry (Figure 3b)	-40 ppm ( $\pm 25$ )	340 ppm
Montmorillonite, 100 W-D cycles—dry (Figure 3c)	-60 ppm ( $\pm 25$ )	480 ppm
Montmorillonite, 100 W-D cycles— $\text{Sr}^{++}$ exchanged-dry (Figure 3d)	-60 ppm ( $\pm 50$ )	680 ppm <sup>2</sup>
Montmorillonite, 0 W-D cycles—wet (Figure 4a) <sup>1</sup>	-27 ppm ( $\pm 5$ )	50 ppm
Montmorillonite, 100 W-D cycles—wet (Figure 4c) <sup>1</sup>	-30 ppm ( $\pm 5$ )	45 ppm
Montmorillonite, 100 W-D cycles— $\text{Sr}^{++}$ exchanged-wet (Figure 4d)	-60 ppm ( $\pm 50$ )	400 ppm <sup>2</sup>

<sup>1</sup> Narrow component.

<sup>2</sup> Imprecise due to low signal/noise ratio.

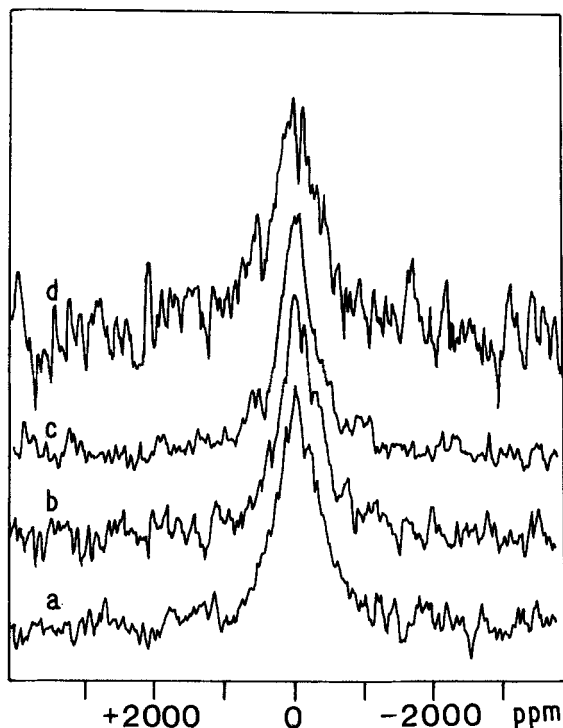


Figure 3.  $^{39}\text{K}$  solid state NMR powder spectra of "dry" (room humidity) Wyoming montmorillonite: a. 0 wetting and drying (W-D) cycles of the original montmorillonite. b. 11 W-D cycles. c. 100 W-D cycles. d. 100 W-D cycles + 4  $\text{Sr}^{++}$  exchanges.

different a and b axis orientations, but  $\cos(2\varphi)$  lies between  $-1$  and  $1$ . With the same assumption that the quadrupole interaction is dominant, the signal intensity for  $c \perp B_0$  should be significant in an interval of width  $\frac{\nu_Q^2 \eta_Q^2}{\nu_L} \approx 600$  ppm (Figure 2b).

In fact, the extreme observed values should correspond to:

$$\nu_{CG(1)} = \nu_{CS} + \frac{\nu_Q^2}{12\nu_L} \{9 - 6\eta_Q + \eta_Q^2\} \quad (4)$$

and to:

$$\nu_{CG(2)} = \nu_{CS} + \frac{\nu_Q^2}{12\nu_L} \{9 + 6\eta_Q + \eta_Q^2\}. \quad (5)$$

In principle, Equations (2), (4), and (5) should allow the determination of  $\nu_{CS}$ , as well as  $\nu_Q$  and  $\eta_Q$ , but the results of such a calculation are of doubtful practical value. An alternative approach is to assume a few trial values for  $\eta_Q$  (e.g., 0, 0.5, and 1) and to use them to calculate  $\nu_Q$ . The obtained estimates for  $\nu_Q$  always lie between 270 and 330 Hz; thus,  $\nu_Q$  for K in vermiculite can be safely estimated to be in the order of 300 kHz (QCC  $\approx$  0.6 MHz).

In Figures 3 and 4, we have plotted the  $^{39}\text{K}$  spectra of montmorillonites with different numbers of W-D

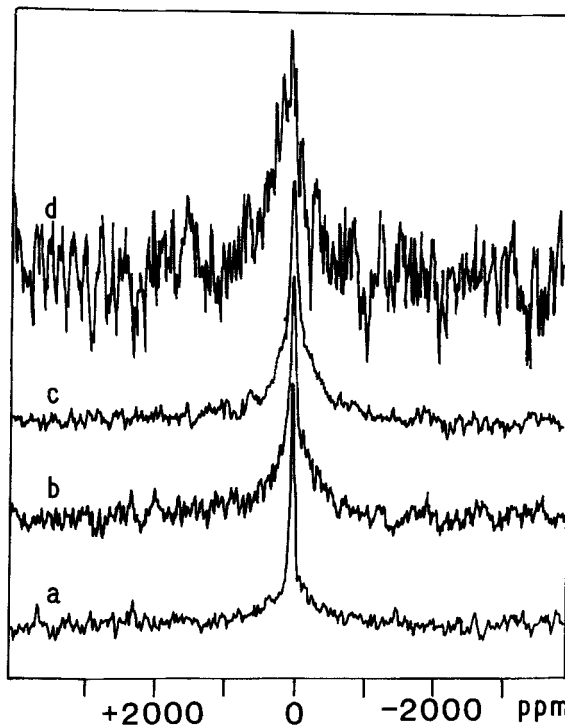


Figure 4.  $^{39}\text{K}$  solid state NMR powder spectra of same samples as in Figure 3, "wet" (paste with 40 wt. % clay). a. 0 W-D cycles. b. 11 W-D cycles. c. 100 W-D cycles. d. 100 W-D cycles + 4  $\text{Sr}^{++}$  exchanges.

cycles. The samples have been observed both in the "dry" state (in equilibrium with room humidity at  $20^\circ\text{C}$ ) and in the "wet" state: signal accumulation was started immediately after preparation of a paste containing 60 wt. %  $\text{H}_2\text{O}$  and 40 wt. % of the dry sample, and lasted for 3 to 6 hours. The spectra of dry and wet samples are represented in Figures 3 and 4, for the samples with 0, 11, and 100 W-D cycles as well as for the 100 W-D sample after  $\text{Sr}^{++}$  exchange. It should be kept in mind that wetting the samples to record their spectra corresponds to the first part of a further W-D cycle.

Whereas all the dry samples exhibit similar spectra, those of the unexchanged wet samples contain two components. Direct comparison shows that the broader component can be exactly superimposed on the signal of the dry sample. It is thus easy to subtract it, leaving only the narrow component (fwhh  $\approx$  50 ppm). Such a decomposition is shown in Figure 5. From a cursory examination, it is clear that the broader component becomes more prominent with increasing numbers of wetting and drying cycles.

In contrast with this behaviour, the  $\text{Sr}^{++}$ -exchanged 100 W-D cycles sample only shows a broad signal, whether in the dry or in the wet state. The overall signal intensity is inferior to the other spectra, as apparent from the lower signal/noise. Peak widths and positions are listed for all samples in Table 1.

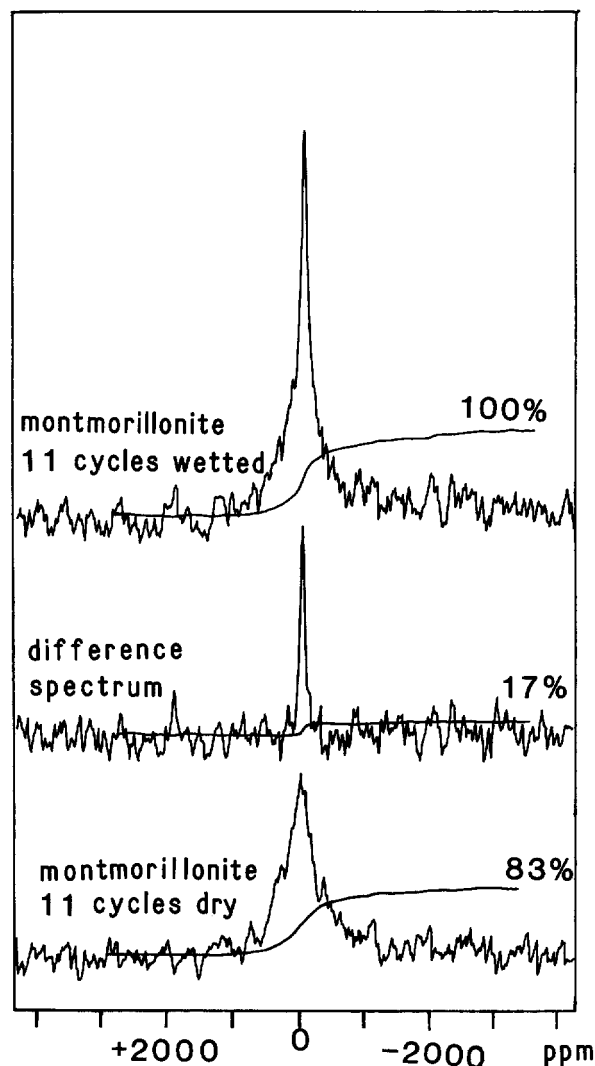


Figure 5. Example of a deconvolution of the  $^{39}\text{K}$  NMR signal into a narrow and a broad component (spectrum 4 d, montmorillonite with 11 W-D cycles, wet).

The XRD powder spectra of the three samples, recorded after the NMR investigations, are shown in Figures 6 and 7 in the region of the 001 peak. Figures 6a, 6b, and 6c show the XRD spectra of the "dry" samples (in equilibrium with room humidity) with 0, 10, and 100 W-D cycles, respectively. Figures 7a, 7b, and 7c are of the same samples in an aqueous slurry with 60 wt. %  $\text{H}_2\text{O}$ , after 4 to 5 hours equilibration.

Whereas the 100 W-D cycles sample has almost exclusively collapsed layers at room humidity ( $d_{001} = 10.1 \text{ \AA}$ ), the other two show larger  $d_{001}$  values that can be interpreted by an interstratification between the well-known 10.  $\text{\AA}$  and 12.4  $\text{\AA}$  forms. The latter is generally assumed to correspond to a crystalline form with the compensating cation coordinated to three water molecules (Mamy, 1970).

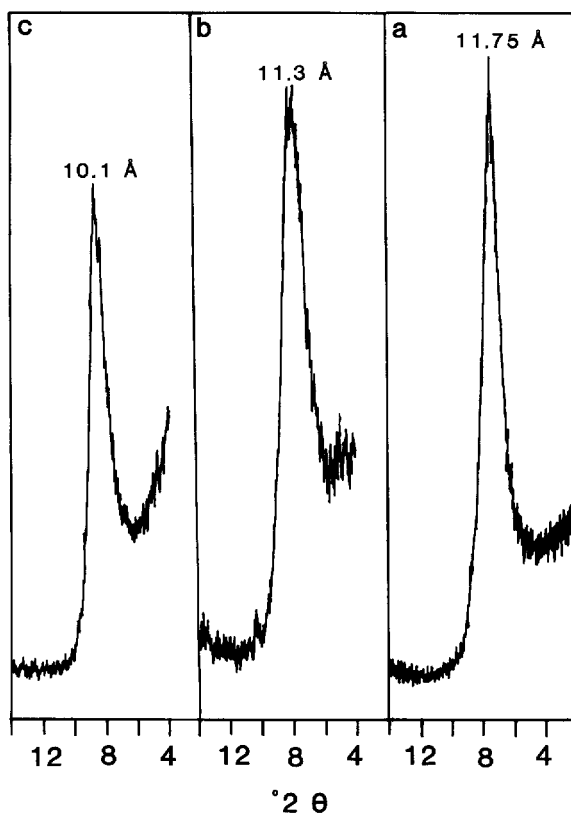


Figure 6. XRD powder spectra in the 001 line region of the montmorillonite samples of Figure 3, "dry" (room humidity). a. 0 W-D cycles. b. 11 W-D cycles. c. 100 W-D cycles.

Preparation of a water slurry causes a minor amount of swelling to 12.4  $\text{\AA}$  in the 100 W-D cycles sample, as evidenced by the displacement of the peak maximum from 10.1 to 10.5  $\text{\AA}$ . In contrast, the 0 W-D sample shows rapid swelling and the 001 line soon disappears. The 11 W-D cycles sample has an intermediate behaviour, with a loss of intensity and displacement to higher spacings of the 001 line.

The samples' surface areas are given in Table 2. The observed increase in surface area with the number of W-D cycles is coherent with observations by Gaultier (1976).

## DISCUSSION

The only purposes of this investigation were to determine, 1) if the  $^{39}\text{K}$  resonance could be observed at all in K silicates with the high magnetic fields currently available; 2) if the signal shape and/or position could be exploited to gain information at a molecular level similar to the possibilities offered by other nuclei such as  $^{23}\text{Na}$  and  $^{133}\text{Cs}$ .

The answer to the first question is clearly positive. We attempted to answer the second one by working on single crystals. This seemed to be the most efficient

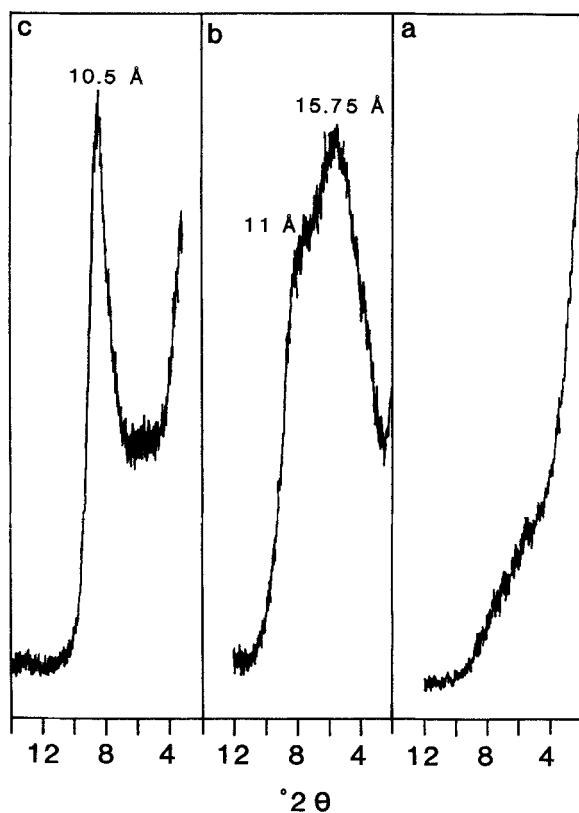


Figure 7. XRD powder spectra in the 001 line region of the montmorillonite samples of Figure 4, "wet" (paste with 40 wt. % clay). a. 0 W-D cycles (4 hour equilibration). b. 11 W-D cycles (20 hour equilibration). c. 100 W-D cycles (20 hour equilibration).

way, since the chemical shift anisotropy and quadrupolar interaction are orientation-dependent and complicate the interpretation of the lineshapes of powder spectra where all orientations are present.

In that respect, the large linewidths observed for the orthoclase and muscovite samples were somewhat disappointing. For muscovite, the most likely explanation is a homogeneous broadening by the interactions of the  $^{39}\text{K}$  spins with paramagnetic Fe centers, due to the relatively high Fe content.

A different explanation is required for the orthoclase

Table 2. Data from NMR, chemical exchange, and surface area analyses pertaining to the distribution of  $\text{K}^+$  between fixed and exchangeable positions, for montmorillonite with different numbers of W-D cycles (see text for explanation).

Number of W-D cycles	Contribution (in %) of narrow component to NMR signal	Contribution (in %) of broad component to NMR signal	% Exchangeable $\text{K}^+$ Gaultier, 1976	% Fixed $\text{K}^+$	Surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )
0	30	70	93	7	26
11	18.5	81.5	59.5	40.5	51
100	12.5	87.5	32	68	75

sample. We verified by polarised light microscopy that the sample indeed consisted of a single crystal domain; however, microprobe analysis revealed that the Si/Al ratio, and thus the degree of Si/Al substitution, varied by a factor larger than 2 among different regions of the sample. This must result in different local environments for K between those regions (inducing different efg values), and thus in heterogeneous broadening, a phenomenon already documented for the  $^{29}\text{Si}$  NMR of feldspars (Engelhardt and Michel, 1987).

In spite of these unfavorable conditions, the resonances of tecto- and phyllosilicates seem to be distinguishable by the position of their center of gravity ( $\delta_{\text{CG}}$ ). The resonance is shifted downfield (i.e., occurs at higher frequencies for fixed Bo) for the tectosilicate ( $\delta_{\text{CG}} = 205$  ppm) vs. the phyllosilicates ( $\delta_{\text{CG}} < 40$  ppm regardless of the orientation). The difference was expected in view of the different molecular environments of  $\text{K}^+$  between the two types of compounds. Further study is required: 1. to generalise the conclusion to other silicates; 2. to evaluate the relative contributions to  $\delta_{\text{CG}}$  of chemical shift and quadrupolar effects, because in general for nuclei with  $I > 1/2$ ;  $\delta_{\text{CG}} = \delta_{\text{CS}} + \delta_{\text{Q}}$ . Such a study is sometimes simplified by the presence of recognisable powder lineshapes, with singularities that allow ready evaluation of the quadrupole coupling constant, but singularities are not observed for our powder samples of montmorillonite. Our rough estimate of  $\nu_{\text{Q}}$  for Llano vermiculite would yield a rather low contribution of  $\delta_{\text{Q}} \approx -15$  ppm.

The spectra of K-vermiculite are better defined than those of muscovite and orthoclase. Indeed, Llano vermiculite contains only a small amount of Fe (<0.3% by chemical analysis), which should minimise broadening by interactions with paramagnetic centers. The signal is narrower by a factor of 3 when  $c \parallel \text{Bo}$  than when  $c \perp \text{Bo}$ , in keeping with the idea that our samples consisted of several domains among which only c had a constant orientation, whereas a and b could vary.

Our powder studies were carried out on montmorillonites submitted to wetting and drying cycles. There are practical reasons to be interested in such samples. It has long been known that wetting and drying cycles result in a steady decrease of the quantity of "exchangeable"  $\text{K}^+$ , the K that can be displaced by other cations. The decrease is accompanied by a partial three-dimensional ordering of the montmorillonite, whereby some of the layers lose the ability to swell under hydration. This phenomenon is thought to be related to the capability of montmorillonite-type minerals to fix irreversibly some of the K that has been introduced into the soil solution, thus making it unavailable for plants (wetting and drying cycles constitute an attempt to mimic in the laboratory some real climatic changes to which topsoils are subjected).

In this context, the existence of two well-defined signals in the  $^{39}\text{K}$  spectrum of wet montmorillonites is

particularly interesting. The broad component is similar to the only component observed in air-dried samples. We know from the XRD spectra that the dry samples consist of interstratifications of forms with layer spacings of 10 Å and 12.4 Å; in both forms the compensating cation is weakly hydrated (probably coordinated to 0 and 3 water molecules, respectively) and has low mobility. Apparently, in our samples,  $^{39}\text{K}$  NMR cannot distinguish between those two forms: both give rise to a fairly large, featureless signal (again, it is conceivable that separate components could be resolved in montmorillonite with lower Fe contents, if the paramagnetic interaction is chiefly responsible for the broadening). Thus, we attribute the broad component to  $\text{K}^+$  in collapsed interlayers and to  $\text{K}^+$  in interlayers swollen at 12.4 Å.

The narrow, liquid-like signal, on the other hand, must correspond to  $\text{K}^+$  in rapid motion, giving rise to motional averaging of the various dipole-dipole and quadrupole-dipole interactions and chemical shift anisotropy. This may have two different origins:  $\text{K}^+$  in completely swollen interlayers ( $>14$  Å) and  $\text{K}^+$  on the external surface of the clay. Under our hydration conditions (slurry with 60 wt. %  $\text{H}_2\text{O}$ ), both are likely coordinated to 6 molecules of  $\text{H}_2\text{O}$ , and thus should resonate at approximately the same frequency. Chemical exchange between these two forms must contribute to the observation of only one resonance. This interpretation is in keeping with similar results recently published for Cd-hectorite (Tinet *et al.*, 1991) and Na-, Cd-, and Cs-vermiculite (Laperche *et al.*, 1990). The results show that the NMR signal of compensating cations in clays is highly dependent on their hydration state.

Now, a comparison with the more classical data from XRD and chemical exchange starts to make sense. In Table 2, we compare the amounts of exchangeable and fixed  $\text{K}^+$  to the relative contribution of the narrow and the broad components to the NMR signal intensity. Such a straight integration of the NMR signals may seem rather naive, since for quadrupolar nuclei signal intensity is not necessarily directly proportional to site population. We tried to obviate this difficulty by the use of selective pulses, whereby simple integration can be used as an approximate working procedure for the sake of comparison. A more sophisticated approach might involve the application of correcting parameters to the integrated intensities given in Table 2, but the main part of the following discussion need not be fundamentally modified.

We can consider that K is distributed between 4 different "pools" or compartments. Let us call: K1, the quantity of K in the interlayers that remain closed ( $d_{001} = 10$  Å) after rehydration; K2, the K in the partly swollen interlayers ( $d_{001} = 12.4$  Å); K3, the K in the completely swollen interlayers ( $d_{001} > 14$  Å); and K4, the K on the external surface.

Table 3. Tentative distribution of  $\text{K}^+$  between different pools, for montmorillonite with different numbers of W-D cycles, in a slurry with 60 wt. % water. K1: amount of K in collapsed layers ( $d_{001} = 10$  Å). K2: amount of K in partly opened layers ( $d_{001} = 12.4$  Å). K3: amount of K in expanded layers ( $d_{001} > 14$  Å). K4: amount of K on the external surface.

Number of W-D cycles	% K1	% K2	% K3	% K4
0	7	63	25.7	4.3
11	40.5	41	10	8.5
100	68	19.5	0	12.5

NMR data can then give access to (K1 + K2) and (K3 + K4). Chemical analysis by ion exchange discriminates fixed potassium (K1) from exchangeable K, presumably K2 + K3 + K4. XRD measurements can provide information on the K1/K2 ratio if layers with  $d_{001} = 10$  Å and  $d_{001} = 12.4$  Å are interstratified. Surface areas are correlated with K4.

Our interpretation explains why, in Table 2, the relative amounts of exchangeable K are correlated with, but always higher than, the contribution of the narrow signal. Indeed, exchangeable K (K2 + K3 + K4) should be higher than mobile K (K3 + K4)—as detected by NMR. Furthermore, it agrees with the absence of a narrow NMR signal for the  $\text{Sr}^{++}$  exchanged sample even after hydration: the exchange should have removed K2, K3, and K4, leaving only K1 to be observed. Here, we have a case where a simple relationship can be established between the effect of a chemical treatment (widely used as an alternative to  $\text{NH}_4^+$  extraction to assess the percentage of fixed K) and the results of a spectroscopic method, which reveal the *in situ* state of the investigated element.

We may try to follow some of the consequences of our interpretation. First, the 100 W-D sample shows no evidence of swelling to  $>14$  Å ( $\text{K3} \approx 0$ ), so that the 12.5% of K contributing to the narrow NMR signal should correspond to K on the outer surface (K4). Assuming that K4 is proportional to the surface area then allows us to estimate its value for the other samples. Subtracting this estimate from (K3 + K4), obtained from the percentage of intensity in the narrow component of the NMR spectrum, yields K3. The difference between exchangeable K and K in the narrow NMR signal gives K2, and K1 simply corresponds to non-exchangeable K.

A tentative distribution of K between these different "pools" in our three samples is given in Table 3. In principle, for samples showing a well-defined 001 line in their XRD spectrum, the position of this line should provide an independent check on the relative amounts of K1 and K2. Our 100 W-D cycles sample is the only one to offer an interpretable spectrum, with a  $d_{001}$  of 10.5 Å. A treatment similar to the one of Hendricks and Teller (1942) shows this to correspond to K1/K2 = 3.54, as compared to our estimate of  $68/19.5 = 3.49$ .

We are aware that several of our assumptions remain open to discussion, but the case of K-montmorillonites illustrates the general principle of positive interplay between spectroscopic and more conventional methods. NMR is seen to provide an independent source of information on the distribution of K among the different forms present in hydrated clays. When used in conjunction with chemical exchange and surface area measurements, quantitative estimates of the various forms can be made. As compared to XRD, the main weakness of NMR seems to lie in the difficulty of distinguishing between K in collapsed and partly swollen interlayers (K1 and K2); however, experience accumulated on other clay systems raises the hope of overcoming this difficulty by the use of low-Fe smectites and of the Magic Angle Spinning (MAS) technique. Since the hydration state of K<sup>+</sup> is different in the two states, the expectation would be to observe distinct NMR signals under those conditions (see Laperche *et al.*, 1991). On the other hand, NMR is obviously superior for observing those forms that do not give rise to good long-range order, such as K<sup>+</sup> in completely swollen interlayers and on the external surface.

A better understanding of the evolution of the K environment at the molecular level will no doubt be helpful in elucidating the mechanisms of K fixation during successive cycles of wetting and drying. In addition, the ability to discriminate between K<sup>+</sup> in swelling and non-swelling interlayers would also be useful for geologists investigating smectite/illite interstratified materials.

More generally, it must be noted that NMR spectroscopy can be applied to natural samples without any prior chemical or physical modification, in contrast with other techniques (for example, CEC determinations necessarily imply a chemical modification of the samples), thus coming close to the aim of an *in situ* characterisation of the physico-chemical state of the element under study.

## CONCLUSIONS

In spite of the preliminary nature of the results reported here, we are convinced that solid-state <sup>39</sup>K NMR holds promise as a tool for characterisation of K containing compounds for the mineralogist working on well-chosen reference minerals. High Fe contents clearly constitute a problem. For the soil scientist, information can be derived on the state and mobility of K in a sample without perturbing pretreatment. Obviously, solid-state NMR will never be a routine technique for the agronomist. It may serve to assess the validity of more conventional techniques, as shown by the example of Sr<sup>++</sup> exchange. For powder samples, fast spinning at the magic angle (or at other angles, in the VASS technique) may provide much additional information.

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