

## STRUCTURAL FLUORINE IN SEPIOLITE

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**Abstract**—Sepiolite from Vallecas-Vicálvaro, Spain, contains 1.3% fluorine. Laser microprobe mass spectrometry of this sepiolite suggests the presence of fragments of  $(\text{SiO}_2)_n\text{OMgF}$  and  $(\text{SiO}_2)_n\text{OMgOH}$ , which are typical of the sepiolite structure. During thermal dehydroxylation, the fluorine in this sepiolite is removed simultaneously with OH groups at about 750°C. Nuclear magnetic resonance spectroscopy (NMR) of  $^{19}\text{F}$  indicates that the fluorine is located in the interior of the sepiolite structure, probably substituting for OH groups, and is homogeneously distributed. In the Vallecas-Vicálvaro sepiolite, about one of every four OH groups bound to  $\text{Mg}^{2+}$  is substituted by fluorine. The kinetics of extraction of  $\text{Mg}^{2+}$  and  $\text{F}^-$  ions by acid treatment (1 N HCl) shows a more rapid extraction of  $\text{Mg}^{2+}$ , with a monotonous decrease of the Mg/F ratio as the extent of extraction increases. These results support the internal location of the fluorine, as suggested by the NMR data.

**Key Words**—Fluorine, Hydroxyl, Laser microprobe mass spectrometry, Dissolution, Nuclear magnetic resonance, Sepiolite.

### INTRODUCTION

Sepiolite is a hydrated magnesium silicate having the following half-unit cell formula (Newman and Brown, 1987):  $(\text{Mg}_{8-y-z}\text{R}^{3+}_y\text{□}_z)(\text{Si}_{12-x}\text{R}^{3+}_x)\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4\cdot\text{R}^{2+}_{(x-y+2z)/2}(\text{H}_2\text{O})_8$ . Structurally (Figure 1), it consists of blocks and channels extending in the c-axis direction. Each structural unit is built up of two tetrahedral silicate layers and a central trioctahedral layer. In the octahedral layer  $\text{Mg}^{2+}$  ions occupy two different structural positions: (1) on the borders of the structural blocks, coordinated to water molecules; and (2) in the interior of the blocks, linked to hydroxyl groups. Due to the similarity of  $\text{OH}^-$  and  $\text{F}^-$  in electronegativity and ionic radius, 1.40 and 1.36 Å, respectively (Pauling, 1960), the substitution of fluorine for hydroxyl groups is plausible in sepiolite as in other clay minerals (Koritnig, 1963).

Fluorine is incorporated into clay mineral structures either during their formation or by hydrothermal alteration (Thomas *et al.*, 1977; Daniel and Hood, 1975). The fluorine content of sepiolite ranges from 0.5% for the sepiolite from New Mexico to 1.3% for the sepiolite from Vallecas, Spain. The results of Alvarez *et al.* (1987) indicate that the fluorine content of samples from the Vallecas deposit is directly related to the MgO content. These authors suggested that the fluorine substitutes for hydroxyls linked to  $\text{Mg}^{2+}$  ions, possibly as a result of hydrothermal alteration, inasmuch as the water surrounding the deposit contains 2 ppm  $\text{F}^-$ .

To ascertain the position of the fluorine in sepiolite, sepiolite from the Vallecas-Vicálvaro deposit was ana-

lyzed by means of conventional techniques, as well as by laser microprobe mass spectrometry (LMMS) and  $^{19}\text{F}$  nuclear magnetic resonance (NMR) spectroscopy. The extraction of  $\text{F}^-$  from the structure by thermal treatment and acid attack was also studied to determine the stability of the  $\text{F}^-$  in the mineral.

### EXPERIMENTAL

#### Materials

The sepiolite sample selected for this study was from the Vallecas-Vicálvaro deposit in Spain. The chemical analysis and  $\text{F}^-$  content (Table 1) are typical of the samples from this locality (Alvarez *et al.*, 1987). The chemicals used were Merck Analytic Grade.

#### Methods

$\text{F}^-$  was determined using a fluoride-selective ion electrode following the modification of Ingram's method (1970) described by Thomas *et al.* (1977), using a Crison 517 digital pH meter. The sample was dissolved for fluorine analysis by alkali fusion with sodium hydroxide in a nickel crucible. The sample was fused by heating it for 15 min over a Bunsen burner (500°C).

Other constituents of the samples were analyzed by atomic absorption spectroscopy using an IL-257 spectrophotometer. The samples were dissolved by alkali fusion with lithium metaborate in a platinum crucible.

The suspensions of sepiolite (5% solids in 1 N HCl) were stirred at 20° and 40°C  $\pm$  0.5°C for various intervals of time, each interval corresponding to an independent experiment. After each treatment the sus-

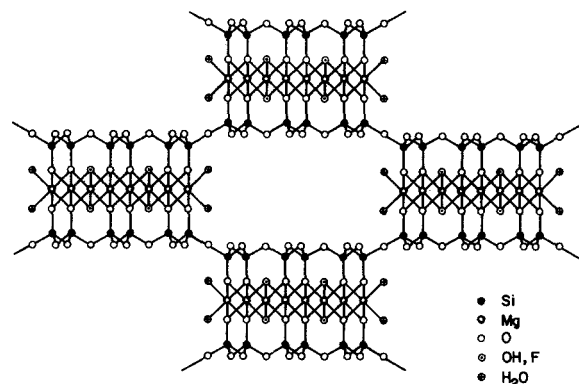


Figure 1. [100] projection of sepiolite structure according to Brauner and Preisinger (1956).

pension was filtered under vacuum, and the concentration of fluoride in the filtrate was determined by the method indicated above. The concentration of Mg and of other minor elements (Al, Ca, Na, K) was determined by atomic absorption spectrometry. The composition of the solid residue was also determined.

An attempt to introduce fluorine into the sepiolite structure was made by treating the sample with  $\text{NH}_4\text{HF}_2$  in methanol (Fijal *et al.*, 1985). The solvent was eliminated in a rotary evaporator, and the treated samples were heated at  $100^\circ\text{C}$  for 8 hr in a Teflon pressure reactor. The sample was then washed with methanol.

#### Apparatus

The  $^{19}\text{F}$ -NMR spectra were obtained in an SXP 4/100 Bruker spectrometer using a frequency of 79 MHz. The NMR data were processed in an Aspect 2000 computer, which allows by successive accumulation the signal/noise ratio to be increased to as much as 50, and the spectrum of the frequency to be obtained by the Fourier transform method. The  $\pi/2$  pulse was  $4 \mu\text{s}$ , and the time between successive accumulations was 2 s.

The LMMS spectra were obtained with a Leybold-Heraeus LAMMA-500 apparatus having the characteristics described by Denoyer *et al.* (1982). With this technique, spectral information could be obtained about both positive and negative ionized fragments in individual particles of the sepiolite (depth resolution  $\approx 1 \mu\text{m}^3$ ).

The X-ray powder diffraction (XRD) diagrams were obtained with a Siemens D-500 diffractometer operating at 35 kV and 25 mA, using Ni-filtered  $\text{CuK}\alpha$  radiation and a scanning rate of  $1^\circ 2\theta/\text{min}$ .

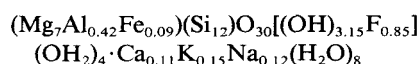
## RESULTS

The sepiolite sample used in this study had a fluorine content of 1.3% (Table 1), typical of the sepiolites from the Vallecas-Vicálvaro deposit (Alvarez *et al.*, 1987).

Table 1. Chemical analysis of sepiolite from Vallecas-Vicálvaro, Spain.

Oxide	Content (%)
$\text{SiO}_2$	62.00
$\text{Al}_2\text{O}_3$	1.72
MgO	22.90
CaO	0.48
$\text{Fe}_2\text{O}_3$	0.56
$\text{Na}_2\text{O}$	0.30
$\text{K}_2\text{O}$	0.58
$\text{F}^-$	1.31
LOI	10.52
Total	100.37

The XRD diagram (Figure 2) is characteristic of a very pure sepiolite. All the observed reflections were assigned to sepiolite with no indication of coexisting crystalline F-containing species, such as fluorite ( $\text{CaF}_2$ ), sellaite ( $\text{MgF}_2$ ), or humite ( $3\text{Mg}_2\text{SiO}_4 \cdot \text{MgF}_2$ ). Transmission electron micrographs (TEMs) revealed exclusively the microfibrillar bundles characteristic of sepiolite. The chemical data (Table 1) conform to the approximate structural formula:



De Waele *et al.* (1984) first reported the presence of fluorine in the sepiolite structure on the basis of LMMS spectra. In the negative mass spectra of a particle of sepiolite, we detected the characteristic signal at  $m/e = 19$ , indicating the presence of  $\text{F}^-$ . Figure 3 shows a typical example of the negative mass spectra of sepiolite, obtained when laser shots of relatively low energy ( $\approx 4 \times 10^{-7}$  J) were focused on an individual mineral particle. In the observed fragmentation pattern, molecular ion peaks of  $[\text{SiOMg}(\text{OH})]^-$  ( $m/e = 85$ ),  $[\text{SiO}_2\text{Mg}(\text{OH})]^-$  ( $m/e = 101$ ), and  $[(\text{SiO}_2)_n\text{OMg}(\text{OH})]^-$  ( $m/e = 117, 177, \text{ and } 237$ ), which are the natural atomic arrangements of these elements in the sepiolite framework (Figure 1), were identified. In addition to these characteristic fragment ions, other ion peaks corresponding to fragments in which OH groups were substituted by F were also observed (Table 2). The systematic difference in two mass units ( $m/e$ ) between consecutive peaks is characteristic of fragments in which F replaces OH.

The  $^{19}\text{F}$ -NMR spectra of sepiolite showed a signal having a half-height width of 1.1 Gauss (Figure 4A). Comparing this peak with those obtained for other magnesium phyllosilicates, such as hectorite from Hector, California, and synthetic Laponite S from Laporte Industries, both of which have larger fluorine contents (5.17% and 7.69% respectively), the width of the peak increases with the fluorine content of the mineral. This increase is probably due to F-F interactions as a consequence of the increasing density of F in the octahedral layers.

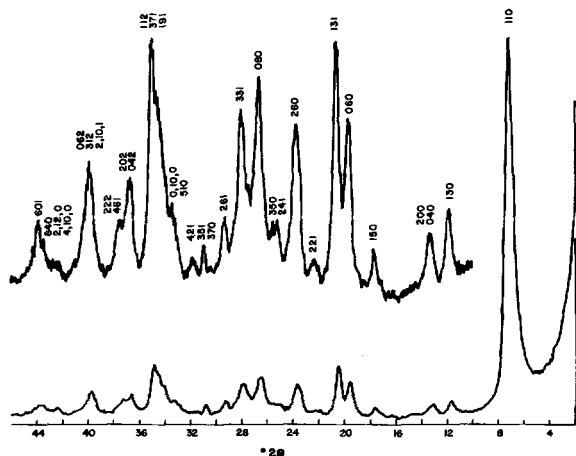


Figure 2. X-ray powder diffraction diagram of sepiolite from Vallecas-Vicálvaro.

To study the thermal stability of the fluorine in sepiolite, the mineral was heated in air at various temperatures for 3 hr. The results (Figure 5) show that no significant removal of F took place until 750°C. At higher temperatures fluorine was lost rapidly. This process coincided with the destruction of the sepiolite structure due to dehydroxylation (Martín Vivaldi and Fenoll Hach-Ali, 1969) and the formation of new crystalline phases (clinoenstatite and protoenstatite), at 900°C, after all of the OH had been lost by the mineral.

The results of the 1 N HCl treatment (Figure 6) at 20° and 40°C show that F<sup>-</sup> and Mg<sup>2+</sup> ions were released simultaneously, although the Mg<sup>2+</sup> was extracted more rapidly than the F<sup>-</sup>. This difference in the rate of extraction became greater as the temperature of the treatment was increased. Prolonged acid treatment (10 days) of sepiolite produced a residual solid having a Mg<sup>2+</sup> and F<sup>-</sup> content of 54 and 32 mmole/100 g, respectively, indicating the difficulty in extracting these elements completely. The <sup>19</sup>F-NMR signal of sepiolite treated with 1 N HCl at 20°C for 8 hr (extraction of about 25% Mg<sup>2+</sup> and 22% F<sup>-</sup>) showed (Figure 4D) the same width as the signal of natural sepiolite, indicating that the

Table 2. Fragments identified in the laser microprobe mass spectrum of sepiolite from Vallecas-Vicálvaro, Spain.

m/e	Assigned fragment
85	[SiOMg(OH)] <sup>-</sup>
87	[SiOMg(F)] <sup>-</sup>
101	[SiO <sub>2</sub> Mg(OH)] <sup>-</sup>
103	[SiO <sub>2</sub> Mg(F)] <sup>-</sup>
117	[SiO <sub>2</sub> OMg(OH)] <sup>-</sup>
119	[SiO <sub>2</sub> OMg(F)] <sup>-</sup>
177	[(SiO <sub>2</sub> ) <sub>2</sub> OMg(OH)] <sup>-</sup>
179	[(SiO <sub>2</sub> ) <sub>2</sub> OMg(F)] <sup>-</sup>
237	[(SiO <sub>2</sub> ) <sub>3</sub> OMg(OH)] <sup>-</sup>
239	[(SiO <sub>2</sub> ) <sub>3</sub> OMg(F)] <sup>-</sup>

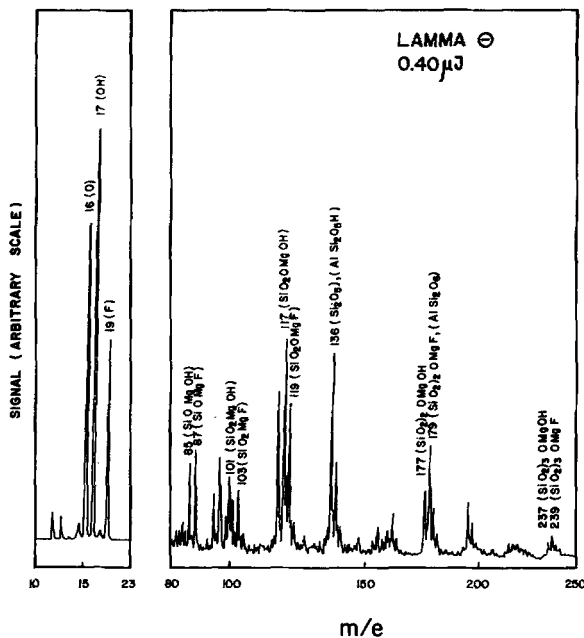


Figure 3. Laser microprobe mass spectrum (negative mode) of sepiolite from Vallecas-Vicálvaro, Spain.

environments of the remaining F<sup>-</sup> was not altered by the acid treatment.

A procedure based in the method used by Fijal *et al.* (1985) to fluorinate montmorillonite was followed in an attempt to incorporate more fluorine into the sepiolite structure. As a result of this drastic treatment with NH<sub>4</sub>HF<sub>2</sub>, the products contained 2 to 5 wt. % of fluorine. The <sup>19</sup>F-NMR spectrum of a sample containing 2.96% fluorine (Figure 4E) showed two peaks of widths 1.0 and 5.6 Gauss, respectively, centered at the same resonance frequency.

### DISCUSSION

The OH groups of sepiolite in the interior of the structural units are each coordinated to three Mg<sup>2+</sup> ions. Two types of structural sites for Mg can be distinguished: those with the OH groups in *trans* disposition (OH-OH distance ~4.1 Å), and those with OH groups in *cis* disposition (OH-OH distance ~2.7 Å). The partial substitution of OH groups by F in these octahedra gave rise to different types of anionic associations, the distribution of which was analyzed by <sup>19</sup>F-NMR spectroscopy. In particular, the second moment (S<sub>2</sub>) deduced from the NMR signal was related to the interatomic distances (r<sub>i</sub>) and the degree of occupancy (n<sub>i</sub>) of the structural sites surrounding the nucleus under study by means of Eq. (1):

$$S_2 = \frac{3}{5} \hbar^2 \gamma_f^2 (I + 1) I \sum_i \frac{n_i}{r_i^6} + \frac{4}{15} \hbar^2 \gamma_s^2 (S + 1) S \sum_i \frac{n_i}{r_i^6} \quad (1)$$

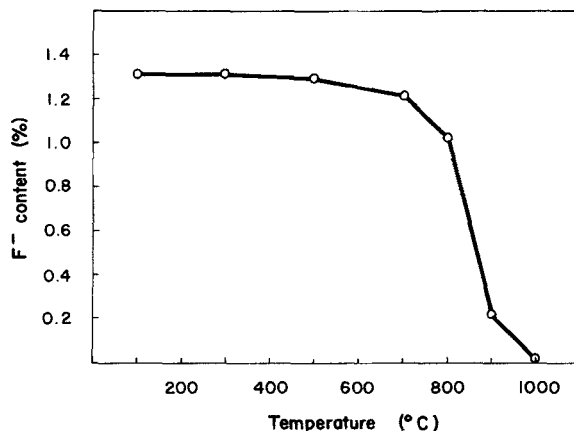
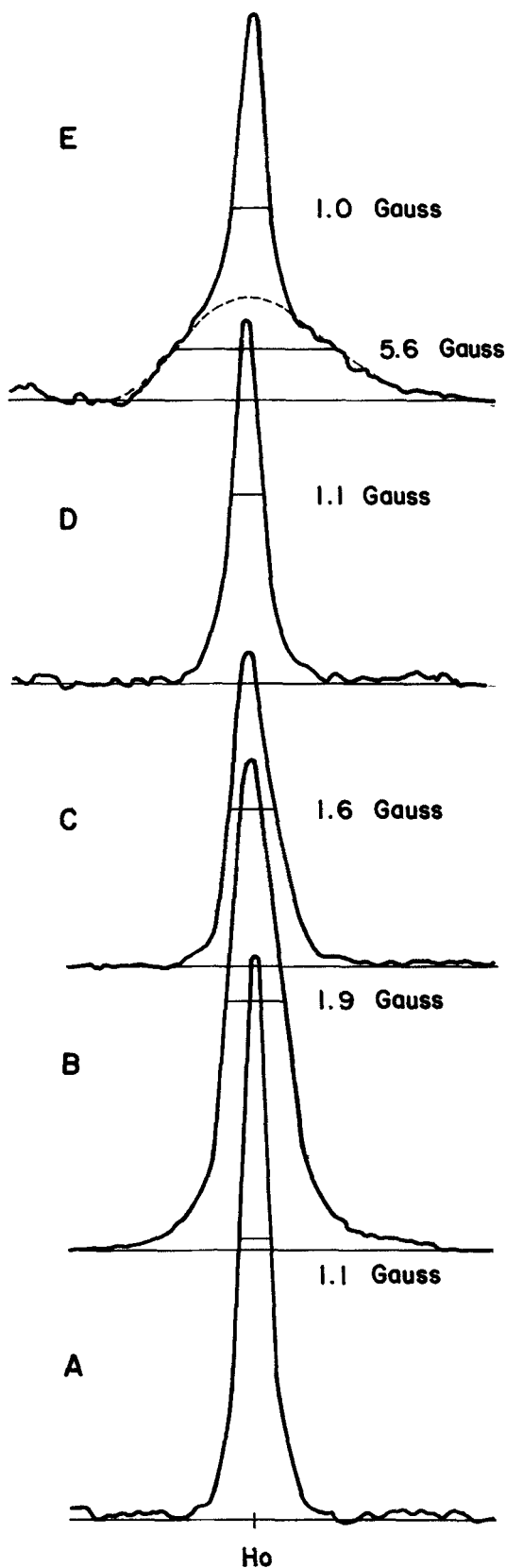


Figure 5. Diminution in fluorine content of sepiolite samples as a function of temperature of treatment.

where  $\gamma_I$  and  $\gamma_S$  are the gyromagnetic constants of nuclei of the same (I) and different (S) types compared with that being studied (Van Vleck, 1948).

If interatomic distances from the literature (Sanz and Stone, 1979) are introduced into Eq. (1), the value of  $S_2$  can be calculated for various degrees of substitution of F for OH in phyllosilicates, structurally related to sepiolite. In Figure 7, the values calculated for random distributions of F<sup>-</sup> and OH<sup>-</sup> ions are compared with those determined from the NMR spectra of sepiolite, hectorite, and Laponite S. Note the substantial degree of agreement. Thus, almost all the fluorine appears to be located inside the structural units of sepiolite, substituting for OH groups. The F is randomly and homogeneously distributed in the octahedral layer of the mineral. The probability of encountering two F<sup>-</sup> ions in *cis* arrangement in the same octahedron (distance F-F = 2.63 Å) is therefore low (<12%). In principle, the localization of F<sup>-</sup> nuclei on the borders of the structural channels, in which the zeolitic water of the structure is situated, should be excluded, because in such an arrangement the F...H<sub>2</sub>O interaction, having a shorter H-F internuclear distance, would give a broader signal than the one found.

The substitution of F for OH in sepiolite was also supported by LMMS analysis, which showed the simultaneous presence of  $(\text{SiO}_2)_n\text{OMgOH}$  and  $(\text{SiO}_2)_n\text{OMgF}$  fragments in the corresponding spectra.

The location of the F in the interior of the structural units explains the thermal- and acid-treatment results. On thermal treatment, fluorine was lost simultaneously with dehydroxylation at about 750°C, probably in the

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Figure 4. <sup>19</sup>F-Nuclear magnetic resonance spectra of: (A) sepiolite from Vallecas-Vicálvaro; (B) Laponite S; (C) hectorite; (D) sepiolite treated with 1 N HCl at 20°C for 8 hr; and (E) sepiolite treated with NH<sub>4</sub>HF<sub>2</sub>.

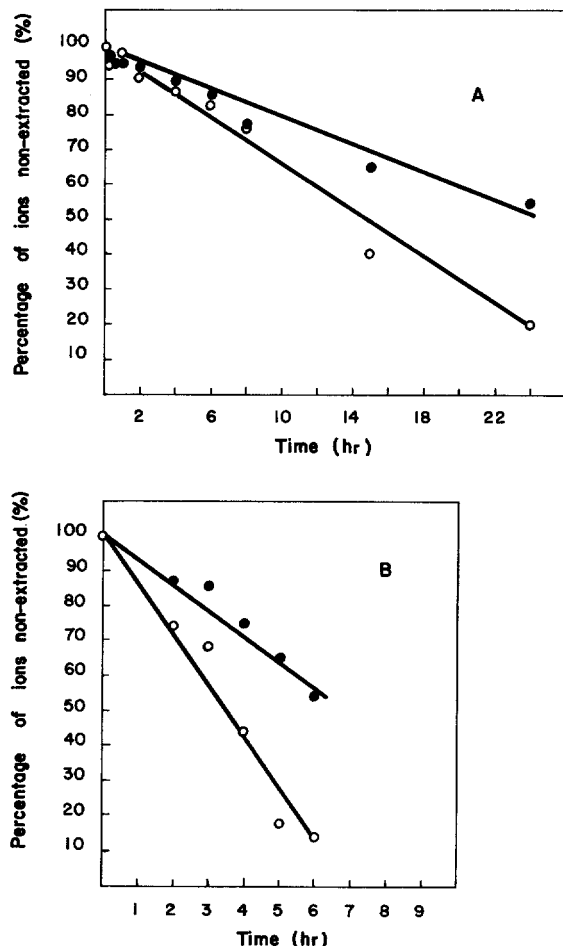


Figure 6. Percentage of ions remaining unextracted, (O) Mg<sup>2+</sup> and (●) F<sup>-</sup>, as a function of time of treatment with 1 N HCl. (A) 20°C; (B) 40°C.

form of HF, which was eliminated together with H<sub>2</sub>O molecules formed by the condensation of OH groups linked to Mg<sup>2+</sup> ions. Also, the acid-treatment data are in agreement with the proposed location of the F<sup>-</sup> ions. The higher rate of extraction of Mg<sup>2+</sup> can be interpreted by a preferential extraction of Mg<sup>2+</sup> from the structural borders, where F is absent. This interpretation is supported by the variation of the Mg/F ratio vs. the degree of extraction of Mg<sup>2+</sup> ions (Figure 8). At first the Mg/F ratio was equal to that of the bulk sepiolite, but it diminished to 1.6 for more intensive acid attack.

The incomplete extraction of Mg<sup>2+</sup> and F<sup>-</sup> ions cannot be due to precipitation of MgF<sub>2</sub> because (1) the XRD diagrams of the residual solid showed no MgF<sub>2</sub> reflections, and (2) the solubility product of MgF<sub>2</sub> was not reached under the experimental conditions ( $K_s = 8 \times 10^{-4}$ ), even supposing a total extraction of the Mg<sup>2+</sup> and F<sup>-</sup>. Also, if the residual solid was treated with a fresh acid solution, little additional Mg<sup>2+</sup> and F<sup>-</sup> was

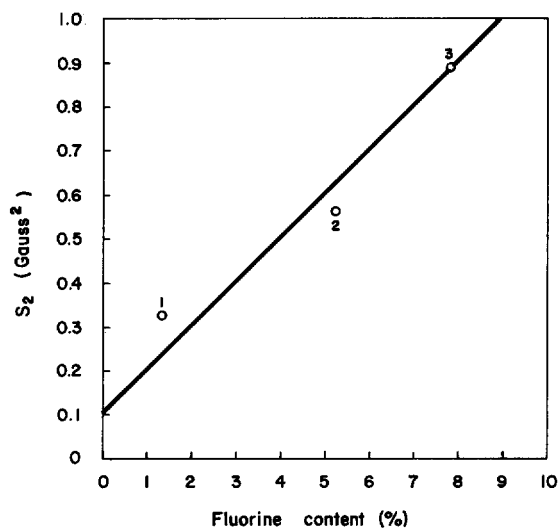


Figure 7. Calculated value of the second moment ( $S_2$ ) as a function of fluorine content.  $S_2$  deduced from the nuclear magnetic resonance spectrum is indicated for (1) sepiolite; (2) hectorite, and (3) Laponite S.

extracted, even if the treatment was repeated several times. The explanation of these observations is probably connected with the lack of diffusion of the ions into the solution, due to the collapse of the channels, which probably resulted in the formation of siloxane bonds between adjacent tetrahedral layers, impeding the removal of the residual Mg<sup>2+</sup> and F<sup>-</sup>. Figure 8 shows that, for different experimental conditions, the Mg/F ratio tended towards unity in extreme conditions. The internal localization of fluorine in sepiolite conferred a high stability with regard to both acid and thermal treatments.

The results obtained from the NH<sub>4</sub>HF<sub>2</sub> treatment of sepiolite showed that new F<sup>-</sup> anions were not incor-

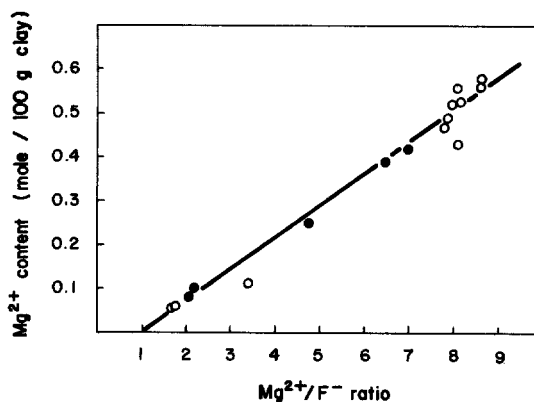


Figure 8. Variation of the Mg/F ratio as a function of the Mg content of untreated sepiolite and sepiolite after acid treatment at (O) 20°C and (●) 40°C.

porated into the interior of the structure replacing OH. The large width of the second component (5.6 Gauss) observed in the  $^{19}\text{F}$ -NMR spectrum (Figure 4E) showed that the incorporated  $\text{F}^-$  ions did not substitute for OH groups of the octahedral layer (maximum expected width = 2.1 Gauss), but were apparently located in regions of high density of  $\text{F}^-$  ions, possibly associated with the  $\text{Mg}^{2+}$  ions in the more external positions of the octahedral layer (border of the structural units). The F-F and F-H interactions between neighboring nuclei were probably responsible for the observed width of the NMR spectrum. These results indicate that  $\text{F}^-$  ions have limited access to the interior of the sepiolite structure where the OH groups are located.

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