

A ^{19}F NUCLEAR MAGNETIC RESONANCE STUDY OF NATURAL CLAYS

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Abstract—A series of natural clays, including 1:1 layer silicates (serpentines, kaolin minerals), smectites, vermiculite, micas, talc, pyrophyllite, sepiolite, and palygorskite, were studied by ^{19}F magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The ^{19}F chemical shift in these layer silicates is characteristic of the structure, in particular, to the local octahedral cation occupancy. Fluoride ions bonded to three Mg octahedral cations have a chemical shift of about -177 ppm and those bonded to two Al cations and a vacancy have a chemical shift of about -134 parts per million (ppm). The shift at -182.8 ppm in hectorite is apparently associated with fluoride bonded to two Al cations and a Li cation. Surprisingly, the difference in chemical shift of the interlayer and inner fluoride in 1:1 layer silicates is insufficient to distinguish these sites. Based on trends in chemical shift, it appears that fluoride substitution for inner hydroxyls in clays with octahedral substitution is not random. Fluoride is apparently preferentially associated with Mg rather than Al in the octahedral sheet as no resonance due to a fluoride bonded to two Al cations and a vacancy is observed in clays such as SAz-1.

Key Words— ^{27}Al , Aluminum, Clay minerals, ^{19}F , Fluorine, MAS, NMR, Solid.

INTRODUCTION

High-resolution magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy has proven to be a powerful tool for obtaining structural information on a variety of mineral systems (Stebbins 1992). The vast majority of this work has centered on ^{27}Al and ^{29}Si NMR structural studies (Engelhardt and Michel 1989). In spite of high NMR sensitivity for fluorine and the fact that many minerals contain F^- substituted for OH^- , there are only a few reports of the use of ^{19}F NMR to obtain structural information in clay minerals. Sanz and Stone (1979) and Santaren *et al* (1990) used relatively low-resolution solid-state NMR techniques, primarily second-moment measurements, to obtain information about the location of F^- in the structure of micas and sepiolite. Recently Huve *et al* (1992a, 1992b) demonstrated the utility of ^{19}F NMR in structural determinations in a variety of natural and synthetic 2:1 layer silicates.

A large gyromagnetic ratio and 100% natural abundance make ^{19}F one of the most sensitive nuclei for study by NMR (Martin *et al* 1980), and although it has been used extensively as a probe nucleus in liquids, it has been used little in solid-state NMR (Harris and Jackson 1991). There are several reasons for this. The large gyromagnetic ratio results in relatively strong dipole-dipole couplings which implies that heavily fluorinated materials will have intrinsically broad lines. Fluorinated systems with large concentrations of protons must be proton decoupled, and the proximity of the ^{19}F and ^1H NMR resonance frequencies makes this proton decoupling very difficult. Additionally, fluorine generally has large chemical shift anisotropies (CSA) that produce severe spinning sidebands under MAS

conditions. All of these factors combine to make ^{19}F high-resolution NMR in solids generally problematic. In spite of these difficulties, there are several publications in the NMR literature that demonstrate the utility and technical requirements for obtaining accurate ^{19}F spectra in solids (Clark *et al* 1986; Kreinbrink *et al* 1990; Harris and Jackson 1991). Clays generally contain only a few percent of fluorine which makes it a magnetically dilute nucleus. Although there are water molecules and hydroxyls in most clays, the density of protons is not so high as to require proton decoupling to obtain high-resolution NMR spectra. Therefore, only the large ^{19}F CSA is an intrinsic impediment to obtaining accurate MAS-NMR spectra of clays.

It is well known that F^- is structurally similar to OH^- in size and charge. Thus, structural hydroxyls in minerals can be replaced by F^- either during the genesis (Thomas *et al* 1977) or subsequent alteration (Daniel and Hood 1975) of the mineral. The natural fluorine content of clays ranges from parts per million to a few percent. Levels of a few tens of ppm are sufficient for ^{19}F MAS-NMR spectroscopy because of the high ^{19}F sensitivity. However, paramagnetic transition metals, particularly iron, pose a significant problem to the use of NMR as a tool to study natural minerals. Although no one has directly addressed the NMR spectral distortions in minerals, an examination of most NMR studies of clays in the literature reveals the use of samples with unusually low iron content because the substitution of paramagnetic iron for aluminum in the octahedral sheets of clay minerals perturbs virtually all NMR experiments performed on clays with high iron content. For example, we were unable to find a sample of serpentine with sufficiently low Fe content to give a useful NMR signal in this study.

This work was originally undertaken to investigate the potential of ^{19}F NMR to study inner vs. interlayer (inner-surface) hydroxyls and their substitution by F^- in kaolinites. As will be seen below, the ^{19}F chemical shift between these sites is apparently insufficient to allow us to make that distinction. However, we discovered that ^{19}F MAS-NMR is a useful technique for investigating the composition of the octahedral sheets in both 2:1 and 1:1 layer silicates and it provides some information on the nature of F^- for OH^- substitution.

EXPERIMENTAL

Materials

The clay minerals used in this study are representative of 1:1, 2:1, and chain-structure layer silicates with varying layer charge. The sources and essential properties of the samples studied are given in Table 1. A lithium-substituted montmorillonite was prepared from Cheto, Arizona, montmorillonite using the following method. A $<2\ \mu\text{m}$ homo-ionic Na-SAz-1 was exchanged with Li^+ . The damp, homo-ionic Li-SAz-1 was placed in a platinum crucible and gradually heated to 300°C . It was held at that temperature for about 40 hours and then gradually brought to room temperature. In principle, this treatment causes the Li ions to migrate through the hexagonal cavities and into unoccupied sites in the octahedral sheet (Hofmann and Klemm 1950; Greene-Kelly 1955; Brindley and Ertem 1971; Calvet and Prost 1971).

NMR spectroscopy

NMR spectra were obtained at room temperature (approximately 27°C) on a Varian Unity-400 spectrometer at nominal frequencies of 376 MHz for ^{19}F and 104 MHz for ^{27}Al . A Varian MAS probe with 7-mm outside-diameter, zirconia rotors and a zirconia stator was used. Although this MAS probe is not entirely fluorine free, we removed as many of the fluoropolymer components as possible to reduce the ^{19}F background. The typical $\pi/2$ pulse width was $6\ \mu\text{s}$ and a 1 s recycle delay was used. The spinning rate was around 6 kHz for ^{19}F spectra but at times, the spinning rate was varied to clearly distinguish spinning sidebands from centerbands. Chemical shifts in fluorine spectra were referenced to external trichloro-fluoromethane. The number of scans varied from 32 for the fluoro-phlogopite to over 10^3 for samples with low F content, and for the serpentine samples, which gave no discernible signal even though they have high fluorine content. Aluminum spectra were acquired using a different 7 mm Varian MAS probe also using zirconia rotors and stator. The rotor speed was 5 to 8 kHz depending on the sample, and a single-pulse sequence was used with a $2\text{-}\mu\text{s}$ pulse, which corresponds to a flip angle of 15° . Chemical shifts were externally referenced to an acidified 0.1 M aqueous solution of AlCl_3 . Ap-

proximately 500 scans were taken for adequate signal to noise in the ^{27}Al spectra. We estimate the error in chemical shift measurement due to the sample substitution technique to be about 0.2 ppm for narrow lines. For some of the very broad lines obtained in this work, errors in chemical shift measurement are associated with determining the maximum in the peak and may be as large as 1–2 ppm in the worst cases.

RESULTS AND DISCUSSION

The ^{19}F shifts in the clays studied fall into three general ranges, near $-134\ \text{ppm}$, $-153\ \text{ppm}$, and $-178\ \text{ppm}$. Table 1 contains the chemical shifts measured for all samples in this study. As will be seen in detail below, each of these ranges of chemical shifts can be correlated with known structural features of the clays.

For clarity, we will present a physical model for the structure and substitution of F^- in clays. This will be followed by discussions of the data for 1:1 clays and 2:1 clays, followed by a discussion of the Li-substituted montmorillonite, and finally a short discussion of the spectral characteristics of ^{19}F NMR as applied to clay minerals.

First we consider the probable location of fluorine in the clay structure. Fluorine is identical in charge and similar in size to the hydroxyl group, OH^- , and it can replace hydroxyls in both 1:1 and 2:1 clays. The inner hydroxyl sites in both 1:1 and 2:1 clays are structurally similar in that they are located at the intersection of three octahedra. Fluoride ion on a hydroxyl site thus has three octahedral sites as nearest neighbors. In this work, the dominant octahedral cations considered are Li, Al, Mg, and \square , representing a vacant site in a dioctahedral structure. In the discussions below, we relate the ^{19}F chemical shifts to the occupancy of the three nearest-neighbor octahedral sites.

1:1 layer silicates

The 1:1 layer silicates studied here are kaolin minerals and contain two distinct types of hydroxyl sites in a ratio of 1:3. Both the inner and interlayer (inner-surface) hydroxyls are directly bonded to two cations of the octahedral sheet but the interlayer hydroxyls are associated with two octahedral cations and have a "vacancy" in the basal plane. Figure 1 contains a representative ^{19}F spectrum of kaolinite. The ^{19}F MAS-NMR spectra have several spinning side bands, but just one NMR line in each spectrum at around $-134\ \text{ppm}$. This single resonance was surprising because we expected to find separate resonances for the inner and interlayer fluorine sites. Additionally, we obtained spectra of dickite and halloysite. The ^{19}F spectra of these minerals are essentially the same as that of kaolinite even though there are differences in both the mode of stacking and the stacking order of these three 1:1 dioctahedral clays.

Among the clay minerals, the 1:1 group contains the greatest number of hydroxyls per unit cell for possible

Table 1. Origin and properties of clays studied.

Mineral name	Origin	Structural formula	^{19}F content (ppm)	Chemical shift (ppm)
1:1 Dioctahedral minerals				
Kaolinites	Cornwall, UK	$\text{Al}_2\text{Si}_2\text{O}_7(\text{OH})_2$	1331	-135.4
	Mesa Alta, New Mexico		543	-135.7
Dickites	St. George	$\text{Al}_2\text{Si}_2\text{O}_7(\text{OH})_2$	2084	-134.8
	San Juanito, Mexico		3428	-134.7
Halloysite	Eureka, California	$\text{Al}_2\text{Si}_2\text{O}_7(\text{OH})_2$	4846	-133.7
1:1 Trioctahedral minerals				
Serpentine	CMS sample ¹	$\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	High	No signal
2:1 Dioctahedral minerals				
Pyrophyllite	CMS sample ¹	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	NA	-133.7
Muscovite	CMS sample ¹	$\text{K}_2\text{Al}_2(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH})_4$	NA	-138.0
	SCu-1, Otay, California	$\text{M}^{+1.25}(\text{Al}_{2.69}\text{Mg}_{1.2}\text{Fe}^{+0.11})(\text{Si}_{7.95}\text{Al}_{0.05})\text{O}_{20}(\text{OH})_4$	1270	-154.6
	SAZ-1, Apache County, Arizona	$\text{M}^{+1.01}(\text{Al}_{2.95}\text{Mg}_{1.2}\text{Fe}_{0.29})(\text{Si}_{7.79}\text{Al}_{0.21})\text{O}_{20}(\text{OH})_4$	3004	-153.2
	Polkville, Mississippi	$\text{M}^{+1.23}(\text{Al}_{2.78}\text{Mg}_{1.16}\text{Fe}_{0.20})(\text{Si}_{7.88}\text{Al}_{0.12})\text{O}_{20}(\text{OH})_4$	6393	-152.9
2:1 Trioctahedral minerals				
Hectorite	Hector, California	$\text{M}^{+1.04}(\text{Mg}_{4.7}\text{Li}_{1.13}\text{Fe}_{0.06})\text{Si}_8\text{O}_{20}(\text{OH})_4$	NA	-176.2, -182.8
Talc	Llano, Texas	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	NA	-177.4
Vermiculite	synthetic	$\text{M}^{+1.97}(\text{Mg}_{5.66}\text{Al}_{0.3}\text{Fe}_{0.02})\text{Si}_{5.72}\text{Al}_{2.28}(\text{OH})_4$	NA	-175.8
Fluoro-phlogopite	CMS sample ¹	$\text{K}_2\text{Mg}_6(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH},\text{F})_4$	NA	-178.0
Sepiolite	CMS sample ¹		NA	-175.3
Palygorskite	CMS sample ¹		NA	-175.3

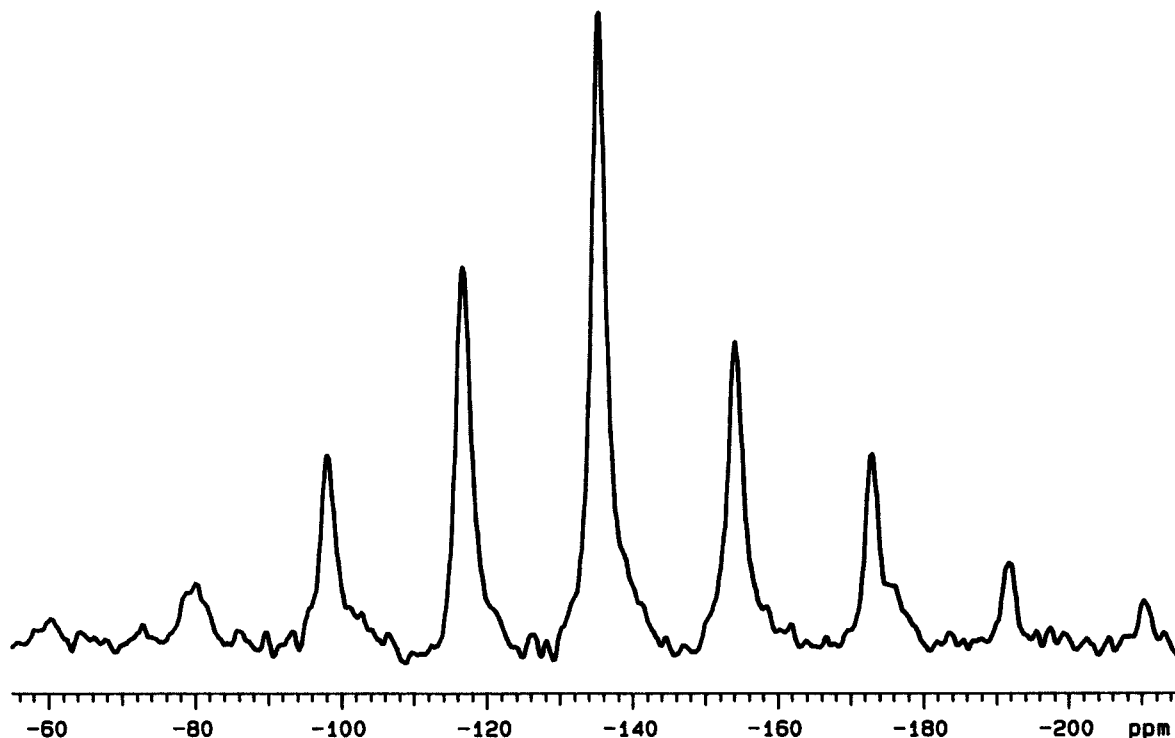


Figure 1. The ^{19}F MAS NMR spectrum of kaolinite from Mesa Alta, New Mexico. Sample spinning speed was approximately 7 kHz. The large central peak is the "isotropic" chemical shift and all other peaks are spinning sidebands as discussed in the text.

fluorine substitution. However, the fluorine contents are relatively low in the samples examined. The existence of fluorine on only the inner sites may explain the existence of only one ^{19}F NMR resonance for kaolinite as well as the lack of significant differences in the ^{19}F chemical shifts for the different layer stacking of kaolinite, dickite, and halloysite since we would expect layer-stacking effects to be most significant at the interlayer sites.

In order to understand the single observed shift, we studied a synthetically fluorinated kaolinite sample given to us by P. Costanzo *et al* (1980). According to studies by Weiss *et al* (1956), the exchange of fluoride for hydroxyls in kaolinite is reversible and appears to be limited to hydroxyl ions at the edges of the silicate sheets and on the basal surfaces, most of the inner hydroxyls are not exchangeable. The synthetically fluorinated sample has essentially the same ^{19}F chemical shift as the natural kaolinite (-136 ppm) although the intensity of the NMR signal is much stronger, indicating that there is extensive fluorination of the sample. This is strong evidence that the inner and interlayer fluoride ions have similar chemical shifts.

We made several attempts to obtain ^{19}F MAS-NMR spectra for several minerals of the serpentine group, to no avail. This lack of success is in spite of the fact that

most serpentines have relatively high fluorine contents. We tried many different samples from different sources. We attempted to remove paramagnetic cations by grinding and treatment with mild acid, but were unable to obtain a useful MAS spectrum. We believe that this failure is due to the relatively high concentration of paramagnetic Fe in most samples and Cu or Ni in some of the samples. These paramagnetic metals are part of the octahedral sheet and cannot be readily removed without destroying the mineral.

2:1 layer silicates

The 2:1 layer silicates examined are chemically more complicated than the 1:1 layer silicates because they have a variety of layer charges, different substitutions in both the octahedral and tetrahedral sheets, and in a few cases, significantly different structures. These differences are reflected in the ^{19}F NMR data. We obtain chemical shifts ranging from about -133 to -183 ppm, depending on the clay structure.

Talc is trioctahedral with a layer charge of zero which implies that all fluorine in the sample must be at a $\{\text{Mg-Mg-Mg}\}$ site. The ^{19}F spectrum has a single peak at -177.4 ppm. Thus, a chemical shift of about -177 ppm is assigned to F^- atoms bonded to $\{\text{Mg-Mg-Mg}\}$. Huve *et al* (1992a) report a similar shift for this type

of site in their recent study of synthetic fluorinated 2:1 trioctahedral layer silicates.

Pyrophyllite is a dioctahedral mineral analogous to talc in having no layer charge and consequently all F⁻ atoms are in sites with {Al-Al-□} nearest neighbors. The NMR spectrum has a single peak at -133.7 ppm. We assign ¹⁹F shifts in the range of -133 ppm to fluorine substitution in sites with two aluminums and a vacancy as nearest neighbors. We also investigated the ²⁷Al NMR spectrum of this sample and obtained a single resonance with a chemical shift of 3.7 ppm. Since ²⁷Al chemical shifts are known to be very sensitive to the coordination of Al (Woessner 1989) and ²⁷Al chemical shifts near zero ppm are assigned to octahedral coordination of Al, we are confident that all Al in the pyrophyllite sample studied is in the octahedral sheet.

In the hectorite sample studied, the fluorine content is particularly high (5.18 wt%). This means that approximately 50% of the hydroxyls in the structure are substituted by fluoride (Thomas *et al* 1977). This is the only sample studied where the ¹⁹F MAS-NMR spectrum consisted of two lines. The chemical shifts are -176.2 and -182.8 ppm. In analogy to the talc sample, we associate the shift at -176.2 ppm with trioctahedral sites containing only magnesium and the line at -182.8 ppm, is attributed to {Mg-Mg-Li} octahedral sites. Again this is in agreement with results reported by Huve *et al* (1992a).

The ²⁷Al MAS-NMR spectrum for SAz-1 shows only one peak at 3.6 ppm. This indicates that for SAz-1 most of the aluminum atoms are indeed in the octahedral sheet. This agrees with the charge distribution known for this sample. Almost 88% of the charge is localized in the octahedral sheet (Jaynes and Bigham 1987) and the structural formula is (M⁺_{1.01}((Al_{2.95}Mg_{1.20}Fe³⁺_{0.25}Fe²⁺_{0.04})(Si_{7.79}Al_{0.21}))O₂₀(OH)₄) (van Olphen and Fripiat 1979). The ¹⁹F NMR spectra for SAz-1 and other montmorillonite clays have only one peak at about -152 ppm. In fact, the octahedral sheet for montmorillonites is primarily {Al-Al-□} sites. We expected the majority of the fluorine to have a resonance at about -134 ppm in analogy to pyrophyllite and a minor peak at some other resonance position for the {Al-Mg-□} sites. We attribute the single resonance at about -152 ppm to {Al-Mg-□} sites, in agreement with the assignment made by Huve *et al* (1992a). This observation and assignment has strong implications and implies that fluoride is not statistically distributed in the structure of montmorillonites but is ordered into {Al-Mg-□} sites preferentially over {Al-Al-□} sites. We address this question experimentally through Li substitution discussed below.

We studied three other readily available montmorillonite samples with differing Al₂O₃/MgO ratios with the goal of looking for a resonance near -134 ppm, associated with the expected {Al-Al-□} sites. Table 2

Table 2. Chemical shifts and Al₂O₃/MgO ratios of montmorillonites.

Origin	Al ₂ O ₃ /MgO	¹⁹ F chemical shifts (ppm)
SCa-1, Otay, Ca	2.5	-154.6
SAz-1, Cheto, Az	2.7	-153.2
#21 Polkville, Miss	4.0	-152.9

contains the ¹⁹F chemical shifts for the three montmorillonites as a function of the Al₂O₃/MgO ratio.

None of these samples had a significant peak near -134 ppm which might be associated with {Al-Al-□} fluorine sites. Although there is a slight trend in the shift data, increasingly upfield shift with an increase in the Al₂O₃/MgO ratio, the magnitude is within experimental errors. By analogy to ²⁹Si NMR results, it is reasonable to expect chemical shifts associated with Mg substitution but a large number of very similar samples must be studied to establish a pattern when the change in the chemical shifts are so small.

Proceeding to samples with a greater layer charge, we examined one vermiculite sample from Llano, Texas, obtained from the Clay Mineral Society, Source Clay Repository. This sample has a single ¹⁹F resonance with a chemical shift of -175.8 ppm. As mentioned above, this chemical shift is associated with the {Mg-Mg-Mg} site in trioctahedral samples.

The muscovite sample examined had a single ¹⁹F resonance at -138 ppm. Although slightly different from the pyrophyllite shift, we associate this resonance with a dioctahedral clay with {Al-Al-□} sites.

The synthetic fluoro-phlogopite sample has a ¹⁹F MAS-NMR spectrum with only a single very strong peak at -178.0 ppm. This ¹⁹F chemical shift is characteristic of trioctahedral {Mg-Mg-Mg} sites which is confirmed by the ²⁷Al MAS-NMR spectrum with a single peak at 68 ppm, consistent with aluminum in tetrahedral sites.

The last two samples are slightly different in structure from normal clays. Sepiolite is a hydrated magnesium silicate. Structurally, it is made up of blocks and channels (Grim 1968). Each structural unit consists of two tetrahedral silicate sheets and a central trioctahedral sheet. This unit is equivalent to a small section of a 2:1 clay. The ¹⁹F MAS spectrum shows only one peak at -175.3 ppm which we assign to F⁻ atoms in a trioctahedral {Mg-Mg-Mg} site. This assignment is entirely consistent with the known structure.

The palygorskite sample examined is from the Georgia-Florida area and has a high fluoride content. The ¹⁹F MAS spectrum of this mineral has only one resonance at -175.3 ppm. This chemical shift is, again, assigned to F⁻ atoms with three Mg atom neighbors. The ²⁷Al spectrum has a single peak at 3.7 ppm, suggesting that all aluminum cations are in the octahedral

sheets. It is interesting that the ^{19}F spectrum is characteristic of {Mg-Mg-Mg} sites, whereas the ^{27}Al spectrum indicates that there are significant octahedral aluminum cations in the sample. If one were to assume a completely random substitution of fluorine in the structure, there would be a peak associated with {Mg-Mg-Al} sites as well. The implication is thus that fluorine is associated with sites with Mg rather than Al as nearest neighbors. This agrees with the montmorillonite data presented above in which fluorine appears to be preferentially associated with Mg over Al in the octahedral sheet.

Substituted 2:1 layer silicates: Li-SAz-1

In order to investigate the apparent association of fluorine with Mg in the octahedral sheet of smectites, we attempted two different chemical modifications of SAz-1. The first modification was an attempt to synthetically exchange fluorine for the inner hydroxyls. We attempted various hydrothermal treatments with aqueous fluoride solutions. These included different pH's, temperatures, pressures, and even using DMSO as a solvent modifier. Our ^{19}F NMR spectroscopy never indicated a measurable uptake of fluorine. The pressures and temperatures used were relatively modest so our failure to exchange fluorine for the inner hydroxyls does not necessarily mean that it cannot be accomplished using more strenuous conditions. The second modification was to diffuse Li into octahedral vacancies. This experiment is based on considerable literature indicating that Li-substituted montmorillonites will irreversibly take up lithium upon heating, reducing the overall layer charge (Hofmann and Klemen 1950; Greene-Kelly 1955; Brindley and Ertem 1971; Calvet and Prost 1971). This is the standard Greene-Kelly method of evaluating the site of layer charge in clays. There are several assumptions in this particular experiment. First, we note that SAz-1 is primarily dioctahedral and that the majority of the layer charge arises from Mg substitution in the octahedral sheet. This is substantiated by the structural formula and the fact that the ^{27}Al NMR spectrum only contains a peak for aluminum in octahedral sites. This means that there are a number of {Al-Mg-□} sites. These sites are regions of negative charge and we assume that Li^+ is electrostatically attracted to such regions. Upon heating, we assume that the Li^+ first enters hexagonal cavities near such sites. On heating to higher temperatures, the Li^+ ion is small enough to migrate through the hexagon of oxygens and into the octahedral sheet. Thus we expect to form {Al-Mg-Li} sites where there had formerly been {Al-Mg-□} sites. Further, the implication is that {Al-Al-□} sites are not converted to {Al-Al-Li} sites because all charge reduction is accomplished with Mg as a nearest neighbor in the octahedral sheet. The ^{19}F NMR spectrum of the exchanged SAz-1 sample shifted

from -152 ppm (natural) to -158 ppm (exchanged). This shift of about -6 ppm is consistent with electronegativity arguments for shifts in such samples. The low electronegativity of Li should cause the ^{19}F signal to be more shielded, although quantitative comparisons with a vacant site are difficult. This shift is also consistent with the observed spectrum of hectorite in which substitution of Li for Mg results in a shift of about -6 ppm. Although we do not expect the shift in going from {Mg-Mg-Mg} to {Mg-Mg-Li} in hectorite to be identical to the shift in going from {Al-Mg-□} to {Al-Mg-Li} the sign and magnitude of the shift are entirely consistent.

Additionally, the fact that there is only a single ^{19}F resonance observed in both the natural and Li-exchanged SAz-1 sample is further evidence for the association of fluorine with {Al-Mg-□} sites. SAz-1 has a CEC $\cong 120$ meq/100g, and the structural formula shows that the majority of the layer charge arises from substitution in the octahedral sheet (Van Olphen and Fripiat 1979). The structural formula and the ^{27}Al NMR data discussed above are strong evidence that the layer charge in SAz-1 is nearly entirely due to Mg-Al substitution in the octahedral sheet. Thus, if the fluorine were statistically distributed through the sample, one would expect to see two ^{19}F NMR resonances, one for {Al-Al-□} and another for {Al-Mg-□} sites. By comparison with other clay samples, the {Al-Al-□} site would be expected to have a resonance at around -134 ppm and no such resonance is observed.

^{19}F spectral characteristics

Based on the NMR results for the layer silicates investigated in this work, the following generalizations can be made. First, the NMR sensitivity of ^{19}F is very high compared with most nuclides, and it is thus possible to obtain useful spectra when the amount of fluorine is in the few-ppm range. Second, the majority of samples we investigated have significant spinning sidebands. We have attempted to make a qualitative evaluation of the source of these sidebands by obtaining static (non-MAS) spectra of many of the clay samples discussed above. The static spectra are somewhat variable but generally have line shapes indicative of chemical shift anisotropy (Fyfe 1983). None of the spectra have the clear, well-defined shift anisotropy patterns of ideal compounds but rather are severely broadened at the edges. There are two plausible sources of this broadening: magnetic dipole couplings to other magnetically active nuclei in the system such as protons or ^{27}Al , or relaxation due to couplings to the paramagnetic ions in the structure. It is likely that both of these mechanisms operate to some extent. We also found that the spinning sidebands are greatest in those samples which we expect to have the highest concentration of paramagnetic cations. We attribute the spinning

sideband patterns to a combination of chemical shift anisotropy and well-known paramagnetic sideband generation (Nayeem and Yesinowski 1988). Unfortunately, little can be done experimentally to eliminate this problem. In order to obtain useful ^{19}F data for these samples, a MAS probe capable of relatively high spinning speeds is essential. Although unavailable to us, spinning rates of 10 kHz or more would be useful in spreading out the spinning sideband patterns. Spectra are acquired at several different spinning rates to move observation "windows" and to assure that no small resonances lurk under the spinning sidebands.

CONCLUSIONS

It is relatively easy to obtain ^{19}F spectra of many clays in spite of their low fluorine content. However, a significant problem arises with clays having high concentrations of paramagnetic cations, notably Fe. Our original goal was to investigate the fluorine occupancy in kaolinites in which there are two different types of hydroxyl sites which might be substituted by fluorine. Surprisingly, those two sites have virtually identical ^{19}F chemical shifts or perhaps fluorine only substitutes for one of the hydroxyls. In either case it was impossible to determine relative substitution of F^- for OH^- at the inner and interlayer sites.

We found that the ^{19}F chemical shift for fluorine atoms substituting for inner hydroxyls is sensitive to the local octahedral cation occupancy. This indicates that ^{19}F NMR might be useful for local structural determinations in clays, and we conclude that fluorine is not randomly distributed in the internal sites. To the extent that we were able to make measurements, fluorine is preferentially ordered onto sites with Mg rather than those with Al in the octahedral sheet. This conclusion appears to be true in montmorillonites in which the preferred fluorine site is in association with {Al-Mg-□} rather than {Al-Al-□} and in palygorskite where the fluorine is found in {Mg-Mg-Mg} sites preferentially over {Mg-Mg-Al} sites. This conclusion agrees with the work of Huve *et al* (1992a, 1992b), who found fluorine in {Al-Mg-□} sites in synthetic montmorillonites. It also agrees with the earlier work of Santaren *et al* (1990) who postulated that fluorine selectively goes to Mg-containing sites.

Migration of Li^+ into the octahedral sheet of a montmorillonite, through ion exchange and heating, was useful in our interpretation of chemical shifts. We are continuing NMR studies of cation migration into octahedral vacancies using ^6Li and ^7Li NMR.

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