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# Structural Changes in Vermiculites Induced by Temperature, Pressure, Irradiation, and Chemical Treatments

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## Abstract

Depending on the treatment, the crystallinity increase of vermiculite may be accompanied by the enhancement of the majority starting phase, and the crystallinity loss may be accompanied by the appearance or disappearance of interstratified phases. Starting vermiculites with high  $K^+$  content in the interlayer have more interstratified phases and lower water content and are less crystalline. The crystallinity loss of vermiculite and therefore the structural disorder increase are caused by the structural water loss. On the contrary, the crystallinity increase is produced by water gain. The vermiculite transformation by structural water loss occurs with temperature increase, vacuum, irradiation with microwaves or ultraviolet, and alcohol or acidic treatment. On the contrary, the transformation by water gain occurs in vermiculites treated with hydrogen peroxide and in those subjected to ionic metal exchange. These treatments provide evaluable information on the relationship between the structure of vermiculites and their industrial applications. The changes suffered by vermiculites due to the treatments applied could give light to ambiguities about their geological origin and hydrothermal and/or supergene processes.

**Keywords:** vermiculite, structural changes, physical and chemical treatments

## 1. Introduction

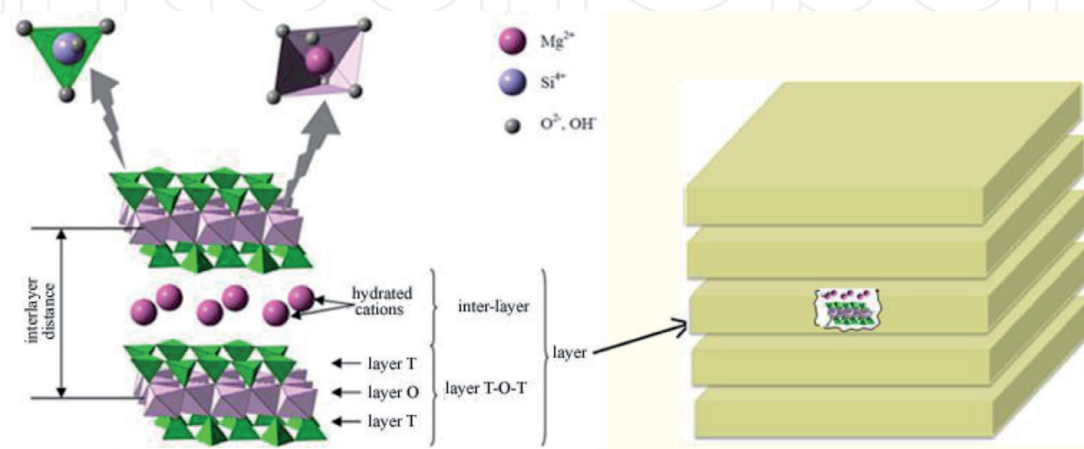
Vermiculite is a mineral that belongs to the phyllosilicate subclass of the silicate class. It has an appearance similar to micas at macroscopic level (**Figure 1**), with varied colors (green, yellow, to brown), leafy habit, hardness about 2, and a density between 2.4 and 2.7 g/cm<sup>3</sup>.

Its structure (**Figure 2**) corresponds to that of the 2:1 group [1], which is composed of two T-O-T layers joined by an interlayer. The T-O-T layer is composed of an octahedral (O) sheet of  $Mg^{2+}$ , located between two tetrahedral sheets (T) of  $Si^{4+}$ . The interlayer is formed by an octahedral sheet of  $Mg^{2+}$  bound to oxygens or  $OH^-$  groups. In addition, it contains water.

In vermiculite, isomorphic substitutions, especially in the tetrahedral sheets of  $Si^{4+}$  to  $Al^{3+}$ , are very common. As a consequence of the positive charge difference, compensation occurs with cations in the interlayer space, mainly  $Mg^{2+}$ , as mentioned before.



**Figure 1.**  
Vermiculite appearance in hand sample.



**Figure 2.**  
Vermiculite structure.

This structure, with spatial group  $C2/c$ , is generally disordered [2], that is, it shows stacking defects that alter the regular alternation of the layers parallel to crystallographic axis  $b$  (Figure 3).

Due to the presence of water and  $\text{OH}^-$  groups, vermiculite can undergo hydration-dehydration processes that depend on various factors such as temperature, pressure, particle size, relative humidity, and chemical composition [1, 3–10].

The hydration state of vermiculites is defined by the number of layers of water in the interlayer space, with phases having zero, one, and two water layers. These phases were named by [11] as 0-WLHS (state of hydration with 0 water layers), 1-WLHS (state of hydration with 1 water layer), and 2-WLHS (state of hydration with 2 water layers), respectively. As an example, for Mg-vermiculite the basal distances are  $9.02 \text{ \AA}$  for 0-WLHS,  $11.50 \text{ \AA}$  for 1-WLHS, and  $14.40 \text{ \AA}$  for 2-WLHS [9–12].

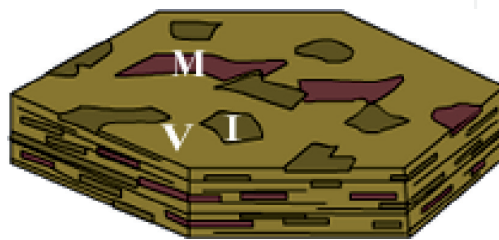
The chemical formula of vermiculite is  $\text{X}_4(\text{Y}_{2-3})\text{O}_{10}(\text{OH})_2\text{M}, n\text{H}_2\text{O}$ , where X represents the tetrahedral positions ( $\text{Si}^{4+}$  y  $\text{Al}^{3+}$ ), Y the octahedral positions ( $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ti}^{4+}$ , etc.), and M the cations located in the interlayer space ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , etc.) to compensate the charges, as a consequence of the isomorphic substitutions.

In addition to the described mineral that corresponds to vermiculite in the strict sense, there are the so-called commercial vermiculites. These vermiculites consist of various interstratified of mica/vermiculite, vermiculite with different states of hydration, mixtures of mica and vermiculite, etc. The distribution of the different phases would be mosaic-type (Figure 4).

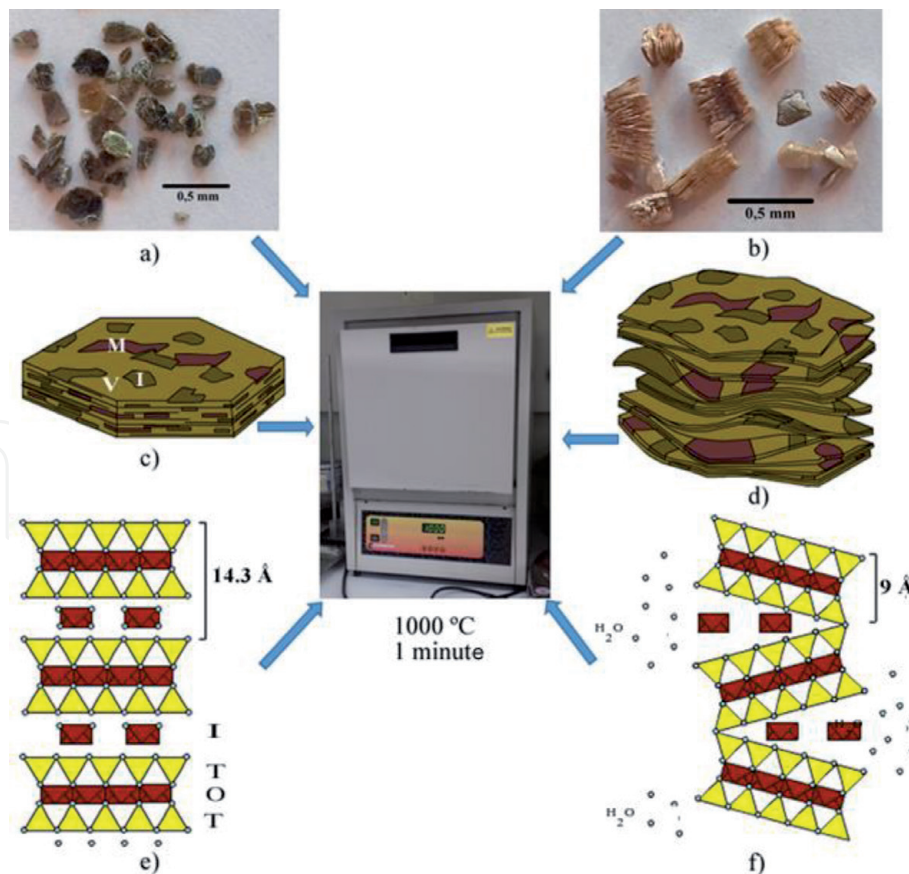
The main characteristic of commercial vermiculites is their exfoliation and expansion capacity when the vermiculite is abruptly heated, and that occurs due to the loss of water molecules located between the silicate sheets (Figure 5).



**Figure 3.**  
 Disordered layers in the vermiculite structure.



**Figure 4.**  
 Mosaic distribution of different phases in a commercial vermiculite (modified from Hillier et al. [15], with permission).



**Figure 5.**  
 Exfoliation mechanism scheme of a commercial vermiculite when heated at 1000°C for 1 minute; (a) commercial vermiculite; (b) exfoliated commercial vermiculite; (c) scheme of the arrangement in domains of the different intergrowth phases in a particle of a commercial vermiculite; (d) diagram of the exfoliated particle; (e) structure of an ideal vermiculite; (f) structure of the exfoliated ideal vermiculite. Note: Schemes (c) and (d) modified from Hillier et al. [15] with permission.

Authors such as [13] and later [14] found that the greatest exfoliation is achieved in the case of regular mica-vermiculite interstratified. Couderc and Douillet [14] associated this fact with the collision, during the “thermal shock,” of the water molecules of the vermiculite sheets with the mica sheets, producing a greater separation between them; Hillier [15] related exfoliation with the mosaic distribution of the different mineral phases within the vermiculite particles. Lateral phase boundaries between vermiculite and other phases (mica, or vermiculite, and chlorite) would prevent vapor from escaping from a particle, resulting in exfoliation when the pressure exceeds the bonding forces that hold the layers together. This type of thermal exfoliation is the oldest and the one that is still used today mostly in the industry.

Vermiculites can be modified by changes in temperature and pressure, chemical treatments, and irradiation, causing physical and structural changes in the mineral [16–24].

One of the most notable physical changes is exfoliation and expansion, which are influenced by factors such as water content, type of cations of the interlayer, and interstratifications of vermiculite [10, 17, 25].

Unmodified and modified commercial vermiculites are characterized by their industrial and technological applications [26–35]. These applications are a function of its physical and chemical properties and the treatment it has undergone, for example, thermal and acoustic insulation, adsorbent of substances, refractories, fire protection, support for hydroponic crops, light concretes, etc. The synthesis of advanced materials such as new glasses of great technological interest constitutes an example of the uses based on chemical applications. Numerous studies on the intercalation of polar organic molecules by clay minerals have been carried out. In addition to water, inorganic or organic substances can be adsorbed in the expandable interlayer space [36, 37].

The objective of this research has been to show the structural changes in commercial vermiculites induced by temperature, pressure, irradiation and chemical treatments, the relationship between these treatments, and crystallinity and the possible causes.

## 2. Methodology

### 2.1 Materials

The investigated vermiculite samples come from Catalão (Goiás, Brazil), Paulistana (Piauí, Brazil), China, Libby (Montana, USA), Benahavis (Málaga, Spain), and Sta. Olalla (Huelva, Spain) to compare. Vermiculite from Catalão (hereinafter Goiás) is associated with an ultramafic complex; Paulistana’s vermiculite (hereinafter Piauí) is found in a hybrid basic rock, probably a lamprophyre [38]. The origin of China’s vermiculites is unknown. The origin and mineralogy of the vermiculite of Sta. Olalla have been extensively studied [39–42]. This vermiculite is formed from phlogopite as a result of the alteration of pyroxenites. Vermiculite from Benahavis occurs in elongated veins, and the host rock is mainly serpentine [43, 44] and can be considered formed by alteration of phlogopite [45].

The weight percent of element oxides of the vermiculites considered in this chapter [10, 46] is in **Table 1** and their water content (%) in **Table 2**.

### 2.2 Vermiculite treatments

#### 2.2.1 Heat treatment

For the experiments with heat [10, 23], two diffractometers were used: Seifert XRD 3000 diffractometer (Scientific-Technical Services of the University of

Sample	Sta. Olalla <sup>1</sup>	Benahavis <sup>1</sup>	Piauí <sup>1</sup>	Goiás <sup>1</sup>	China W <sup>1</sup>	China G <sup>1</sup>	Palabora <sup>1</sup>	Libby <sup>2</sup>
SiO <sub>2</sub>	35.9	37.0	39.9	40.7	43.2	35.6	41.1	38.7
TiO <sub>2</sub>	0.3	2.5	1.1	0.8	1.0	1.2	1.2	1.2
Al <sub>2</sub> O <sub>3</sub>	15.8	14.1	9.3	11.5	11.9	11.0	10.0	13.0
Cr <sub>2</sub> O <sub>3</sub>	0.0	0.0	0.1	0.0	0.2	0.4	0.0	1.0
FeO	3.3	7.6	6.7	9.6	4.3	4.6	7.9	8.6
MnO	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.1
MgO	24.1	21.9	25.5	18.0	24.3	21.8	23.3	20.6
CaO	0.3	0.1	0.2	0.0	0.4	0.9	0.2	0.0
Na <sub>2</sub> O	0.1	0.1	0.0	0.1	0.7	3.5	0.1	0.3
NiO	0.0	0.1	0.0	0.0	0.0	0.1	0.1	0.0
K <sub>2</sub> O	0.0	0.0	3.5	1.1	7.5	5.6	6.0	9.7

<sup>1</sup>Marcos et al. [9].

<sup>2</sup>Marcos and Rodríguez [46].

**Table 1.**  
 Weight percent of element oxides.

	Water content (%)
Sta. Olalla <sup>1</sup>	25.6
Piauí <sup>1</sup>	14.0
Goiás <sup>1</sup>	13.6
China O <sup>1</sup>	17.6
China G <sup>1</sup>	12.3
Palabora <sup>1</sup>	13.4
Libby <sup>2</sup>	10.3

<sup>1</sup>Marcos et al. [9].

<sup>2</sup>Marcos and Rodríguez [46].

**Table 2.**  
 Water content (%).

Oviedo) at 30 mA and 40 kV; Cu-K $\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ;  $2\theta$  range of  $3\text{--}20^\circ$ ;  $2^\circ$  scans of  $0.02^\circ$  per step; and a count time of 20 s per step and Bruker AXS diffractometer (Plasma Physics Laboratory, National University, Manizales headquarters) at 30 mA and 40 kV (Cu-K $\alpha$  radiation;  $\lambda = 1.5418 \text{ \AA}$ ),  $2\theta$  range of  $3\text{--}40^\circ$ ,  $2\theta$  scans of  $0.1^\circ$ , and a count time of 20 s per step.

With an increase of T, the behavior of the vermiculites was different depending on the composition of the vermiculite and the type of heating (ex situ or in situ).

The result with heating ex situ at  $1000^\circ\text{C}$  for 1 minute was an expanded and exfoliated light product composed of enstatite in the purest vermiculites (with Mg<sup>2+</sup> or Mg<sup>2+</sup> and K<sup>+</sup> in the interlayer) Sta. Olalla and Benahavis and mica and enstatite in the commercial vermiculites (with K<sup>+</sup> and/or Na<sup>+</sup> and/or Ca<sup>2+</sup> in the interlayer). The exfoliation of the latter was much greater than that of the former.

The diffraction patterns made with temperature increase ( $40\text{--}140^\circ\text{C}$ ) in situ using the Seifert XRD 3000 equipment, and a powder sample showed the coexistence of the 2-WLHS phases with two layers and one layer of water, and the 1-WLHS phase was revealed. In the patterns made with the Bruker AXS

diffractometer, the last phase did not appear, and it was observed that the structure practically collapsed at 100°C, phase 1-WLHS reappearing as temperature increases.

With gradual increase in T in situ, dehydration of the vermiculites could be observed until practically reaching collapse, although the behavior was different depending on whether the samples contained  $Mg^{2+}$  or  $Mg^{2+}$  and  $K^+$  in the interlayer or  $K^+$  and/or  $Na^+$  and/or  $Ca^{2+}$ . In the former dehydration appears to be restricted to 1-WLHS, and dehydroxylation begins at lower temperatures and is faster than in the latter, in which already dehydrated vermiculite coexists with a similar structure to mica.

### 2.2.2 Pressure treatment

The experiments at atmospheric pressure  $P = 1.4 \cdot 10^{-2}$  mbar and  $P = 2.4 \cdot 10^{-4}$  mbar were carried out on both powder samples and exfoliation flakes of three vermiculites from Sta. Olalla (Huelva, Spain), Paulistana (Piauí, Brazil), and Western China [9]. A Seifert XRD 3000 diffractometer from the Scientific-Technical Services of the University of Oviedo was used. The conditions of use were 30 mA and 40 kV (Cu- $K\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ), range  $2\theta$  between 2 and  $70^\circ 2\theta$ , speed  $0.02^\circ 2\theta/20$  s. Two commercial Leybold pumps (Trivac D 2.5 E (up to  $10^{-2}$  mbar) and Turbovac TMP 50 (up to  $10^{-4}$  mbar)) were used for the vacuum experiments.

The effect of vacuum, like that of temperature, causes dehydration of vermiculite but with a different evolution through the different states of hydration. In fact, under vacuum, the process appears to inhibit itself to a state of hydration with one layer of water (1-WLHS). The role of T is inhibited against that of pressure. The Sta. Olalla vermiculite gave rise to the formation of three different interstratified phases: two phases characterized by an interstratification with interplanar distances,  $d = 11.5\text{--}13.8 \text{ \AA}$  and  $d = 9.6\text{--}11.5 \text{ \AA}$ , respectively, and another phase with  $d = 13.8 \text{ \AA}$ .

Under vacuum,  $P = 1.4 \cdot 10^{-2}$  mbar, in the Sta. Olalla, vermiculite phase 2-WLHS was observed with two layers of water coexisting with phase 2-WLHS but with a layer of water. In Piauí vermiculite, the evolution of the most characteristic reflection was more remarkable since it disappears, appearing in phase 1-WLHS.

The effect was faster with powder samples, and phase 2-WLHS quickly transforms to phase 1-WLHS.

### 2.2.3 Irradiation treatment

#### 2.2.3.1 Microwave irradiation

The transformations undergone by the vermiculites subjected to microwave irradiation (at 800 W and exposure times from 10 to 20 s) were characterized by X-ray diffraction [24]. A PHILIPS X'PERT PRO X-ray diffractometer was used, at 40 mA and 45 kV, Cu- $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), range of  $3\text{--}70^\circ 2\theta$ , steps of  $0.02^\circ$ , and a count time 1 s per step.

Microwave irradiation of vermiculite samples caused much less water loss than they do when subjected to sudden high-temperature heating; it also caused exfoliation of the material. From a structural point of view, the X-ray diffraction patterns of the vermiculites of Sta. Olalla, China, and Libby showed loss of crystallinity and disorder.

#### 2.2.3.2 Ultraviolet irradiation

The changes induced by ultraviolet (UV), short wave (254 nm), and long (356 nm) radiation at different times (1 hour, 1 day, and 1 week) in vermiculites from Sta. Olalla, Libby, and China were studied by using X-ray diffraction [46]. A PHILIPS X'PERT PRO X-ray diffractometer was used, at 40 mA and 45 kV,

Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), range of  $3\text{--}10^\circ 2\theta$ , steps of  $0.007^\circ$ , and a count time 1 s per step. Crystallite size and structural deformation were evaluated using PANalytical software (X'Pert Plus).

In the powder samples of Sta. Olalla, Libby, and China, a decrease in the intensity of the most characteristic reflections was observed as well as a decrease in the size of the crystallite and an increase in deformation. The results were more significant for powder vermiculite from China than for Sta. Olalla and Libby vermiculites, probably due to the coexistence of different hydration states, interstratifications, and superstructures in the initial vermiculite in China. The water loss in these long and short UV irradiated samples for 168 hours was 4 and 4.5% for the Sta. Olalla sample, 0.9 and 1% for the Chinese sample, and 6.4 and 7% for the Libby sample. In the exfoliation flake samples, an increase in the intensity of the most characteristic reflection is observed, in addition to a larger crystallite size and a lower percentage of deformation, so that the crystallinity increased.

#### 2.2.4 Chemical treatment

By **ion exchange of metals** ( $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) for the  $\text{Mg}^{2+}$  of the interlayer in the vermiculite-Mg of Sta. Olalla (Huelva, Spain).

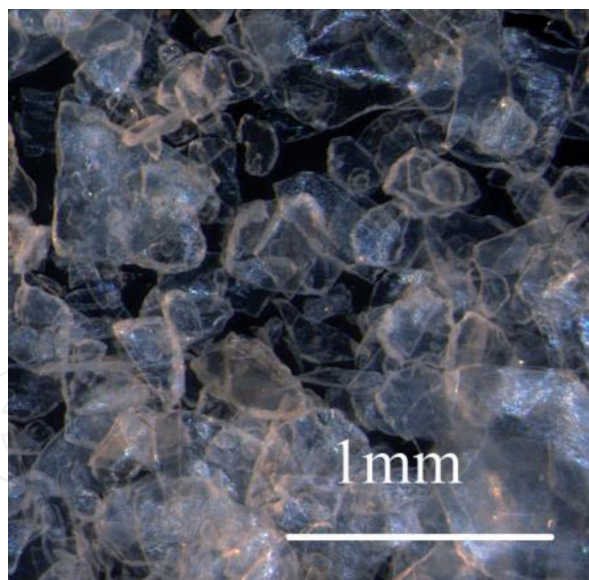
In the case of nickel [35], an aqueous solution of  $\text{Ni}^{2+}$  acetate was used, and in the case of iron [47],  $\text{FeCl}_2$  and  $\text{FeCl}_3$  solutions were used. The crystal structures of the nickel and iron vermiculites were refined using the DIFFaX+ program [48] (and a later version). The characterization was carried out with X-ray diffraction by transmission using an InEL XRD RG3000 cobalt tube vertical diffractometer ( $\lambda = 1.7890 \text{ \AA}$ ) (40 kV, 35 mA) and an InEL CPS 120 detector, in the  $2\theta$  range of  $4\text{--}70^\circ$  (step  $0.03^\circ$ , total acquisition time of 5400 s). Refinement confirmed the similarity of the  $\text{Ni}^{2+}$ -,  $\text{Fe}^{2+}$ -, and  $\text{Fe}^{3+}$ -vermiculites with the Mg-vermiculite. In the  $\text{Fe}^{2+}$ -vermiculite reflections corresponding to the akaganeite ( $\beta\text{-FeOOH}$ ) (JCPDS card 01-075-1594), a phase that was corroborated by Mössbauer spectroscopy (16%) was observed, a technique that also allowed showing the presence of said phase (3%) in the  $\text{Fe}^{3+}$ -vermiculite. Only vermiculite was detected in the  $\text{Ni}^{2+}$ -vermiculites obtained from the starting vermiculite, while in the one obtained from the homoionized starting vermiculite (with brucite -Mg  $(\text{OH})^{2-}$ ), a brucite phase with magnesium and nickel was also detected. In this refinement it was found that  $\text{Ni}^{2+}$  and  $\text{Fe}^{2+}$  also enter the octahedral layer, although there was no evidence for  $\text{Fe}^{3+}$ .

##### 2.2.4.1 Acid activation with $\text{HNO}_3$

Nitric acid treatment at 4 and 8 M was used at room temperature and different treatment times on the purest vermiculite from Sta. Olalla and two commercial vermiculites from Goiás and China, respectively [49]. To quantify potential loss of mass or water, 1 mL of each sample was weighed pre- and post-acidic treatment, and their volume post-treatment was measured. To identify any structural change, X-ray diffraction patterns were taken with a PANalytical X'pertPro diffractometer using 40 mA and 45 kV (Cu-K $\alpha$  radiation;  $\lambda = 1.5418 \text{ \AA}$ ),  $2\theta$  scans  $5\text{--}35^\circ$ ,  $2\theta$  step scans of  $0.007^\circ$ , and a counting time of 1 s per step. TEM high-resolution microscope with a resolution of  $1.9 \text{ \AA}$  between points and  $1.0 \text{ \AA}$  between lines was used to obtain TEM and selected area electron diffraction (SAED) micrographs with its accompanied CCD camera (Gatan).

Vermiculites treated with acid suffered (a) slight delamination and color (**Figure 6**); (b) weight loss (**Table 3**) due to the mass and water loss; (c) inhomogeneous cation leaching, probably achieved to transfer iron from those octahedral sheets to clusters deposited on vermiculite layers (**Figure 7**) [50–53] (and in the samples with





**Figure 6.**  
Color of treated vermiculite from Sta. Olalla.

Samples	HNO <sub>3</sub> molarity	Time	Weight loss (%)
Sta. Olalla	4	1	70
		7	75
	8	1	72
		7	70
Goiás	4	1	12
		7	14
	8	1	47
		7	47
China	4	1	22
		7	27
	8	1	53
		7	52

Marcos et al. [49].

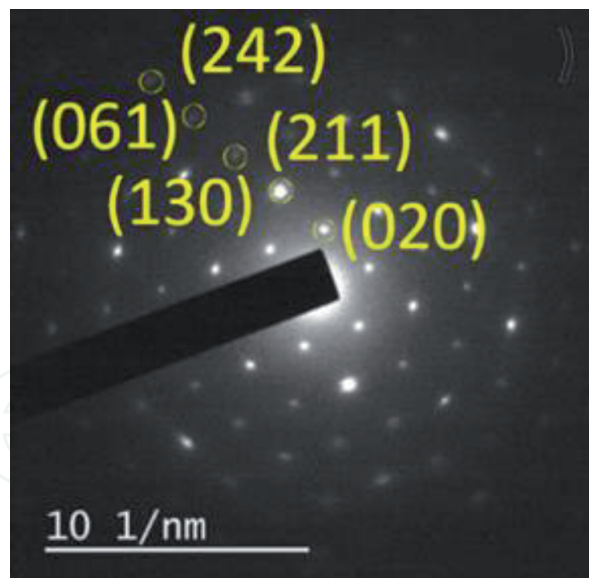
**Table 3.**  
Weight loss (%) in the treated samples.

high iron content, this element would have prevented further leaching of cations but not water loss); and (d) structural transformation that resulted in the formation of lamellar products with low crystallinity and order, composed by amorphous silica and other phases whose identity and percentage varied depending on the vermiculite type.

## 2.2.5 Thermal and chemical treatment

### 2.2.5.1 Thermal treatment and subsequent reaction with metal ions solution (Cr<sup>3+</sup> y Ni<sup>2+</sup>)

For the experiments with Cr<sup>3+</sup> [54] and Cr<sup>6+</sup> [55], commercial vermiculite from China thermo-exfoliated at 900°C for 1 minute was used. With Ni<sup>2+</sup>, commercial from Piauí (Brazil) and China, vermiculites thermo-exfoliated at 1000°C for 1 minute were used [35].



**Figure 7.**  
TEM and SAED micrograph of polycrystalline goethite in Goiás vermiculite .

Vermiculite characterization after  $\text{Cr}^{3+}$  adsorption was performed with X-ray diffraction using a Bruker AXS D8 Advance diffractometer with an Anton Paar HTK1200 oven at room temperature and  $900^\circ\text{C}$  for 1 minute. The equipment conditions were 30 mA and 40 kV, Cu- $\text{K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), range of  $3\text{--}40^\circ 2\theta$ ,  $0.1^\circ$  steps, and a count time of 20 s per step.

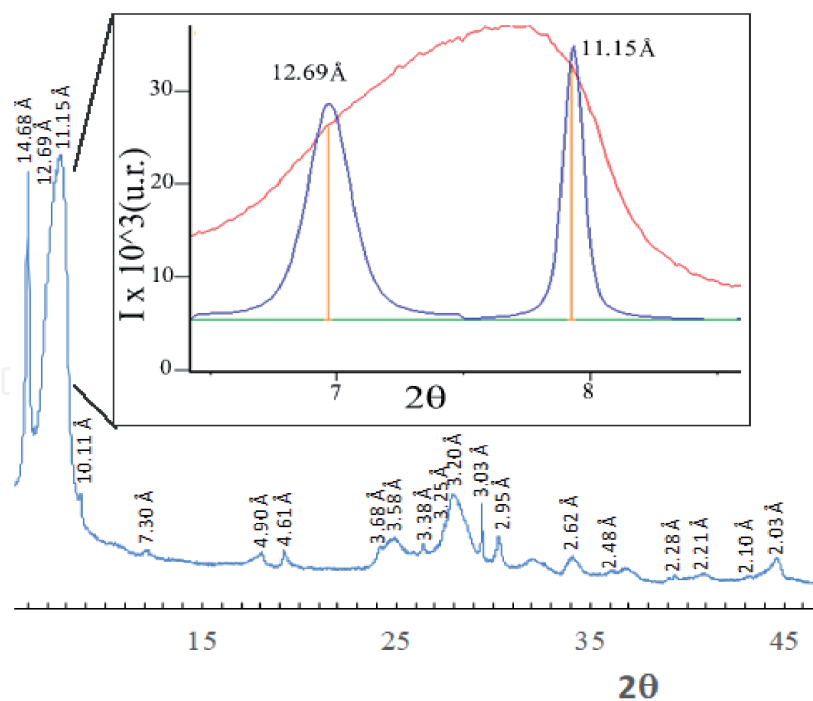
The X-ray spectra of Chinese vermiculite after having been in contact with a solution of synthetic seawater and dissolved  $\text{Cr}^{3+}$  with concentrations of 0.75 and 2.0 ppm suggested that the mica-like phase of the exfoliated vermiculite would have been transformed back into a vermiculite-like structure, similar to that of the original sample. In contrast, in the X-ray spectrum of Chinese vermiculite after having been in contact with distilled water solution and dissolved  $\text{Cr}^{6+}$  with concentrations of 1 ppm (**Figure 8**), no change is observed.

#### 2.2.5.2 Hydrogen peroxide

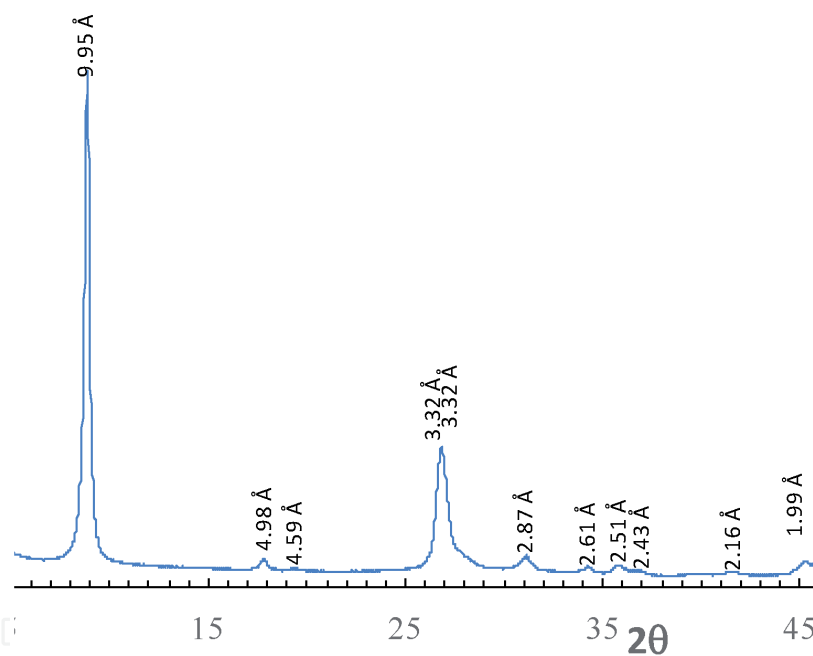
Several experiments with vermiculite samples from Sta. Olalla (Huelva, Spain), Libby (Montana, USA), and Goiás (Brazil), in both powder and flakes forms, were carried out [56]: (a) treatment with 30% and 50% hydrogen peroxide solution, at different times for each sample; (b) irradiation with microwaves for 20 s of Libby and Goiás samples; and (c) treatment with 30% and 50% hydrogen peroxide solution in the microwave oven for 20 s of vermiculite samples from Goiás. X-ray diffraction was used to identify structural changes. For the powder samples, a PHILIPS X'PERT PRO diffractometer was used at 40 mA and 45 kV, Cu- $\text{K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), range of  $3\text{--}70^\circ 2\theta$ , steps of  $0.02^\circ$ , and a count time 1 s per step. For the flake samples, a Seifert XDR 3000 T/T diffractometer was used at 30 mA and 40 kV, Cu- $\text{K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), range of  $2\text{--}10^\circ 2\theta$ , steps of  $0.02^\circ$ , and a time of 20 s count per step. The results showed that the vermiculites hardly underwent changes at the structure level, despite the change in appearance and textural (color, exfoliation, corrugation, undulations) (**Figure 6**). The three vermiculites—Sta. Olalla, Goiás, and Libby—showed a slight increase in the intensity of the main reflection. The change was slower in powder form than in flake samples, at least in Libby vermiculite.

**Alcohol** (methanol, ethanol, propanol, butanol).

The structural changes of commercial vermiculites treated with alcohol and alcohol for 1 month and subsequent microwave irradiation for 20 seconds were



(a)

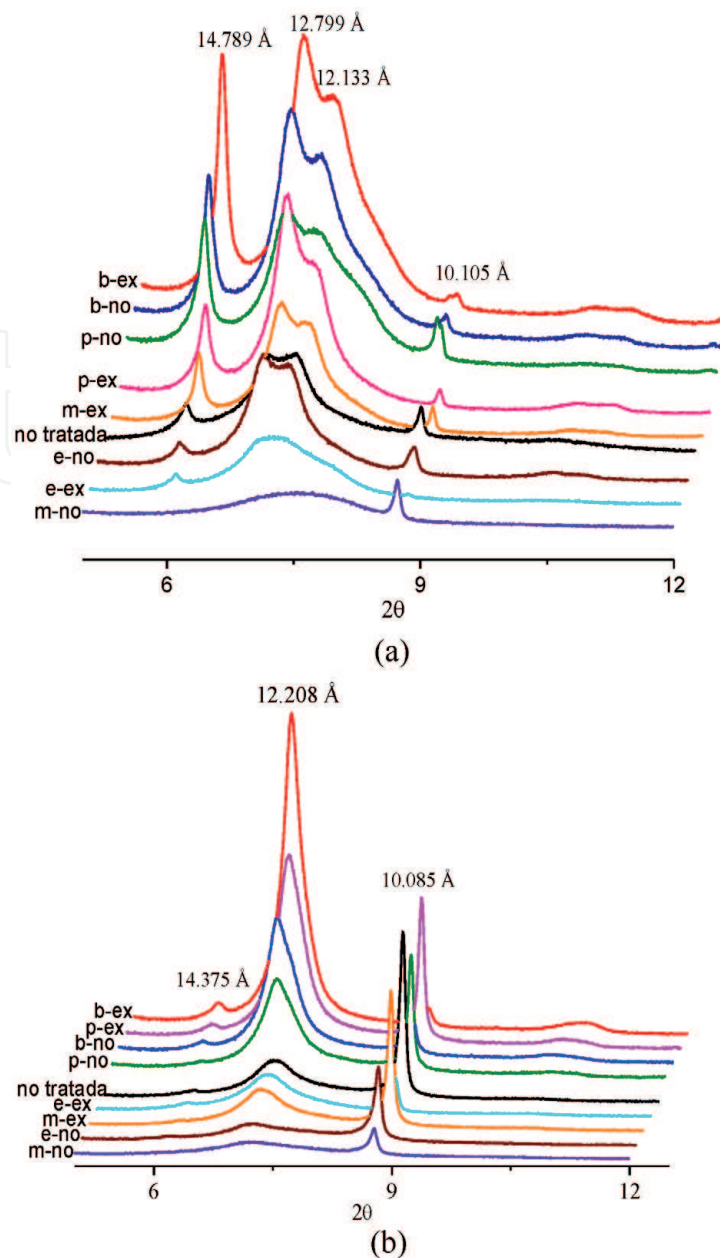


(b)

**Figure 8.**

X-ray diffraction of the starting Chinese vermiculite and abruptly heated at 900°C for 1 minute (a) and after having been in contact with 1 ppm  $\text{Cr}^{6+}$  in distilled water (b).

analyzed using X-ray diffraction [57, 58]. The equipment used was a PHILIPS X'PERT PRO diffractometer, at 40 mA and 45 kV, Cu- $\text{K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), range of 3–12° $2\theta$ , steps of 0.007°, and a count time of 1 s per step. Changes in the intensity and position of the basal reflections were used to indicate changes in the structural order and in the hydration states. In Sta. Olalla vermiculite, the intensity of the most characteristic reflection decreased with all the alcohols and times investigated. In the Chinese and Libby vermiculites, the intensity of the most characteristic reflections with methanol and ethanol also decreased, while with propanol and butanol, as a function of time, there was an increase in intensity and optimization of the profile of the aforementioned reflections and incipient appearance of phases with different hydration states (in Chinese vermiculite).



**Figure 9.** X-ray diffraction of the samples from China (a) and Libby (b) treated with alcohol for 1 month and subsequent microwave irradiation for 20 seconds (Marcos et al. [59]). Note: m = methanol, e = ethanol, b = butanol, p = propanol, ex = exfoliated, no = no exfoliated.

The diffraction spectra for the vermiculite particles from China and Libby treated with alcohol for 1 month and subsequent microwave irradiation for 20 seconds, exfoliated and non-exfoliated, are shown in **Figure 9** [59]. In these vermiculites treated with butanol or propanol and subsequent microwave irradiation, it should be noted that the crystallinity and the order of phases 2- and 2-1-WLHS of the exfoliated and non-exfoliated particles improved in relation to the untreated ones, except in Chinese exfoliated particles after butanol treatment and subsequent microwave irradiation. The opposite occurred with methanol or ethanol treatment and subsequent microwave irradiation, except in the Chinese exfoliated particles after methanol treatment and subsequent microwave irradiation.

### 3. Discussion

The structural modifications of the investigated vermiculites treated thermally, with vacuum, or irradiation or chemically, consist of the phase transformation

and the increase or loss of crystallinity and, therefore, the increase or decrease of the structural order. Depending on the treatment, the increase in crystallinity may be accompanied by the appearance of the majority starting phase, and the loss of crystallinity may be accompanied by the appearance or disappearance of interstratified phases.

Vermiculite responds to an increase of  $T$  by transforming its structure, which affects its applications. It is a dynamic process that depends on the composition, size, and shape of the particle, relative humidity, and process conditions (in situ or ex situ heating). With  $T$  increase, the transformations occur due to dehydration, greater in the purest vermiculites and less in the most micaceous ones. With abrupt ex situ heating, at  $1000^{\circ}\text{C}$ , with powder samples, the purest vermiculites are transformed into enstatite and the least pure into mica and enstatite; in both cases they appear expanded and exfoliated. With gradual heating in situ, at  $1000^{\circ}\text{C}$  and in flake samples, the structure practically collapses in the purest and the most micaceous vermiculites; although it fails to do so, its crystallinity is very low. Dehydration would occur by the escape of water in the form of steam. This escape would occur when the vapor pressure exceeds the bonding forces that hold the layers together, causing exfoliation and expansion [15]. The process occurs faster in powder samples than in flake samples.

The effect of the vacuum is similar to that of the temperature increase; the transformation also occurs by dehydration, although the process seems to be inhibited to a state of hydration with a layer of water (1-WLHS), without additional dehydration of the samples up to a state of hydration of zero layers of water (0-WLHS). The loss of water was less than with an increase in  $T$ . The process is slower than with an increase in temperature in situ since the pressure does not imply an increase in the activation energy as with the first. In addition, it was shown that the dehydration process occurs through different interstratified states in vermiculite. This result has been related to the content of  $\text{Mg}^{2+}$  cations in the interlayer, due to its affinity with water molecules. The purest vermiculite of Sta. Olalla showed the most complex dehydration process due to its higher magnesium content in the interlayer. Due to its affinity for water, the higher the content of the cation, the greater the difficulty in eliminating water molecules. When the temperature and the vacuum are acting simultaneously, the sample is dehydrated just after the vacuum is established, and the temperature has no additional effect. The process, as with temperature increase, occurs more quickly in powder samples than in sheet samples.

Microwave irradiation of vermiculite samples caused a loss of water much lower than what they suffer when subjected to sudden heating at high temperature. The said dehydration was slower than with vacuum or with sudden heating at  $1000^{\circ}\text{C}$ . As a consequence, the phase with  $d = 13.8 \text{ \AA}$  in Sta. Olalla, for example, could not be observed. The crystallinity loss and structural disorder is attributable to the water loss. There was no collapse of the structure or formation of new phases, probably because this loss was much lower than that produced at a temperature higher than that produced by microwave radiation. The expansion process began in the flake center and advanced toward the edges. The alignment and reorientation of the water dipoles with the applied field generated internal friction that caused the heating of the vermiculite and the vaporization of many of the water molecules. The explanation of steam escape and exfoliation would be the same as when the temperature rises.

The decrease in crystallinity and structural order in vermiculite powder samples irradiated with long and short UV is also attributable to the water loss. On the contrary, in crystalline samples the crystallinity and structural order increased. In this case there was surely rehydration by ambient humidity adsorption.

In the chemical treatment by ion exchange of  $\text{Ni}^{2+}$  or  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  metals by the  $\text{Mg}^{2+}$  of the interlayer in the Mg- vermiculite of Sta. Olalla, the decrease in the interplanar distance  $d_{002}$  has been interpreted as due to the interaction of the cation and a possible modification of the interactions between the exchanged cation and the TOT sheets, due to both the nature of the new cation and the variations in the quantity and distribution of the  $\text{H}_2\text{O}$  molecules that it induces. The formation of brucite in the homoionized starting vermiculite could be due to the homoionization process itself, consisting of introducing the vermiculite in a solution of  $\text{MgCl}_2$  in order to eliminate possible impurities such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , etc., coexisting with  $\text{Mg}^{2+}$ . In the vermiculite intercalated with nickel from this homoionized vermiculite, a brucitic phase with magnesium and nickel was also detected.

According to Ravichandran and Sivasankar [50], the reaction with nitric acid first caused the replacement of the exchangeable cations ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) by protons, which will subsequently attacked the layers. Secondly, partial leaching of  $\text{Al}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  from the tetrahedral and octahedral layers occurred. The silicon remained in the form of amorphous silica and quartz; this lasts in a very low percentage, which disappeared with the increase of the acid concentration in any of the samples. The Sta. Olalla sample suffered greater leaching of cations and water loss than the Goiás and China samples, whose high iron content would have prevented further leaching of other cations.

The heat treatment of the vermiculites and subsequent reaction with synthetic seawater solutions with  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$  would have caused the reappearance of the starting vermiculite, by rehydration. Probably, its union with the water trapped in the thermo-exfoliated structure may have made this structure closer to the original, that is, the mica-like structure would have moved back to that of the vermiculite. In aqueous solution  $\text{Cr}^{3+}$  would be in the form  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{Ni}^{2+}$  as  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ; in both cases its adsorption in thermally expanded vermiculites would be controlled by different cooperative mechanisms: (1) cation exchange and (2) surface complexation reactions [60–63]. It is important to note that a very low percentage of  $\text{Ni}^{2+}$  could have precipitated in the pores or on the surface of vermiculite such as magnesium and nickel hydroxide, according to the findings in unheated  $\text{Ni}^{2+}$ -,  $\text{Fe}^{2+}$ -, and  $\text{Fe}^{3+}$ -vermiculites [35, 47]. The cation exchange process would be favored by the fact that  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$  have an ionic radius (0.69 and 0.78 Å, respectively), similar to that of  $\text{Mg}^{2+}$  (0.72 Å). This ion exchange process would have taken place considering that the product resulting from the heating of vermiculite would constitute a heterogeneous system formed by one or more disordered crystalline phases (mica type) with hydroxyl groups and some cations between layers of the original phase and molecules of water.

This transformation would have occurred due to the rehydration of the sample in the adsorption process, which should be directly related to the characteristics of the cation involved [64]. The transformation in both cases would be consistent with the investigations carried out by Derkowski and McCarty [65] on the rehydration of dehydroxylated smectite in an environment of low water vapor. The equilibrium occurs in the solid/liquid interface, where the available centers located on the surface could be exchanged with the species in the solution. This adsorption process would be the opposite of what happens to vermiculite when it expands to 900°C.

The transformation could have occurred due to two aspects: on the one hand, the ionic exchange of ions of the interlayer with  $\text{Na}^+$  and other ions of the saline solution and on the other hand the lower force of attraction with the water of the interlayer which has  $\text{Na}^+$  in relation to  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  [66]. In the case of no transformation because there was no hydration or dehydration, since there was no change in weight before and after the adsorption of the ion by expanded vermiculite, probably due to the characteristics of the cation involved [64].

In the case of the adsorption of  $\text{Ni}^{2+}$  by vermiculite, the behavior would have been similar to that of the adsorption of  $\text{Cr}^{3+}$  [54], although it would have to be confirmed experimentally.

The reaction with hydrogen peroxide showed textural rather than structural changes. The water content (**Table 4**) was practically the same in both the Goiás and Libby samples treated with  $\text{H}_2\text{O}_2$  and untreated. The absence of hydration-dehydration is the cause of no phase transformation.

The leached cations, in greater quantity those of the interlayer ( $\text{Na}^+$ ,  $\text{K}^+$ , etc.) than those of the tetrahedral and octahedral layers, would be replaced by the  $\text{H}^+$  ions of the solution [21]. These ions gave rise to two effects: (1) increase of the pH of the solution and (2) corrosion of the vermiculite particles.

The structural changes of commercial vermiculites treated with alcohol, dehydration-hydration, and disorder-order would be related to the replacement of water by alcohol in a very low percentage, with weight loss and, depending on the type of vermiculite, appearance of phases with state of hydration of less layers of water. The structural changes of commercial vermiculites treated with alcohol and subsequent irradiation with microwaves consist of an increase or decrease in crystallinity and order. The results indicated dehydration-hydration and structural order-disorder that would be related to the entry of alcohol into vermiculites by water replacement, that is, by loss of water. The changes occurred in a manner similar to those produced with temperature and vacuum and were less pronounced for the purest vermiculite.

Structural changes of vermiculites induced by the above mentioned treatments provide evaluable information on the relationship between the structure of vermiculite and their industrial applications. In vermiculite applications as intumescent fire barriers [67–69] where exfoliation at low temperatures is required, the treatment type, in this case microwave irradiation, is more important than the structural change suffered by vermiculite. In the case of vacuum, not only the type of treatment but also the structural changes suffered by the vermiculite influence, since under pressure the vermiculite could act as a deposit mineral and host contaminating elements. Vermiculite irradiated with ultraviolet radiation could be used as material for optoelectronic devices because this radiation is less penetrating and easier and cheaper to obtain than gamma radiation [70].  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ -vermiculites maintain its paramagnetic character; and  $\text{Ni}^{2+}$ -vermiculite behaves as a two-dimensional spin-glass system in which planar ferro- and antiferromagnetic interactions compete, responsible for the complex magnetic behavior found.  $\text{Ni}^{2+}$ -vermiculites are interesting materials to study experimentally or

Samples	Treatment					H <sub>2</sub> O wt (%)
	—	Microwave irradiation	1000°C	H <sub>2</sub> O <sub>2</sub>		
				30%	50%	
Sta. Olalla	25.6	24.9	4.9 <sup>a</sup>			
Goiás	12.1	12.2	5.6	12.1 12.7 <sup>b</sup>	12.1 12.9 <sup>b</sup>	
Libby	10.3	11.1	3.4	10.9	11.4	

<sup>a</sup>Marcos et al. [10].

<sup>b</sup>Samples treated with alcohol and irradiated simultaneously with microwaves.

**Table 4.**

Water content (%) obtained by thermogravimetry of untreated and treated samples of Sta. Olalla, Goiás, and Libby.

in simulations, with applications to physics, chemistry, materials science, and artificial neural networks in computing [71]. Alcohol treatment and subsequent microwave irradiation may be the procedure for obtaining purest vermiculite from a less pure sample. Nitric acid treatment of vermiculites with high iron content resulted in a lamellar products with high porosity, important in many applications such as low cost and efficient and sustainable adsorbent for dyes and metals [60, 72–74]. It is important to highlight how exfoliated vermiculites can remain unchanged depending on the valence of the adsorbed ion and the salinity and pH of the medium.

Consequently, the relationship between structural changes of vermiculite and the chemical and physical treatments could contribute to predicting the structural order–disorder of the vermiculite; the obtaining of purest vermiculite; the environmental fate of toxic metals, such as cesium (radioactive metal) in contaminated areas; and developing methods to extract these metals from contaminated soils or waters [75].

Further, the changes suffered by vermiculites due to the treatments applied could give light to ambiguities about their geological origin due to hydrothermal and/or supergene processes. However, most and possibly all macroscopic vermiculite and interstratifications of vermiculite and other phases (mica, chlorite) are believed to be of supergene origin [76, 77]. The changes suffered by vermiculites due to hydrogen peroxide treatment and ionic metal exchange, with water gain, could point to this origin, corroborating both the field and laboratory evidence in early times [76]. Regarding the treatments that involve water loss in vermiculites, it is not discarded that a more detailed study helps to reveal data related to the hydrothermal origin. Some aspects observed in the transformations caused by treatments with water loss could coincide with field observations [78, 79].

#### **4. Conclusions**

Starting vermiculites with high  $K^+$  content in the interlayer have more interstratified phases and lower water content and are less crystalline.

The crystallinity loss and therefore the structural disorder increase are caused by the structural water loss. On the contrary, the crystallinity increase is produced by water gain.

The vermiculite transformation by structural water loss occurs with temperature increasing, vacuum, irradiation with microwaves or ultraviolet, and both alcohol and acidic treatment. On the contrary, the transformation by water gain occurs in vermiculites treated with hydrogen peroxide and in those subjected to ionic metal exchange.

Structural changes of vermiculites induced by the abovementioned treatments provide evaluable information on the relationship between the structure of vermiculite and their industrial applications. The said relationship would allow predicting the structural order-disorder of the vermiculite, the obtaining of purest vermiculite, or the environmental fate of toxic metals.

The changes suffered by vermiculites due to the treatments applied could give light to ambiguities about their geological origin and hydrothermal and/or supergene processes. Early field and laboratory evidence and current experiments showing changes in vermiculites caused by treatment with hydrogen peroxide and ion-metal exchange, with water gain, could point to a supergenic origin. Regarding the treatments that involve water loss in vermiculites, it is not discarded that a more detailed study helps to reveal data related to the hydrothermal origin.



## **Conflict of interest**

The author declares that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this chapter.

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