

THE BEHAVIOR OF Fe IN GROUND AND ACID-TREATED VERMICULITE FROM SANTA OLALLA, SPAIN

CELIA MAQUEDA^{1,*}, AGUA SANTAS ROMERO¹, ESMERALDA MORILLO¹, JOSÉ L. PÉREZ-RODRÍGUEZ², ANTON LERF³, AND FRIEDRICH ERNST WAGNER⁴

¹ Instituto de Recursos Naturales y Agrobiología (CSIC), Apdo 1052, 41080 Sevilla, Spain

² Instituto de Ciencia de Materiales de Sevilla (UNSE-CSIC), Americo Vespucio 49, 41092 Sevilla, Spain

³ Walther-Meissner-Institut, Bayerische Akademie der Wissenschaften, Walter-Meissner-Strasse 8, Garching D-85748, Germany

⁴ Physik-Department EI5, Technische Universität München, Garching D-85748, Germany

Abstract—The preparation of porous materials from clay minerals by selective leaching is of interest because it yields residues with large specific surface areas that can be used as adsorbents of contaminants or as catalysts. Grinding produces surface modifications and therefore may significantly influence the leaching behavior. The aim of this paper is to study the effect of grinding and leaching on the structure of the vermiculite from Santa Olalla, Spain, using ⁵⁷Fe Mössbauer spectroscopy, X-ray diffraction, infrared spectroscopy, and specific surface area (S_{BET}) measurements. The study shows that grinding destroys the long range order of the vermiculite, but leaves the local structure in the environment of the Fe atoms intact, at least up to a grinding time of 10 min. The Mössbauer study shows that there is no Fe³⁺ in the tetrahedral sheets and that grinding does not lead to a significant oxidation of the structural Fe. Vermiculite ground for 4 min and leached with 1 M HCl solution at 80°C over a 24 h period was decomposed to X-ray amorphous silica with a very large specific surface area ($S_{\text{BET}} = 720 \text{ m}^2 \text{ g}^{-1}$) and with total pore volume of $0.586 \text{ cm}^3 \text{ g}^{-1}$, whereas an unground sample leached with the same acid concentration yielded a specific surface area of only $504 \text{ m}^2 \text{ g}^{-1}$. Most of the Mg²⁺ and Al³⁺ are removed from the ground sample after leaching with 1 M HCl, while large percentages of Fe₂O₃ remain with the X-ray amorphous silica. In unground vermiculite leached with 1 M HCl, a considerable amount of vermiculite remains in the residue. A sample ground for 4 min and treated with 0.25 M HCl also shows the typical vermiculite Mössbauer spectrum with an Fe²⁺/Fe³⁺ ratio similar to that of the unground vermiculite. The samples ground for 2 or 4 min and treated with 1 M HCl solution have an orange color and, according to the Mössbauer spectra, only Fe³⁺ remains. Mössbauer spectra of these samples taken at 4.2 K reveal the presence of akaganéite.

Key Words—Acid Leaching, Grinding, Mössbauer Spectroscopy, Surface Properties, Vermiculite, X-ray Amorphous Silica.

INTRODUCTION

The preparation of porous materials from clay minerals by selective leaching involves the dissolution of a portion of the clay components by treatment with acid solutions. The extent and kinetics of the clay decomposition depend on several factors: the nature of the octahedral and tetrahedral cations, temperature, treatment time, the nature and concentration of the acid, the type of clay, the particle size, and the ratio of acid to solid (Breen *et al.*, 1995; Madejová *et al.*, 1998; Novak and Cicel, 1978; Vicente-Rodríguez *et al.*, 1996; Komadel, 2003; Temuujin *et al.*, 2003a). Selective leaching with acid has been used for preparing porous silica from various clay minerals including chrysotile (Suquet, 1989), antigorite (Kosuge *et al.*, 1995), montmorillonite (Shinoda *et al.*, 1995), kaolinite (Okada *et al.*, 1998), pyrophyllite (Temuujin *et al.*, 2003b),

chlorite (Okada *et al.*, 2005), montmorillonite, synthetic saponite, and phlogopite (Okada *et al.*, 2006). Vermiculite has also been used to prepare porous silica. Suquet *et al.* (1991, 1994) reported a surface area of $270 \text{ m}^2 \text{ g}^{-1}$ for the Llano vermiculite, and Temuujin *et al.* (2003a) and Okada *et al.* (2006), using vermiculite from Transvaal, South Africa, obtained surface areas of $672 \text{ m}^2 \text{ g}^{-1}$ and $647 \text{ m}^2 \text{ g}^{-1}$, respectively. The experimental conditions used by Suquet *et al.* (1991, 1994), Temuujin *et al.* (2003a), and Okada *et al.* (2006) were: acid concentrations of 1 M HCl, 2 M HCl, and 1 M H₂SO₄ at a solid/acid mass ratio of 1:20, 1:40, and 1:50 for 2 h, 2 h, and 5 h, respectively. The South African raw vermiculite used in the latter two studies has a large K⁺ content in the interlayer space (K_{0.53}), yielding X-ray diffraction (XRD) patterns with peaks of high intensity at 12.6 Å and 12.05 Å, and another broad peak at 25.2 Å (Temuujin *et al.*, 2003a), which may be attributed to a biotite-vermiculite mixed-layer mineral, together with some vermiculite (peak at 1.45 nm).

Vermiculite has a 2:1 layer structure with Mg²⁺ serving almost exclusively as the interlayer cation. The interlayer cations are more leachable than the octahedral

* E-mail address of corresponding author:

celia@irnase.csic.es

DOI: 10.1346/CCMN.2008.0560307

cations, and the latter are more leachable than the tetrahedral cations. The chemical composition and, in particular, the substitutions occurring in the octahedral and tetrahedral sheets, play an important role in the selective leaching. Vermiculites show a high degree of substitution of Al and Fe in their structure. Temuujin *et al.* (2003a) suggest that substitution of Si^{4+} by both Al^{3+} and Fe^{3+} in the tetrahedral sheet gives rise to silica of a greater surface area than that obtained from a mineral with only Al^{3+} substitution. This observation is attributed by the authors to the slower leaching of Fe^{3+} compared to Al^{3+} , resulting in the stabilization of the tetrahedral silica sheets and preventing further condensation, which would lead to a decrease in the surface area. Independent of the correctness of this interpretation, these results show that Fe may affect the leaching of clay minerals. It is therefore important to know more about the local environment of the Fe probe sites and its change during leaching. The determination of the distribution of the Fe between and within the octahedral and tetrahedral sheets before and after grinding and leaching of vermiculite are difficult to determine. The most suitable method is Mössbauer spectroscopy.

Grinding produces surface modifications of clays. Even grinding for short times induces a considerable particle-size reduction in vermiculite. Increasing grinding time leads to severe structure degradation with loss of the lamellar shape of the crystallites and a progressive amorphization with formation of hard agglomerates by cold-welding (Sánchez-Soto *et al.*, 1995; Pérez-Maqueda *et al.*, 2004). The resulting structural defects, the increase in the surface area, and the porosity produced by grinding should influence significantly the leaching behavior, as happens with talc and pyrophyllite (Temuujin *et al.*, 2002, 2003b). Grinding could also affect the dissolution of Fe by acid treatment of vermiculite.

Taking the above considerations into account, the aim of this paper was to use chemical analysis, XRD, Fourier transform infrared (FTIR) spectroscopy, specific surface area (S_{BET}) measurements, and scanning electron microscopy (SEM) to study the effects of grinding and leaching on the structure of the Santa Olalla vermiculite. Most importantly, however, Mössbauer spectroscopy will help to elucidate the fate of the structural Fe during leaching.

EXPERIMENTAL

Vermiculite from Santa Olalla (Huelva, Spain) was used as the starting material. Its half-unit-cell composition is $(\text{Si}_{2.64}\text{Al}_{1.36})(\text{Mg}_{2.48}\text{Fe}_{0.324}\text{Fe}_{0.036}\text{Al}_{0.14}\text{Ti}_{0.01}\text{Mn}_{0.01})\text{O}_{10}(\text{OH})_2\text{Mg}_{0.439}$ (Pérez-Maqueda *et al.*, 2001). Large flakes were ground in a knife mill (Netzsch ZSM-1, Germany) and sieved. Vermiculite particles $<80\ \mu\text{m}$ in size were used for the experiments. This material is referred to hereafter as V.

Grinding experiments were carried out with batches of 10 g of vermiculite using a vibratory mill (Herzog HSM-100), which works through friction and impact at 1500 rpm. Grinding times of 2 min (V2m) and 4 min (V4m) were selected for the subsequent acid treatments because these samples were found to have maximum specific surface areas (S_{BET}) before leaching.

Vermiculite samples ($<80\ \mu\text{m}$) left untreated (V) and ground for 2 and 4 min (samples V2m, V4m) were leached with HCl solutions of different concentrations, 0.25 M [samples V (0.25 M), V2m (0.25 M), V4m (0.25 M)] and 1.0 M [samples V (1 M), V2m (1 M), V4m (1 M)] at a solid/acid mass ratio of 1:20. The suspensions were maintained at 80°C with stirring for 24 h. The samples were cooled and washed with distilled water until the supernatant was free of acid. The samples were then dried at 60°C overnight.

The chemical compositions were determined by X-ray fluorescence (XRF) (Siemens, SRS 3000) and atomic absorption spectroscopy (AAS) (Perkin Elmer, model 1120B). A direct examination of the particles was carried out using a scanning electron microscope (Jeol, JSM 5400). X-ray diffraction patterns were obtained using a Siemens Kristalloflex D-5000 diffractometer at 36 kV and 36 mA with $\text{CuK}\alpha$ radiation and a graphite monochromator. Infrared spectroscopy was carried out using KBr pellets with a Nicolet 510P FTIR Spectrometer. The pellets were also heated for 24 h at 110, 200, 300, and 400°C .

The S_{BET} was determined using the Brunauer Emmet Teller (BET) method. The adsorption of N_2 was measured using a Micromeritics 2200 A model (Norcross, Georgia) automatic system. The samples were out-gassed by heating at 200°C under a flow of helium for 12 h. The data were recorded at p/p_0 between 0.0005 and 0.99. The micropore-size distributions were determined using the Horvath-Kawazoe method (1983).

The Mössbauer spectra were recorded with a conventional spectrometer using a sinusoidal velocity waveform and a source of ^{57}Co in Rh. Low-temperature measurements were performed in a liquid He bath cryostat with both source and absorber cooled to 4.2 K. Isomer shifts (IS) are given with respect to the source and can be converted to shifts relative to α -iron at the same temperature as the absorber by adding 0.11 mm/s. In order to account for distributions of the quadrupole splittings (QS) around the mean values for each doublet, the spectra were fitted with Voigt profile lineshapes grouped into quadrupole doublets. Wherever warranted by an asymmetrical broadening of the doublets, a correlation between the Gaussian distribution of the quadrupole splittings and the isomer shifts was constructed. Because the left components of all Fe^{3+} and Fe^{2+} doublets are unresolved, the IS for the two Fe^{2+} doublets required to obtain good fits was assumed to be the same. In some cases, texture effects had to be modeled. A broad background, attributable to magnetic hyperfine interac-

Table 1. Surface areas and chemical composition of unground, ground, and acid-leached vermiculites with HCl solution at two concentrations (0.25 and 1 M).

Sample	Surface area (m ² g ⁻¹)	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃
V	15.40	43.60	32.15	15.62	7.50
V (0.25 M)	73.23	49.71	21.28	20.12	7.33
V (1 M)	504.28	81.78	6.00	7.05	4.04
V2m	32.05	43.66	31.87	15.47	7.74
V2m (0.25 M)	261.45	50.65	19.49	21.10	7.48
V2m (1 M)	689.11	84.03	1.01	1.80	12.01
V4m	33.29	43.62	31.98	15.57	7.57
V4m (0.25 M)	308.37	50.73	18.44	21.86	7.41
V4m (1 M)	720.26	82.59	1.01	1.60	13.55

tions of slowly relaxing paramagnetic Fe³⁺ ions was found even in some of the room-temperature spectra and approximated by a broad Voigt profile.

RESULTS AND DISCUSSION

The chemical composition and surface area of the starting material (Table 1) are in good agreement with values determined by different methods and published elsewhere (Perez-Rodriguez *et al.*, 2003).

Grinding does not change the chemical composition significantly (Table 1). The surface area of the ground samples is about twice as large as that of the starting vermiculite (Table 1). The effect of grinding on the structure of the vermiculite, however, is dramatic. The XRD patterns of the original and of the ground vermiculite after different grinding times revealed that a decrease in intensity and broadening of the 00 l diffraction peaks occurs as a function of grinding time and indicates a loss of periodicity perpendicular to the layer plane (Figure 1). Perez-Maqueda *et al.* (2004) showed a decrease in particle size after grinding this

vermiculite for 4 min. The crystallite size has not been calculated because in this sample there is a contribution of both the small particle size and the random displacement and imperfection in crystal order (mainly produced by edge alteration) to the broadening of the 00 l diffraction. The basal reflections disappear completely after grinding for 15 min (not shown in Figure 1). The particle size reaches a minimum value after grinding for 2 and 4 min. At longer grinding times a progressive agglomeration of the particles leads to an enlargement of the particles in spite of increasing amorphization. After 4 min of grinding, the samples show the greatest surface area, in agreement with the smallest particle size.

In contrast, the Mössbauer spectra of the vermiculite are only slightly affected by grinding (Table 2, Figure 2). The spectra of the original vermiculite (V; Figure 2 top left) and of the ground sample (V4m; Figure 2, top right) can be interpreted as a superposition of three doublets. One represents Fe³⁺, the other two, Fe²⁺, all in octahedral positions. According to the criteria given by Rancourt *et al.* (1992), we could not identify Fe³⁺ in tetrahedral sites. The IS as well as the

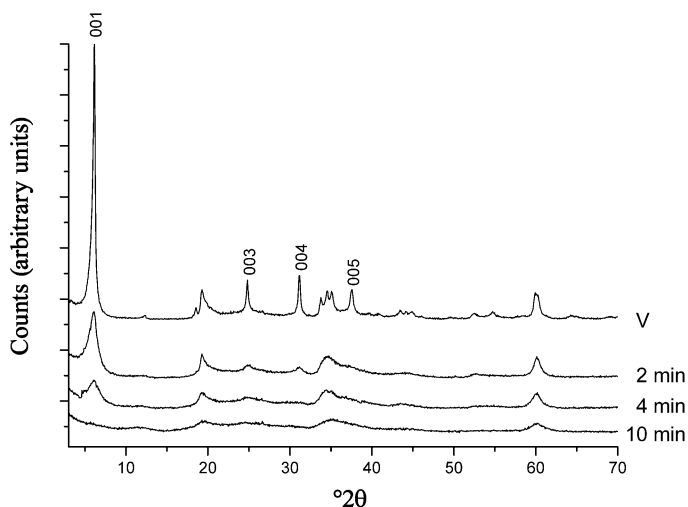


Figure 1. XRD patterns of unground vermiculite (V), and of vermiculite ground for 2, 4, and 10 min (V2m, V4m, V10m).

Table 2. Room-temperature values of the isomer shifts (IS [mm s^{-1}], given vs. the $^{57}\text{Co}:\text{Rh}$ source), quadrupole splittings (QS [mm/s]), and relative areas (A [%]) of the different Fe sites in the vermiculite from Santa Olalla after grinding and/or HCl leaching. For comparison, the data for the starting material are given.

Specimen	Fe^{3+}			Fe^{2+}					
	IS	QS	A	Site 1			Site 2		
				IS	QS	A	IS	QS	A
V	0.27	1.05	90.2	0.99	2.67	5.8	0.99	2.28	4.0
V (1 M)	0.23	0.82	94.7	0.99	2.65	2.7	0.99	2.12	2.6
V4m	0.25	0.93	91.1	0.99	2.76	4.3	0.99	2.27	4.6
V4m (0.25 M)	0.25	0.89	94.0	0.99	2.72	3.1	0.99	2.10	2.9
V4m (1 M)	0.26	0.67	100	—	—	—	—	—	—

QS of the Fe^{3+} site became slightly smaller after grinding (Table 2). The changes in IS and QS of the Fe^{2+} components upon grinding are small, and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is almost unaffected. This is surprising, since grinding in the vibratory mill is considered a highly energetic process.

The FTIR spectra of V and the ground sample (V4m) are almost identical (Figure 3). The spectra of the starting material and the ground sample are similar to the spectra for Santa Olalla vermiculite published previously (de La Calle *et al.*, 1996; Avilés, 1998), showing the essential absorption bands assigned to OH, Si–O, Al–O, and Mg–O lattice vibrations. Between 4000 and 3000 cm^{-1} , there is a broad band attributed to structural OH-groups and water. After heating the pellet

of V at 300°C the water absorption bands decrease and bands at 3700 cm^{-1} and 3650 cm^{-1} appear, which can be assigned to structural OH groups surrounded by ($\text{Mg}^{2+} \text{Mg}^{2+} \text{Mg}^{2+}$) and ($\text{Mg}^{2+} \text{Mg}^{2+} \text{R}^{3+}$) in the octahedral sheets, respectively. In the heated pellet of V4m, the spectra show a strong decrease in the intensity of these bands, indicating that grinding destroys the structural OH bands. The discrepancy between the XRD results on the one hand and the Mössbauer and IR spectra on the other, shows clearly that grinding destroys the long-range order of the vermiculite, but leaves the local structure around the probe atoms intact, at least up to a grinding time of 4 min.

Acid leaching, however, changed the vermiculite substantially and the acid attack is enhanced further by

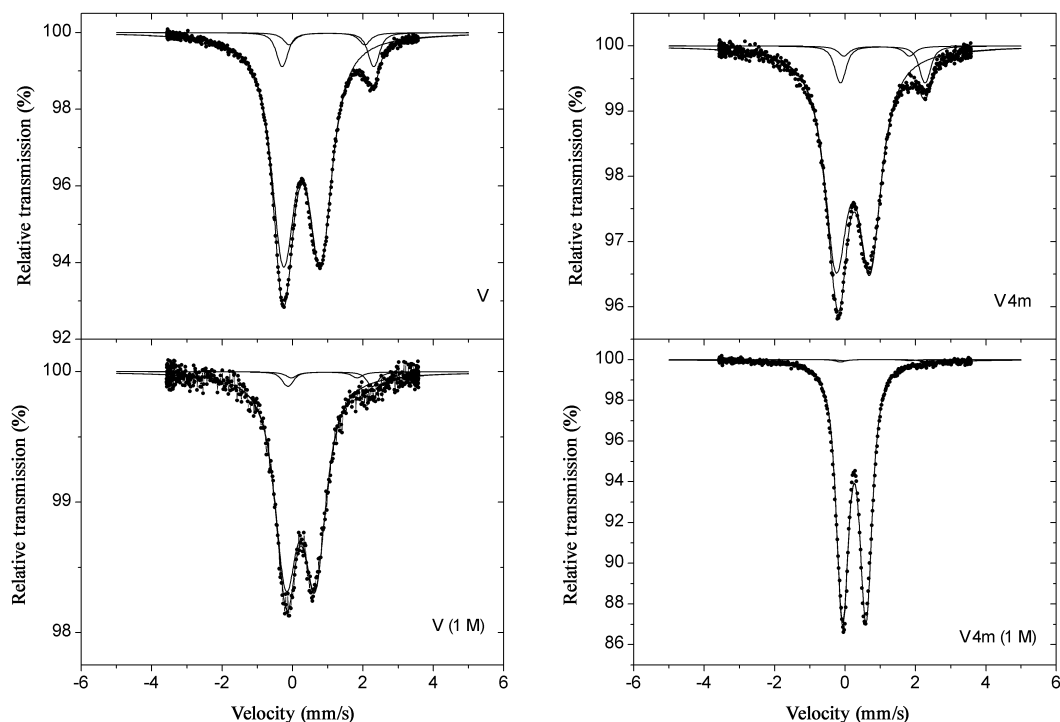


Figure 2. Room-temperature Mössbauer spectra for the original Santa Olalla vermiculite (V), vermiculite ground for 4 min (V4m), and both treated with 1 M HCl.

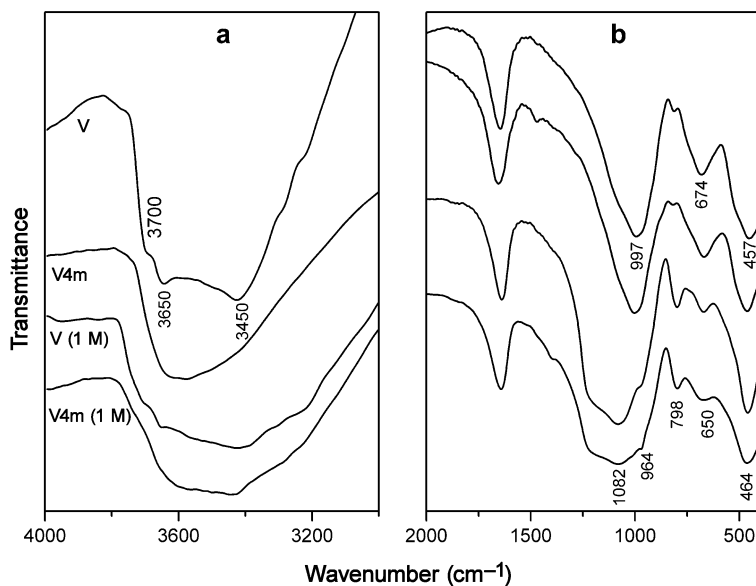


Figure 3. FTIR spectra of unground vermiculite (V) and vermiculite ground for 4 min (V4m) and treated with 1 M HCl [V (1 M), V4m (1 M)]: (a) samples heated at 300°C; and (b) at room temperature.

grinding. This was already demonstrated by the chemical composition of the solids remaining after leaching (Table 1). The SiO_2 contents are similar for the unground and ground samples, and they increased with increasing acid concentration (Table 1). The maximum SiO_2 content found was $\sim 84\%$. This value is less than that (99.7%) obtained for vermiculite by Temujin *et al.* (2003a), but those authors had leached with 2 M HCl for 2 h. The MgO content decreased with increasing acid concentration and only a few % of Mg remained in the sample after leaching with 1 M HCl solution. The concentration of Al_2O_3 in the leaching residue increased on leaching with 0.25 M HCl, and then dropped sharply during leaching with 1 M HCl (Table 1). The increased Al concentration found on leaching with 0.25 M HCl arose because Mg^{2+} and some Fe had been removed, while Al^{3+} was still largely undissolved. After leaching the ground samples (V2m and V4m) with 1 M HCl solution, the Al content decreased to $\sim 1.5\%$, indicating that practically all the Al had been leached from both the octahedral and the tetrahedral sheets (Table 1). In the unground V sample, a large percentage of Al remained in the solid, even after treatment with 1 M HCl. This may suggest that the Al is less leachable, probably because it is mainly located in the tetrahedral sheets of the Santa Olalla vermiculite. The leaching behavior of our sample is in good agreement with the observation of Kalinowski and Schweda (2007).

Iron turns out to be the least soluble element except for Si, under the leaching conditions applied in this work. The Fe content of the samples leached with 0.25 M HCl solution is diminished only slightly with respect to the original vermiculite (Table 1). Thus, only a very small proportion of Fe has been leached, together

with Mg. This is confirmed by the concentration of Fe found in the solution after the acid attack, which corresponded to 0.95% of the total Fe content. After leaching with 1 M HCl, however, there are important differences in the Fe content of the unground and the ground samples. The unground specimen shows a significant decrease in the Fe_2O_3 content, to $\sim 4\%$. On the other hand, the ground vermiculites show a strong increase in Fe_2O_3 , which reaches concentrations of 12.0% and 13.6% in V2m and V4m, respectively, as a consequence of the removal of Mg and Al. Summing up the results for the ground samples, one can state that in 0.25 M HCl, very little Fe^{3+} and some Mg^{2+} are dissolved, while virtually all Mg^{2+} and most of the

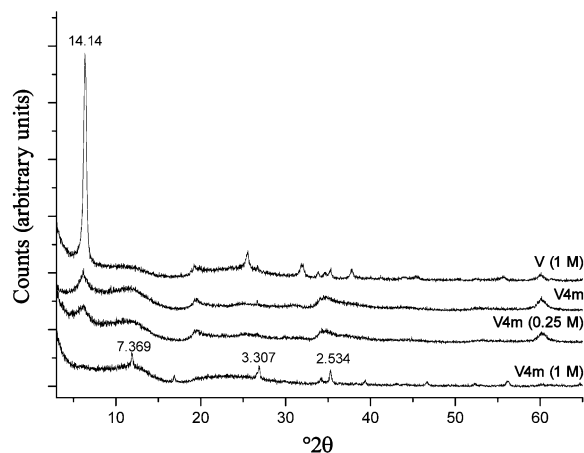


Figure 4. XRD patterns of unground vermiculite, of vermiculite treated with 1 M HCl [V (1 M)], and of vermiculite ground for 4 min (V4m) and leached with 0.25 and 1 M HCl [V4m (0.25 M), V4m (1 M)].

Al^{3+} , including that in the tetrahedral sheet, are removed in 1 M HCl. The solid remaining after grinding and acid leaching consists mainly of oxides of Si and Fe.

The XRD pattern of the original vermiculite sample treated with 1 M HCl (Figure 4) shows severe attack on the mineral (compare with the V pattern in Figure 1), although the 001 diffraction peak at 14 Å is still present at low intensity, and higher-order 00 l reflections are still visible, indicating that part of the vermiculite has resisted the acid attack. The XRD pattern of V4m after leaching with 1 M HCl no longer shows any characteristic vermiculite peak. Instead, new peaks at 7.396 Å, 3.307 Å, 2.534 Å, *etc.* appear; these can be assigned to akaganéite (β -FeOOH). According to the chemical analysis, the dominant material after leaching is silica. These results indicate that the residue after leaching consists of X-ray amorphous (porous) silica and akaganéite formed from the structural Fe of the vermiculite. The residual solid obtained after leaching has an orange color whereas the residue of original vermiculite leached with 1 M HCl is light yellow.

The FTIR spectra of V and V4m after leaching with the 1 M HCl solution (Figure 3) are very similar. The dominant features are absorption bands at 1082 cm^{-1} , 798 cm^{-1} , and 464 cm^{-1} , which can be assigned to the stretching and bending vibrations of SiO_4 tetrahedra (Farmer, 1974). These features are typical of X-ray amorphous silica. In the acid-treated original vermiculite, a peak at 997 cm^{-1} indicates that not all of the vermiculite has been destroyed. The band at 964 cm^{-1} probably originates from the formation of Si-OH groups (silanosilation; Temuujin, 2003a) in the leached product. The band at 674 cm^{-1} of V, V4m, and V (1 M HCl) can be attributed to the ν_3 mode of Mg-OH. A small, broad absorption band at 650 cm^{-1} , appearing in sample V4m (1 M), could originate from the akaganéite since Mg is almost released from the lattice. The IR spectra of V (1 M), after heating, correspond to bands at 3700 cm^{-1} and 3650 cm^{-1} , indicating that some vermiculite still remains in the residue after acid treatment. These bands do not appear in sample V4m (1 M). In both samples, the band at 3450 cm^{-1} has been more difficult to remove during the heating, probably due to the silanosilation of the leached products.

The room-temperature Mössbauer spectrum of the ground vermiculite (V4m) is still nearly the same as that of the original vermiculite (Figure 2, Table 2), except for a slight decrease in the QS and IS values and a slight broadening of the lines. This shows that grinding has little influence on the local environment of the Fe. Grinding alone also leaves the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio unchanged and hence causes neither oxidation nor reduction. The spectra of the original vermiculite leached with 1 M HCl (V 1 M) and of the ground vermiculite treated with 0.25 M HCl (V4m 0.25 M) show a reduced $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, either because of oxidation or because of preferential dissolution of Fe^{2+} . Again, a decrease in

QS and IS is observed, indicating a moderate change in the local environment of the Fe^{3+} . A substantial change in the Mössbauer spectrum is observed on leaching the ground vermiculite in 1 M HCl [sample V4m (1 M)]. Now the QS has decreased to 0.66 mm/s and the lines are much narrower than in all other cases, the latter showing that a well defined Fe compound has been formed.

The XRD results suggest that this compound is akaganéite, and this is confirmed by the Mössbauer spectra taken at 4.2 K (Figure 5). At this temperature, the spectra of the original vermiculite (V) and of the ground vermiculite, leached in 0.25 M HCl, are still very similar, exhibiting the dominant Fe^{3+} quadrupole doublet, a minor doublet of Fe^{2+} and a broad component that can be attributed to slow paramagnetic relaxation of some of the Fe^{3+} in the octahedral sheets of the

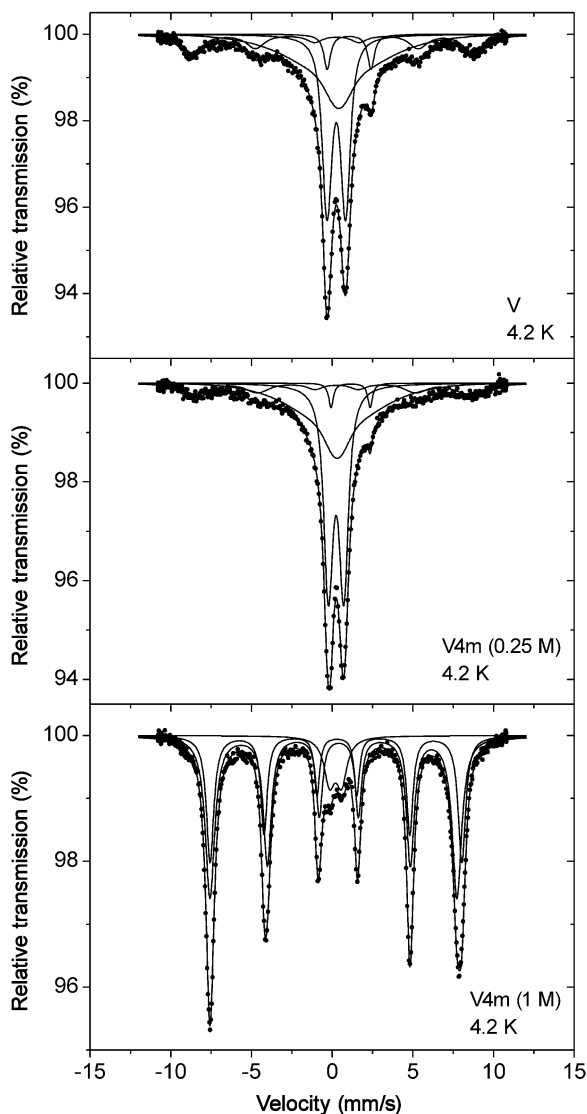


Figure 5. Mössbauer spectra taken at 4.2 K.

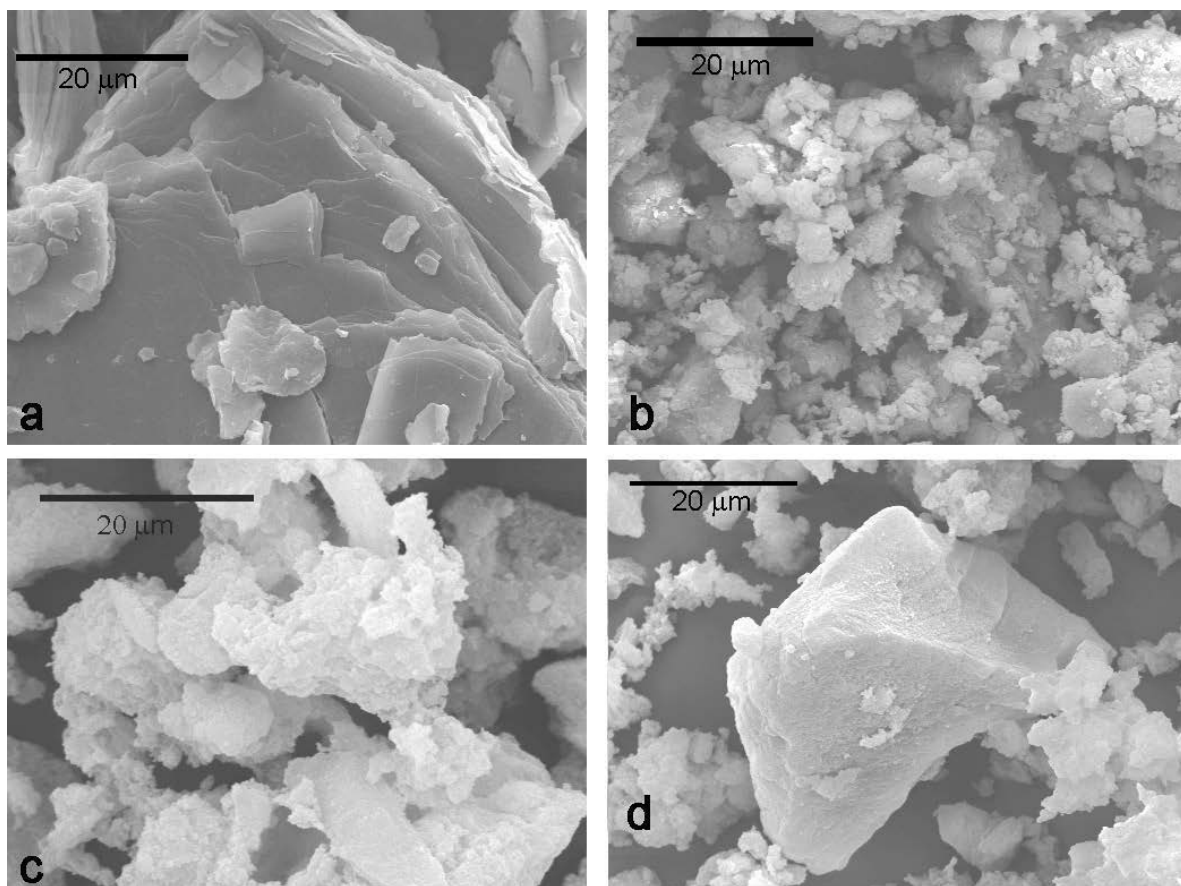


Figure 6. SEM images of (a) unground vermiculite; (b) vermiculite ground for 4 min; (c) and then leached with 1 M HCl (c and d). Note the change in magnification.

vermiculite, the six-line pattern with a hyperfine field of ~ 53 T being caused by Fe^{3+} ions relaxing more slowly than those which yield the broad but structureless pattern. This indicates the strong resistance of the vermiculites against acid attack. This observation is in excellent agreement with the experiments by Kalonowski and Schweda (2007), and with the Mössbauer data presented by Ferrow (2002). The spectrum of sample V4m (1 M) is altogether different. The dominant magnetically split part is the typical six-line pattern of akaganéite (Murad, 1979), which can be fitted by a superposition of two sextets with slightly different hyperfine fields (48.4 and 47.5 T), and significantly different quadrupole interactions (-0.33 and -0.06 mm/s). The additional weak quadrupole doublet may represent a minor remnant fraction of the vermiculite phase.

The SEM image of the vermiculite ground for 4 min (V4m) shows a significant decrease in the particle size (Figure 6b) when compared with the original vermiculite (V, Figure 6a); in addition, the edges of the sample are altered extensively. After leaching [V4m (1 M)], the particles seem to increase their volume due to swelling or delamination (Figure 6c, note the increase in the

magnification), and the subsequent transformation to X-ray amorphous silica. Particles keeping their hexagonal shape, but extending perpendicular to the plate

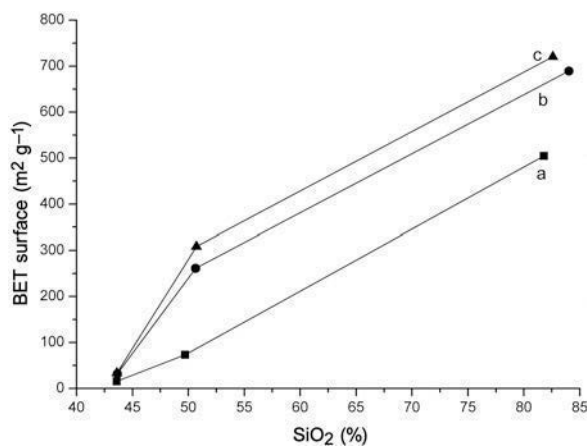


Figure 7. Relationship between SiO_2 percentages and BET surface area (S_{BET}): (a) original vermiculite, and leached with 0.25 M and 1 M HCl; (b) vermiculite ground for 2 min and leached with 0.25 M and 1 M HCl; (c) vermiculite ground for 4 min and leached with 0.25 M and 1 M HCl.

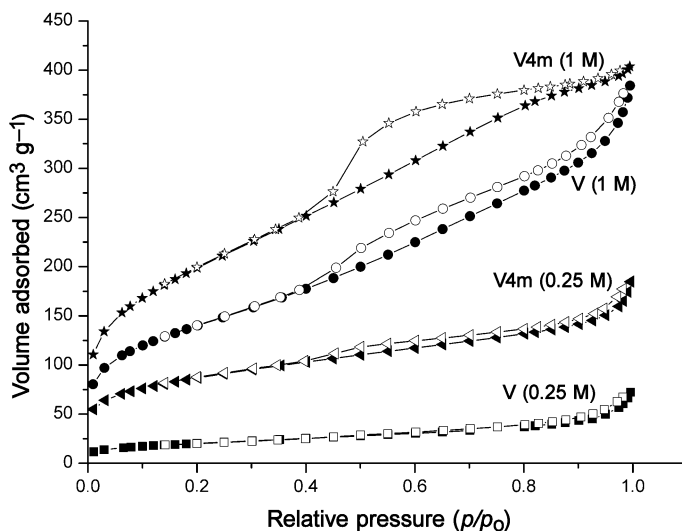


Figure 8. Nitrogen adsorption isotherms of unground vermiculite and of vermiculite ground for 4 min and leached with 0.25 M [V (0.25 M), V4m (0.25 M)] and 1 M HCl [V (1 M), V4m (1 M)].

dimension (Figure 6d), are not so rare. However, there is no evidence for akaganéite crystallites, although XRD and Mössbauer spectroscopy show unambiguously the presence of a substantial amount of akaganéite in this sample. In addition, microprobe analysis revealed an homogeneous distribution of Fe and Si in the samples. This can only be understood if the akaganéite particles are smaller than the spot diameter of the electron beam used for the microprobe analysis, *i.e.* $<0.1 \mu\text{m}$ crystallites that are homogeneously distributed in the silica network and too small to be resolved in the SEM images.

Acid-leached clay minerals are of interest because of their large surface areas. The specific surface areas (S_{BET}) increased as a function of the SiO_2 content (Figure 7) when the concentration of the leaching acid was increased. The greatest S_{BET} value was found for the vermiculite ground for 4 min (V4m) and leached with 1 M HCl, reaching a value of $720 \text{ m}^2/\text{g}$. This is greater than the values found by Temuujin *et al.* (2003a) and Okada *et al.* (2006) ($672 \text{ m}^2/\text{g}^{-1}$ and $647 \text{ m}^2/\text{g}^{-1}$, respectively) which are considered to be among the largest values reported for porous materials obtained from clay minerals by leaching. The specific surface area (S_{BET}) obtained from the original sample after treatment with 1 M HCl was only $504 \text{ m}^2/\text{g}^{-1}$. This value is in good agreement with the value obtained by Temuujin at the same acid concentration, but at a shorter reaction time. Little difference was observed between samples ground for 2 (V2m) and 4 min (V4m), and the considerably smaller surface area of the leached, unground vermiculite clearly indicates the effect of pretreatment by grinding.

The nitrogen adsorption-desorption isotherms of the V and V4m vermiculite after leaching with 0.25 M and 1 M HCl solution [V (0.25 M), V (1 M), and V4m (0.25 M), V4m (1 M)] are of type I in the IUPAC

classification, characteristic of microporous materials (Figure 8). The presence of mesopores is also revealed by the hysteresis that appears in the isotherms. The isotherms become more like type IV after grinding and increasing the concentration of the acid solution. Significant differences occur in the isotherms of the unground and the ground vermiculites leached with 1 M HCl solution.

The representation of pore diameter against differential pore volume shows a peak at $\sim 7 \text{ \AA}$ diameter for both the unground and the ground samples. The intensity of the peak increases in the ground sample. This value is in fair agreement with the value of 6 \AA obtained by Temuujin *et al.* (2003a) for the South African vermiculite. Temuujin *et al.* (2003a) concluded that the large surface area is due to the stabilization of the tetrahedral sheets by the Fe ions incorporated. However, we established almost the same values for surface area, though our vermiculite did not incorporate any Fe^{3+} in the tetrahedral sheets. Thus, it is more likely that the finely divided Fe oxyhydroxide is responsible for stabilizing the large surface areas obtained.

This could be a general phenomenon, since residual Fe has often been described in acid-treated clays, when the concentration of the acid used for leaching was $<3 \text{ M}$ (*e.g.* Breen *et al.* 1997; Rhodes and Brown, 1995; Cseri *et al.*, 1995). This is also true for commercially available samples (Cseri *et al.* 1995).

ACKNOWLEDGMENTS

The authors thank the Spanish Comisión Interministerial de Ciencia y Tecnología (CICYT) for financial support under project no. AGL-2005-0164, and the Junta de Andalucía, through project no. P06-FQM-1909, and PAI RMN 166.

REFERENCES

- Avilés, M.A. (1998) Síntesis de materiales cerámicos avanzados mediante la reducción carbotérmica de vermiculita. PhD thesis, Universidad de Sevilla, Spain.
- Breen, C., Madejová, J., and Komadel, P. (1995) Characterization of moderately acid-treated, size-fractionated montmorillonites using IR and MAS NMR spectroscopy and thermal analysis. *Journal of Materials Chemistry*, **5**, 469–474.
- Breen, C., Zahoor, F.D., Madejová, J., and Komadel, P. (1997) Characterization and catalytic activity of acid-treated, size-fractionated smectites. *Journal of Physical Chemistry B*, **101**, 5324–5331.
- Cseri, T., Békássy, S., Figueras, F., Cseke, E., de Menorval, L.C., and Dutartre, R. (1995) Characterization of clay-based K catalysts and their application in Friedel-Crafts alkylation of aromatics. *Applied Catalysis A*, **132**, 141–155.
- De la Calle, C., Suquet, H., and Pons, C.H. (1996) Evolution of benzylammonium-vermiculite and ornitine-vermiculite intercalates. *Clays and Clay Minerals*, **44**, 68–76.
- Farmer, V.C. (1974) *The Infrared Spectra of Minerals*. Monograph 4, Mineral Society, London. 539 pp.
- Ferrow, E.A. (2002) Experimental weathering of biotite, muscovite and vermiculite: A Mössbauer spectroscopic study. *European Journal of Mineralogy*, **14**, 85–95.
- Horvath, G. and Kawazoe, K. (1983) Methods for calculation of effective pore size distribution. I. Molecular sieve carbon. *Journal of Chemical Engineering, Japan*, **16**, 420–475.
- Kalinowski, B.E. and Schweda, P. (2007) Rates and non-stoichiometry of vermiculite dissolution at 22°C. *Geoderma*, **60**, 367–385.
- Komadel, P. (2003) Chemically modified smectite. *Clay Minerals*, **38**, 127–138.
- Kosuge, K., Shimada, K. and Tsunashima, A. (1995) Micropore formation by acid treatment of antigorite. *Chemistry of Materials*, **7**, 2241–2246.
- Madejová, J., Bujdak, J., Janek, M., and Komadel, P. (1998) Comparative FT-IR study of structural modifications during acid treatment of dioctahedral smectites and hectorite. *Spectrochimica Acta A*, **54**, 1397–1406.
- Murad, E. (1979) Mössbauer and X-ray data on β -FeOOH (akaganéite). *Clay Minerals*, **14**, 273–283.
- Novak, I. and Čičel, B. (1978) Dissolution of smectites in hydrochloric acid: II. Dissolution rate as a function of crystallochemical composition. *Clays and Clay Minerals*, **26**, 341–344.
- Okada, K., Shimai, A., Takei, T., Hayashi, S., Yasumori, A., and Mackenzie, K.J.D. (1998) Preparation of microporous silica from metakaolinite by selective leaching method. *Microporous and Mesoporous Materials*, **21**, 289–296.
- Okada, K., Arimitsu, N., Kameshima, Y., Nakajima, A., and Mackenzie, K.J.D. (2005) Preparation of porous silica from chlorite by selective acid leaching. *Applied Clay Science*, **30**, 116–124.
- Okada, K., Arimitsu, N., Kameshima, Y., Nakajima, A., and Mackenzie, K.J.D. (2006) Solid acidity of 2:1 type clay minerals activated by selective leaching. *Applied Clay Science*, **31**, 185–193.
- Pérez-Maqueda, L.A., Caneo, O.B., Poyato, J., and Pérez-Rodríguez, J.L. (2001) Preparation and characterization of micron and submicron-sized vermiculite. *Physics and Chemistry of Minerals*, **28**, 61–66.
- Pérez-Maqueda, L.A., Jiménez de Haro, M.C., Poyato, J., and Pérez-Rodríguez, J.L. (2004) Comparative study of ground and sonicated vermiculite. *Journal of Materials Science*, **39**, 5347–5351.
- Pérez-Rodríguez, J.L., Pérez-Maqueda, L.A., Poyato, J., and Lerf, A. (2003) Layer modification by mechanical treatment of the Santa Olalla vermiculite. *Solid State Phenomena*, **90–91**, 515–520.
- Rhodes, C.N. and Brown, D.B. (1995) Autotransformation and aging of acid-treated montmorillonite catalysts: a solid state ^{27}Al NMR study. *Journal of the Chemical Society, Faraday Transactions*, **91**, 1031–1035.
- Rancourt, D.G., Dong, M.Z., and Lalonde, A.E. (1992) Mössbauer spectroscopy of tetrahedral Fe^{3+} in trioctahedral micas. *American Mineralogist*, **77**, 34–43.
- Sánchez-Soto, P.J., Ruiz-Conde, A., Avilés, M.A., Justo, A., and Pérez-Rodríguez, J.L. (1995) Mechanochemical effects on vermiculite and its influence on the synthesis of nitrogen ceramics. In: *Ceramics: Charting the Future* (P. Vicenze editor). Techna Srl., Spain.
- Shinoda, T., Onaka, M., and Izumi, Y. (1995) Proposed models of mesopore structures in sulfuric acid-treated montmorillonites and K10. *Chemistry Letters*, **7**, 495–496.
- Suquet, H. (1989) Effect of dry grinding and leaching on the crystal structure of chrysotile. *Clays and Clay Minerals*, **37**, 439–445.
- Suquet, H., Chevalier, S., Marcilly, C., and Barthomeuf, D. (1991) Preparation of porous materials by chemical activation of the Llano vermiculite. *Clays and Minerals*, **26**, 49–60.
- Suquet, H., Franck, R., Lambert, J.F., Elsass, C.M., and Chevalier, S. (1994) Catalytic properties of two pre-cracking matrices: a leached vermiculite and Al-pillared saponite. *Applied Clay Science*, **8**, 349–364.
- Temuujin, J., Okada, K., Jadamba, T.S., Mackenzie, K.J.D., and Amarsanaa, J. (2002) Effect of grinding on the preparation of porous material from talc by selective leaching. *Journal of Materials Science Letters*, **21**, 1607–1609.
- Temuujin, J., Okada, K., and Mackenzie, K.J.D. (2003a) Preparation of porous silica from vermiculite by selective leaching. *Applied Clay Science*, **22**, 187–195.
- Temuujin, J., Okada, K., Jadamba, T.S., Mackenzie, K.J.D., and Amarsanaa, J. (2003b) Effect of grinding on the leaching behaviour of pyrophyllite. *Journal of the European Ceramic Society*, **23**, 1277–1282.
- Vicente-Rodríguez, M.A., Suarez, M., Bañares-Muñoz, M.A., and González, J.D. (1996) Comparative FT-IR. Study of the removal of octahedral cations and structural modifications during acid treatment of several silicates. *Spectrochimica Acta A*, **52**, 1685–1694.

(Received 4 April 2007; revised 17 March 2008; Ms. 0011; A.E. P. Heaney)