^{19}F MAS-NMR STUDY OF STRUCTURAL FLUORINE IN SOME NATURAL AND SYNTHETIC 2:1 LAYER SILICATES

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Abstract—High-resolution solid-state, fluorine-19, magic-angle spinning-nuclear magnetic resonance spectroscopy (MAS-NMR) was used to study natural and synthetic fluorinated 2:1 layer silicates of known composition. This technique enabled us to determine directly the coordination of structural fluorine and it was found to be sensitive to both the chemical nature of the octahedral elements (Al, Mg, Li) and the type of octahedral sheet (di- or trioctahedral). The observed chemical shifts at -132, -152, -176 and -182 ppm (relative to $CFCl_3$) were assigned to different environments of fluorine. The results were then used to characterize synthetic 2:1 layer silicates with unknown octahedral composition.

Key Words—Clay minerals, ^{19}F MAS-NMR, Fluorine, Layer silicates, Silicates, Smectites.

INTRODUCTION

High-resolution magic-angle spinning-nuclear magnetic resonance (MAS-NMR) spectroscopy of solids is a powerful tool for understanding the fine structure of materials such as clay minerals (Smith *et al.,* 1983; Thompson, 1984; Sanz and Serratosa, 1984; Kinsey *et al.,* 1985; Weiss *et al.,* 1987). In this paper, high-resolution solid-state fluorine-19 MAS-NMR data for a variety of fluorinated 2:1 layer silicates are reported for the first time.

It is generally agreed that substitution of hydroxyl groups by fluorine atoms occurs in clay minerals. The similarity of both their electronegativity and radius allows this substitution in most types of layer silicates. Fluorine atoms are bonded to clay structures during their formation (Thomas *et al.,* 1977) or by hydrothermal alteration (Daniel and Hood, 1975), but also during their synthesis in a fluoride medium (Granquist and Township, 1966; Torii and Iwasaki, 1987; Huve *et al.,* 1991). For a long while, the determination of the fluorine content of clay minerals was difficult. Thanks to the use of the fluoride-selective electrode (Frant and Ross, 1966) new data could be obtained (Thomas *et al.,* 1977). The F content in clay minerals ranges from a few ppm in nontronite (API, Colfax, Washington) to more than 50,000 ppm in hectorite (API 34a, Hector, California) (Thomas *et al.,* 1977). Minerals such as taeniolite $[K(Mg_2Li)Si_4O_{10}F_2]$ are fully substituted. In the clays obtained by synthesis in a fluoride medium, or fluorinated by a post-synthesis treatment, a variable number of hydroxyl groups may be substituted by fluorine atoms.

The substitution of fluorine atoms for hydroxyl groups has been studied by various methods, namely by ^1H and ^{19}F broad-band nuclear magnetic resonance (Sanz and Stone, 1979; Santaren *et al.,* 1990). Sanz and Stone

determined the distribution of iron(II), fluorine, and hydroxyl groups in octahedral sheets of phlogopite, and Santaren *et al.* studied the structural fluorine in sepiolite. ^{19}F MAS-NMR has proven to be a better tool for the study of fluorine in solids (Yesinowski and Mobley, 1983; Clark *et al.,* 1986; Raudsepp *et al.,* 1987; Kreinbrink *et al.,* 1990; Delmotte *et al.,* 1990).

The present paper will demonstrate that it is possible to determine the composition of the octahedral sheets of 2:1 layer silicates, and possibly the distribution of the octahedral elements (such as Al, Mg, Li), from ^{19}F MAS-NMR signals. First, a series of essentially pure, highly crystalline and well-known fluorinated natural and synthetic layer silicates were analyzed by ^{19}F MAS-NMR. Then a series of synthetic fluorinated layer silicates of unknown composition was characterized using the results obtained.

EXPERIMENTAL

Materials

The fluorinated samples selected for this study are chemically representative of the 2:1 layer silicates. Their half unit cell holds three octahedra. Dioctahedral layer silicates contain two octahedral elements, primarily Al and a vacancy. Trioctahedral silicates contain three octahedral elements, primarily Mg. If the 2:1 layers are not electrically neutral the excess layer charge is balanced by various interlayer cations. Both the dioctahedral and trioctahedral layer silicates were examined by ^{19}F MAS-NMR in this study. The samples were of different origins. The trioctahedral hectorite was from *Hector, California,* and the dioctahedral montmorillonite from Camp Berteau, Morocco. They are well-known, pure natural samples and were used as reference materials for the ^{19}F MAS-NMR chemical shifts (Table 1). Barasym SMM 100 is a pure synthetic di-

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Table 1. Characteristics of the natural and synthetic fluorinated 2:1 layer silicate samples of known composition.

Mineral name	Origin	Structural formula (half-unit cell)[1]	^{19}F chemical shift (ppm)[2]			
			Type I	Type II	Type III	Type IV
TRIOCTAHEDRAL MINERALS						
Hectorite	Hector, California, USA	$C_y(Si_4)(Mg_{3-y}Li_y)O_{10}(OH,F)_2$ [3]			−176.2	−182.8
Trioctahedral 2:1 layer silicate	Synthetic	$(Si_4)(Mg_3)O_{10}(OH,F)_2$ [4]			−176.5	
DIOCTAHEDRAL MINERALS						
Montmorillonite	Camp Berteau, Morocco	$C_z(Si_4)(Al_{2-y-z}Fe_yMg_z)O_{10}(OH,F)_2$ [5]		−152.0		
Barasym SMM 100	Synthetic	$C_x(Si_{4-x}Al_x)(Al_2)O_{10}(OH,F)_2$ [6]	−131.9			
Dioctahedral 2:1 layer silicate	Synthetic	$C_x(S_{4-x}Al_x)(Al_2)O_{10}(OH,F)_2$ [4]	−133.2			

[1] C: monovalent interlayer cation.
[2] From $CFCl_3$.
[3] Adapted from Köster, H. M. (1982).
[4] This study.
[5] Adapted from Calvet, R. and Prost, R. (1971).
[6] Adapted from Granquist, W. T. and Pollack, S. S. (1967).

octahedral 2:1 layer silicate (Granquist and Township, 1966) that was supplied by the Institut Français du Pétrole (I.F.P.). It can be described as a random interstratified material containing ⅔ illite-like sites and ⅓ smectite-like sites (Wright et al., 1972) (Table 1).

For a pure trioctahedral-Mg and an essentially pure dioctahedral-Al 2:1 layer silicate (Table 1), a series of samples of unknown composition (Table 2) were obtained by synthesis from starting materials containing various Al_2O_3/MgO ratios and the same content of SiO_2 and fluorides (Huve et al., 1991).

NMR spectroscopy

The NMR spectra were obtained on a Bruker MSL 300 spectrometer at a frequency of 282 MHz for ^{19}F using a 5 mm high-speed Doty probe without ^{19}F background. An ordinary one-pulse cycle was applied under MAS condition with a spinning rate of 8 to 10 kHz. Typically, 15° pulses (3 μs) with a 5 s recycle delay were used. 180 scans were accumulated. All spectra were obtained for a spectral width of 125 kHz. $CFCl_3$ was used as a reference for the ^{19}F chemical shifts.

RESULTS

Except for hectorite (Figure 1), there is only one signal on each spectrum. The smaller peaks on each side of the strong line are spinning side-bands (indicated by *). These arise from the magic-angle spinning process and can be distinguished from the true signal because their positions vary with the spinning speed.

The ^{19}F MAS-NMR spectrum of the very pure and strongly-fluorinated hectorite (Figure 1) shows two peaks at −182.8 and −176.2 ppm, indicating that two nonequivalent sites are present. The weak intensity of the spinning side bands compared to that of the main

signal may be explained by the absence of dipolar, quadrupolar, and paramagnetic effects.

The montmorillonite (Figure 1) shows one peak at −152.0 ppm and a significant side-band structure. These spinning side bands were more pronounced than in the previous sample's spectrum and may be attributed to a quadrupolar anisotropic effect rather than to a paramagnetic effect due to Fe(III). Indeed, the octahedral sheets contain mainly Al, with some Fe(III) and Mg substituted for Al. The signal was weak as 2415 scans were necessary. This was because of the low fluorine content of this sample (0.1–0.2%) and presumably due to the large paramagnetic effect of Fe(III). Alvarez et al. (1987) found that the fluorine present in natural deposits is directly related to their MgO content, therefore, it was assumed that the F atoms were bonded to octahedral Mg (Mg-Al-□) rather than to octahedral Al (Al-Al-□). This assumption may explain why only one signal is observed.

The pure Barasym SMM 100 sample also shows a single peak, but at −131.9 ppm, indicating the exis-

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The □-symbol represents a cation-free octahedral site vacancy.

Table 2. Characteristics of the synthetic fluorinated 2:1 layer silicate samples of unknown composition.

Al_2O_3/MgO ratio of the starting mixtures	^{19}F chemical shifts (ppm)[1]			
0.08	—	−153.1		−176.7
0.22	−132.6	−152.9		−176.2
0.50	−132.6	−153.1		—
4.00	−133.4	−153.2		—

[1] From $CFCl_3$.
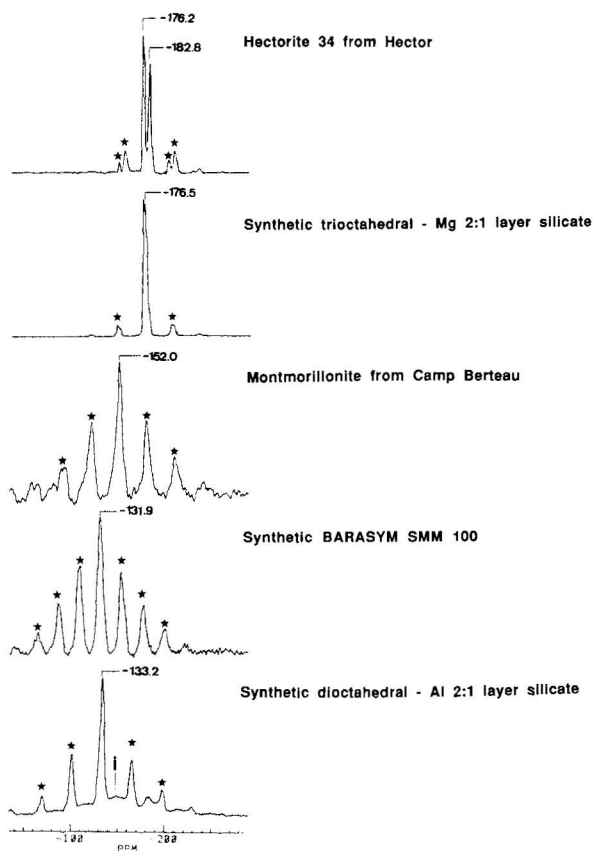
Figure 1. ¹⁹F MAS-NMR spectra of the known natural and synthetic fluorinated 2:1 layer silicates (5 s recycle time, 3 μs 15° pulse excitation). 180 scans were accumulated, except for the montmorillonite sample—2415 scans. Stars identify spinning side bands; i = impurity.

the existence of more than one fluorine site, but all sites would be very similar. The dioctahedral sample shows only one major peak at -133.2 ppm compared with the -131.9 ppm signal observed for Barasym SMM 100 (type I). The broad band near -148 ppm is attributed to the fluoro-complex $AlF_xOH_y \cdot zH_2O$ detected by XRD as a minor impurity.

The following assumptions can be made: (1) The -132 ppm (type I) chemical shift corresponds to F atoms in dioctahedral sheets containing mainly Al atoms (Barasym SMM 100 and synthetic dioctahedral 2:1 layer silicate). (2) The -176 ppm (type III) chemical shift is characteristic of F atoms in trioctahedral sheets containing mainly Mg atoms (hectorite and synthetic trioctahedral 2:1 layer silicate). (3) According to the known octahedral sheet composition, the -152.0 and -182.8 ppm chemical shifts may characterize F atoms in dioctahedral sheets containing Al and Mg atoms and in trioctahedral sheets containing Mg and Li, respectively (type II and IV).

DISCUSSION

Trioctahedral minerals

As mentioned above, the type III signal (-176 ppm) observed for hectorite and the synthetic trioctahedral 2:1 layer silicate is attributed to F atoms bonded to three Mg (Mg-Mg-Mg configuration) on the basis of the similarity of both the ¹⁹F chemical shifts and spinning side-band structure. It is well known that two types of structural sites for Mg atoms can be distinguished in trioctahedral minerals such as phlogopite: one with the OH groups or F atoms in a *trans*-position and the other with these species in a *cis*-position (Sanz and Stone, 1979). The partial substitution of the OH groups by F atoms gives rise to four non-equivalent but very similar F atoms sites: those with one F atom and one OH group in the same octahedron in a *cis*- or *trans*-position and those with two F atoms in a *cis*- or *trans*-position. This correlates well with the ¹⁹F NMR signals observed for the synthetic trioctahedral 2:1 layer silicate (two peaks and two shoulders centered at -176.5 ppm).

In the end-member trioctahedral minerals, the F atoms are bonded to three Mg atoms. The partial substitution of Mg by other elements such as Li is possible, as in hectorite. This kind of substitution is generally minor because the excess layer charge needs to be neutralized. If the assumption is made that ⅓ of the Mg atoms are substituted by Li in a few unit cells, the type IV signal (-182.8 ppm) may be the result of such a substitution (Mg-Mg-Li).

Dioctahedral minerals

Again, because of the similarity in both the ¹⁹F chemical shifts and spinning side-band structure observed for the Barasym SMM 100 and the synthetic diocta-

tence of only one F-atom site (Figure 1). Several spinning side bands of high relative intensity are present.

The four NMR signals observed so far are considered to characterize four different F sites denoted type I (-131.9 ppm), type II (-152.0 ppm), type III (-176.2 ppm) and type IV (-182.8 ppm), respectively. To complete the assignment of these chemical shifts, two samples of well-known composition (Table 1) were synthesized:

(1) a fluorinated trioctahedral-Mg 2:1 layer silicate containing neither octahedral nor tetrahedral Al, and (2) a fluorinated dioctahedral-Al 2:1 layer silicate containing no Mg in the octahedral sheets (Huve *et al.*, 1991).

For the trioctahedral sample, a major peak was found at -176.5 ppm (Figure 1) that coincides with the -176.2 ppm signal observed for hectorite (type III). The similarity of the spinning side-band structure of both samples indicates that the F-atom sites are essentially equivalent. In fact, for the synthetic sample, the signal can be resolved into two peaks at -175.3 and -176.7 ppm, and two shoulders. That may imply

hedral 2:1 layer silicate, the type I signal (-132 ppm) is attributed to F atoms bonded to two Al atoms and to a vacancy (Al-Al-□ configuration). In montmorillonite, Al is partly substituted by Mg and the F atoms are bonded to one Al, one Mg, and a vacancy (Al-Mg-□) rather than to two Al atoms and a vacancy (Al-Al-□). Therefore, the type II signal (-152.0 ppm) observed for the montmorillonite sample is assigned to F in a Al-Mg-□ configuration.

Electronegativity and nucleus shielding

An increasing electronegativity of the octahedral elements reduces the shielding of the fluorine nucleus. There is a less-negative chemical shift because of the lower electron density around these F atoms. Fluorine atoms may have two or three octahedral elements of different nature (Al, Fe, Mg, Li) in their environment. The electronegativity values of Al, Mg, and Li, 1.5, 1.2, and 1.0, respectively (Pauling, 1960), could explain the different chemical shifts. For the hectorite containing Mg and Li atoms in octahedral sheets, two 19F chemical shifts are observed (-176 and -182 ppm). The low electronegativity of Li tends to increase the shielding of the fluorine nucleus, thus the chemical shift of 19F may be displaced to more negative values when the F atoms are coordinated to Li. Consequently, the -182 ppm signal is attributed to F atoms bound to two Mg and one Li (Mg-Mg-Li configuration). The same observation is made for dioctahedral layer silicates with two Al atoms and one vacancy or with one Al, one Mg, and one vacancy and -132 and -152 ppm chemical shifts, respectively. Due to the possible fraction of possible substituted octahedral elements (one-third, trioctahedral; one-half, dioctahedral), the effect of the shielding is less important for trioctahedral layer silicates (6 ppm chemical shift variation, -176 to -182 ppm) than for dioctahedral ones (20 ppm, -132 to -152 ppm).

Spinning side bands, quadrupolar effect, and isotopic abundance

As seen above the spinning side-band structures observed are quite different. In the trioctahedral minerals, they are weak and narrow (Figure 1, hectorite and synthetic trioctahedral 2:1 layer silicate). In the dioctahedral minerals, they are strong and broad (Figure 1, montmorillonite and synthetic dioctahedral 2:1 layer silicate). Although both Al and Mg are quadrupolar nuclei, fluorine is subjected to a higher quadrupolar effect when bonded to Al than to Mg. This may be attributed to their isotopic abundances that are 10% for 25Mg and 100% for 27Al. The different spinning side-band intensities are also due to the inherent difference in the geometry of the F environment in tri- or dioctahedral materials. Indeed, the F environment in the trioctahedral minerals is very symmetrical, whereas it is very asymmetrical in the dioctahedral case.
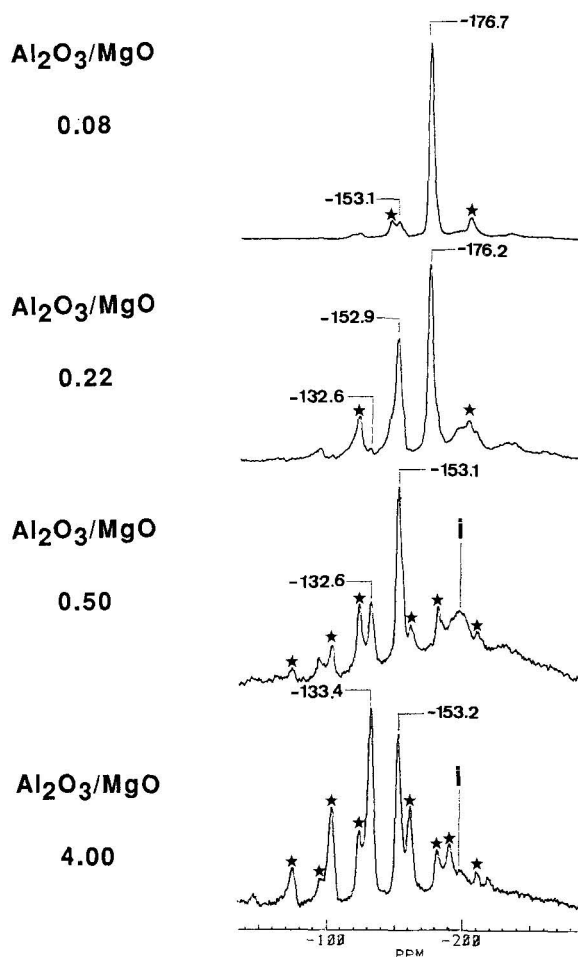

Figure 2. 19F MAS-NMR spectra of a series of synthetic fluorinated 2:1 layer silicates (180 scans at 5 s recycle time, 3 μs 15° pulse excitation). The stars identify spinning side bands; i = MgF$_2$ impurity.

Application to synthetic 2:1 layer silicates of unknown composition

The results of 19F MAS-NMR spectroscopy as described and discussed above were used to characterize the octahedral sheet compositions of a series of synthetic fluorinated 2:1 layer silicates. Their XRD patterns show the 060 reflections corresponding to both tri- and dioctahedral (1.52 Å and 1.49 Å, respectively) components. The intensities of the two (060) reflections vary with the Al$_2$O$_3$/MgO ratio of the mixture at the start. The same was observed by Harward and Brindley (1964) who found that as the Mg content of the gel increased and Al decreased, there is a tendency to form separate mineral phases. Our samples with a high Al$_2$O$_3$/MgO ratio contain MgF$_2$ as a minor impurity. For a

small Al_2O_3/MgO ratio of the starting mixture, less MgF_2 is present and the layer silicate phases contain more fluorine. The NMR spectra of the samples (Figure 2) show a continuous evolution with the Al_2O_3, MgO and F content of the reaction mixture, but the chemical shifts vary stepwise from -176 to -132 ppm (Table 2). The broad band between -195 and -197 ppm is attributed to MgF_2 (Kreinbrink *et al.*, 1990). The observed chemical shift values of -132, -153, and -176 ppm are similar to those of F atoms of types I, II, and III, respectively. This may indicate that the samples contain dioctahedral-Al sheets (-132 ppm), dioctahedral-Al,Mg sheets (-153 ppm), and trioctahedral-Mg sheets (-176 ppm), either separately or in interstratified phases.

CONCLUSION

^{19}F MAS-NMR spectroscopy is a new and powerful tool to study fluorinated materials. In microporous solids such as layer silicates or zeolites, the fluorine content is low, ranging from 1 to 10%. Therefore, the F atoms are weakly coupled making this technique extremely useful (Delmotte *et al.*, 1990). For layer silicates, it offers the possibility of exploring octahedral sheet compositions by taking advantage of the influence of the octahedral elements (Al, Mg, Fe, Li . . .) on bonded fluorine. The high resolution of the technique enables the determination of several types of fluorine sites. There is no evidence in the literature that the chemical shifts observed in this study have been reported previously. New characterizations of natural or synthetic layer silicates and clay minerals may be established. Under appropriate experimental conditions, ^{19}F MAS-NMR spectroscopy is a sensitive method and is inherently quantitative (spin ½ for the F nucleus). Further work is in progress to study other natural or synthetic layer silicates and clay minerals of various compositions, and to determine quantitatively the occupancy of a given fluorine site.

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