Expansion behaviour of commercial vermiculites at 1000 °C

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A B S T R A C T

Commercial vermiculites from different places were studied in order to know the cause of their different behaviour after abrupt heating at 1000 °C. Mössbauer spectroscopy provided Fe²⁺ and Fe³⁺ contents and allowed identification of both tetrahedral and octahedral iron. The Fe²⁺ content was higher in type-2 vermiculites (with K⁺ or Na⁺ and/or Ca²⁺ with or without Mg²⁺ as the principal interlayer cations) than in type-I vermiculites (with Mg²⁺ or Mg²⁺ and K⁺ (<1) as the principal interlayer cations). The higher iron content seemed to facilitate the fixing of potassium ions. This was responsible of the larger expansion after abrupt heating at 1000 °C for 1 min.

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1. Introduction

Vermiculites have been extensively investigated because of their remarkable physical and chemical properties: low thermal conductivity and density, refractory behaviour, and high cation exchange capacity, properties that lead to various industrial applications (Strand and Stewart, 1983; Hindman, 1992; Bergaya et al., 2006). They present a wide variety of physical–chemical properties as a result of their lamellar structure, of their layer charge, of disorder effects, and of their ability for dehydration–rehydration and the associated swelling processes (Mathieson and Walker, 1954; Shirouzu and Bailey, 1966; Grim, 1968; Brown and Brindley, 1980; de la Calle and Suquet, 1988; de la Calle et al., 1988; Bergaya et al., 2006). Vermiculites have water interlamellar layers and, consequently, can undergo dehydration–hydration processes which depend on temperature, pressure, chemical composition, particle size and relative humidity (Mathieson and Walker, 1954; Vail and Hesse, 1992; Collins et al., 1992; Reichenbach and Beyer, 1994, 1995; Ruiz-Conde et al., 1996; Marcos et al., 2003, 2009). The hydration properties of 2:1-clay minerals are controlled to a large extent by the interlayer cations (for instance, see Hendricks et al., 1940; Mooney et al., 1952; Suquet et al., 1975; Bergaya et al., 2006).

When vermiculite is heated at ≈1000 °C during a short period of time, the water situated between layers is rapidly vaporized, exerting a disruptive effect upon the particles, in industry called exfoliation. As a consequence, a highly porous material is formed and finds many industrial uses. The vermiculite particles are expanded to twenty or thirty times of their original size normal to the basal cleavage plane. Several authors (Midgley and Midgley, 1960; Couderc and Douillet, 1973; Justo et al., 1989; Marcos et al., 2009) found that the greater expansion is achieved in the case of mixed-layer vermiculite–mica minerals or mixed-layer vermiculite minerals containing vermiculite in different hydration states. Justo et al. (1989) pointed out that the chemical composition would influence the process of exfoliation. According to Couderc and Douillet (1973), the higher expansibility of the interstratified minerals is due to the fact that water molecules escaping from the interlamellar space collide with mica layers, moving them away from the vermiculite layers. The explanation of these authors is questionable because hitting of water molecules against mica layers should be similar to vermiculite layers. On the other hand, pure vermiculites with a higher content in interlamellar water than interstratified vermiculites would have a higher expansibility, however, the opposite effect occurs.

According to the interlayer cationic composition the commercial vermiculites were divided in two types (Marcos et al., 2009): type-I with Mg²⁺ or Mg²⁺ and K⁺ (<1) as the principal interlayer cations, and type-2 with K⁺ (approximately = or >1) and/or Na⁺ and/or Ca²⁺ with or without Mg²⁺ as the principal interlayer cations. Type-I vermiculites transform to enstatite with small amounts of mica-like materials. Type-2 vermiculites transform to mica-like materials with minor amounts of enstatite. Type-2 vermiculites show higher expansion and higher specific surface than type-I ones.

The goal of this paper is to explain the cause of the different expansion of commercial vermiculites, after abrupt heating at 1000 °C, on the basis of the chemical composition.

2. Experimental

The commercial vermiculite samples investigated were collected from Catalão (Goiás, Brasil), Paulistana (Pauli, Brasil), Palabora (South Africa), and China (East, West and G). Vermiculites from Sta. Olalla (Huelva, Spain) and Benahavis (Málaga, Spain) were also collected for...
The Catalão vermiculite, hereafter Goiás, is associated to an ultra-mafic complex. The vermiculite from Paulistana, hereafter Piauí, occurs in a hybrid basic rock, probably a lamprophyre (Hennies and Stellin, 1978). In the Palabra complex in the Republic of South Africa, phlogopite is progressively transformed into vermiculite following the sequence: phlogopite → mixed-layer → vermiculite (Badreddine, 1988). Although the alteration of phlogopite into vermiculite is considered to be the result of a weathering process caused by ordinary groundwater, Gevers (1949) proposed the influence of magmatic fluids to explain the origin of vermiculite. The authors could not identify the exact origin of the China vermiculites. The origin and mineralogy of the Sta. Olalla vermiculite were extensively studied (González García and García Ramos, 1960; Velasco et al., 1981; Justo, 1984; Luque et al., 1985). This vermiculite was formed from a mica identified as a phlogopite resulting from the alteration of pyroxenites. The Benahavis vermiculite occurs in elongated veins and the host rock is principally serpentinite (López González and Barrales Rienda, 1972; Justo, 1984) and it can be considered formed by alteration of phlogopite (Justo Erbez et al., 1983).

X-ray diffraction patterns and chemical analyses of samples were previously published by Marcos et al. (2009) except for that one from Benahavis, for which the X-ray diffraction pattern and chemical analyses were carried out in the same conditions as for the other samples.

The Mössbauer spectra of eight samples were recorded at 295 K with a constant acceleration spectrometer which utilized a room temperature rhodium matrix Co57 source and was calibrated at room temperature with a constant acceleration spectrometer which utilized a container was filled with ca. 74 mg/cm² of powder, except for the Sta. Olalla absorber that the amount was 114 mg/cm².

3. Results and discussion

The X-ray diffraction pattern at room temperature obtained for the Benahavis sample was similar to that pure one of Sta. Olalla and showed the most intense reflection, at d = 14.36 Å, a reflection that is the characteristic (002) reflection of vermiculite (ICPDS card 16-613). After heating at 1000 °C for 1 min the Benahavis vermiculite showed enstatite X-ray pattern (ICPDS card 19-768) (Fig. 1).

The results of the chemical analyses for all the samples in mass % of the elements as oxides reached the thousandths. The mass content of the oxides did not add to 100 since the electron microprobe did not detect the light elements such as hydrogen and oxygen, elements that are present as water molecules and hydroxyl groups in the structure. These compositions were similar to those published for vermiculites (Föster, 1963; Grim, 1968; Justo, 1984; Justo et al., 1986) and the small differences could result from the presence of other element oxides in small quantity, such as Cr2O3 or MnO (Föster, 1963; Norrish, 1973). The iron oxide content was below 10% in all samples.

The small K₂O content (Justo et al., 1986) supports the pure character of the vermiculites of Sta. Olalla and Benahavis, and the major K₂O content of other samples might indicate that these samples are not pure vermiculites (Veide, 1978). X-ray diffraction patterns of the purest samples showed only reflections for Mg–vermiculite with two-water layer, whereas other samples showed the coexistence of phases of vermiculite with zero-, one- and two-water layers and interstratifications of vermiculites with hydration states different.

Iron may occur in both the octahedral and tetrahedral sheets of vermiculites. Electron microprobe analysis did not distinguish between Fe²⁺ and Fe³⁺ contents, important aspect to obtain the cationic distribution in the structure. Mössbauer spectroscopy was a way of knowing the contents of Fe²⁺ and Fe³⁺ in the tetrahedral and octahedral sheets of crystalline structure (Coe, 1984; Dyar, 1987; Badreddine et al., 2000).

The 295 K Mössbauer spectra of eight commercial vermiculites from different origins are in Fig. 2. Except for the Palabra and China W samples, they were analyzed with four symmetric doublets and their parameters are in Table 2. Among the four doublets, two with isomer shifts of ca. 1 mm/s and two with isomer shifts of ca. 0.4 mm/s were assigned to Fe²⁺ and Fe³⁺, in the octahedral M1 and M2 sites, respectively. The relative areas of each pair of doublets were constrained in the ratio of 1:2, in agreement with the relative population of the M1 and M2 sites (Goodman and Wilson, 1973; Bancroft and Brown, 1975; Sanz and Stone, 1977; Sanz et al., 1978; Badreddine et al., 2000). For the Goiás sample, the small amount of Fe³⁺, ca. 2%, did not permit a fit with two Fe²⁺ doublets and was fitted with only one doublet.

The Fe²⁺ doublets had isomer shift and quadrupole splitting values, which agree with octahedral Fe²⁺ in the M1 and M2 sites (Coe, 1984), see Fig. 3. The quadrupole splitting of the Fe³⁺ M1 sites was larger than that of the Fe³⁺ M2 sites, whereas the quadrupole splitting of the Fe²⁺ M1 sites was smaller than that of the Fe²⁺ M2 sites. This difference occurs because the valence and lattice contributions to the electric field gradient at the Fe²⁺ sites have opposite signs (Dyar, 1987; Badreddine et al., 2000; Badreddine et al., 2002). Hence, the lattice contribution at the M1 site was larger than that at the M2 site. For the Fe³⁺ ions, the only contribution to the electric field gradient is lattice

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**Table 1**

Chemical analyses (mass %) of the studied vermiculites obtained from microprobe analysis.

<table>
<thead>
<tr>
<th></th>
<th>Sta. Olalla</th>
<th>Benahavis</th>
<th>Piauí</th>
<th>Goiás</th>
<th>China W</th>
<th>China G</th>
<th>Palabra</th>
<th>China E</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>35.928</td>
<td>37.001</td>
<td>39.940</td>
<td>40.673</td>
<td>43.221</td>
<td>35.647</td>
<td>41.070</td>
<td>36.609</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.329</td>
<td>2.493</td>
<td>1.125</td>
<td>0.790</td>
<td>1.013</td>
<td>1.161</td>
<td>1.248</td>
<td>1.159</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.030</td>
<td>0.035</td>
<td>0.062</td>
<td>0.014</td>
<td>0.162</td>
<td>0.389</td>
<td>0.023</td>
<td>0.028</td>
</tr>
<tr>
<td>MnO</td>
<td>0.135</td>
<td>0.119</td>
<td>0.044</td>
<td>0.082</td>
<td>0.008</td>
<td>0.037</td>
<td>0.028</td>
<td>0.017</td>
</tr>
<tr>
<td>CaO</td>
<td>0.294</td>
<td>0.128</td>
<td>0.204</td>
<td>0.034</td>
<td>0.401</td>
<td>0.916</td>
<td>0.180</td>
<td>1.172</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.124</td>
<td>0.074</td>
<td>0.039</td>
<td>0.123</td>
<td>0.711</td>
<td>3.545</td>
<td>0.149</td>
<td>0.004</td>
</tr>
<tr>
<td>NiO</td>
<td>0.000</td>
<td>0.075</td>
<td>0.020</td>
<td>0.015</td>
<td>0.038</td>
<td>0.056</td>
<td>0.057</td>
<td>0.062</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.033</td>
<td>0.011</td>
<td>3.539</td>
<td>1.069</td>
<td>7.483</td>
<td>5.614</td>
<td>6.012</td>
<td>6.489</td>
</tr>
<tr>
<td>Total</td>
<td>80.052</td>
<td>83.494</td>
<td>86.407</td>
<td>81.944</td>
<td>93.458</td>
<td>84.800</td>
<td>89.879</td>
<td>89.823</td>
</tr>
</tbody>
</table>

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Fig. 1. X-ray diffraction pattern of the Benahavis sample abruptly heated to 1000 °C for 1 min.
contribution and hence, the quadrupole splitting of the Fe\(^{3+}\) M1 sites was larger than that of the Fe\(^{3+}\) M2 sites.

In contrast, in the China W sample, one additional Fe\(^{3+}\) doublet with an isomer shift of 0.17 mm/s, was assigned (Coey, 1984) to tetrahedral Fe\(^{3+}\). The difference between the tetrahedral and octahedral isomer shifts was illustrated in the two left rectangles in Fig. 2.

The Piauí and Palabora spectra showed visual evidence of a line at ca. 0.45 mm/s, an evidence, which according to Rancourt et al. (1992), was a clear indication of the presence of tetrahedral Fe\(^{3+}\). Hence, an additional doublet with an isomer shift of ca. 0.2 mm/s was assigned to Fe\(^{3+}\) in tetrahedral site.

The commercial Palabora sample contains ca. 36% of the total iron content as tetrahedral Fe\(^{3+}\), in agreement with the studies of a ‘ferriphlogopite’ by Annersten et al. (1971). Further, the Fe\(^{2+}\) content of ca. 18%, is close to that measured in a sample collected at the Palabora Complex of South Africa, ~23% (Badreddine et al., 2000).

The content of Fe\(^{2+}\) and Fe\(^{3+}\) was obtained by Mössbauer spectroscopy and their values are in Table 2. Mössbauer spectra of Piauí, China W and Palabora samples (Fig. 2) confirmed the Fe\(^{3+}\) occupation in the tetrahedral sites, probably as a consequence of the lower extent of oxidation in these vermiculites.

The distribution of cations between octahedral and tetrahedral sites according to Föster (1963) for calculating structural formulas was as follows: (a) all the silicon was allotted to the tetrahedral group, together with enough Al\(^{3+}\) to bring the total to 4.00. When there was not enough Al\(^{3+}\) to complete the tetrahedral group, Fe\(^{3+}\) was then allotted to the tetrahedral group to complete it. (b) Any remaining Al\(^{3+}\) and Fe\(^{3+}\), with the Fe\(^{2+}\), Ti\(^{4+}\), Cr\(^{3+}\), Mn\(^{2+}\), plus all the Mg\(^{2+}\) or enough Mg\(^{2+}\) to fill three positions were assigned to the octahedral group. (c) Any remaining Mg\(^{2+}\), plus the Ca\(^{2+}\), Na\(^{+}\), and K\(^{+}\), were finally assigned to interlayer positions. This assignment order might be arbitrary (Luca and Cardile, 1989; Luca, 1991a,b; Luca and Maclachlan, 1992; Manceau et al., 2000; Gates et al., 2002). On the one hand, the tetrahedral iron was underestimated. Mössbauer spectroscopy was a way to identify the tetrahedral iron. On the other hand, the manner of distributing Mg\(^{2+}\) cations between octahedral and interlayer positions might result in a minimum of interlayer Mg\(^{2+}\); some of the Mg\(^{2+}\) assigned to octahedral positions might actually be interlayer Mg\(^{2+}\). The best mean of ascertaining how the Mg\(^{2+}\) should be distributed is to determine the amount of interlayer Mg\(^{2+}\) displaced by cation exchange.

The cations in Table 3 were obtained using the MINPET program (MINPET GEOLOGICAL SOFTWARE, 146 DV Chateau Masson-Angers, Quebec, Canada). The calculations were based on 24 anions: 20 structural oxygens and 4 OH groups. The distribution of cations between octahedral and tetrahedral sites was made according to Föster (1963) but considering the contents of octahedral and tetrahedral Fe\(^{2+}\) and octahedral Fe\(^{3+}\) calculated from the contents of these cations obtained with Mössbauer, because electron microprobe analyses only provided information on total iron content (Fe\(_{tot}\)).

The content of tetrahedral and octahedral cations was 100% except in China W and China E samples with values of 82.7% and 74.2%, respectively, for octahedral sheet. The interlayer Mg\(^{2+}\)–cation content was zero in these last vermiculites, however, some of the Mg\(^{2+}\) might belong in interlayer positions and be exchangeable.

Except for the Sta. Olalla, Benahavis, China W and China E samples, the Si/Al ratio in tetrahedral sites was larger than the value of ca. 3.00 reported earlier (Herrero et al., 1985).

Fig. 2. The 295 K Mössbauer spectra of the eight samples studied. Black crosses indicate experimental data points. The solid line drawn to the data points corresponds to the calculated least-squares fitting. The other solid lines show the individual components contributing to the fit (see text for more details).
The structural formulas for the samples are given below. The labelling scheme was as follows: 1—Sta. Olalla, 2—Benahavis, 3—Piauí, 4—Goiás, 5—China W, 6—China G, 7—Palabora, 8—China E.

\[
\begin{align*}
& (Mg_{0.76}K_{0.20}Ca_{0.03}Na_{0.04})Mg_{0.42}Al_{0.58}Fe_{0.41}O_{20}(OH)_{4} \\
& (Si_{5.68}Al_{2.32})O_{20}(OH)_{4} \\
& (Mg_{0.62}Ca_{0.22}Na_{0.16})Mg_{0.41}Al_{0.58}Fe_{0.41}O_{20}(OH)_{4} \\
& (Si_{5.73}Al_{2.27})O_{20}(OH)_{4} \\
& (Mg_{0.66}K_{0.20}Ca_{0.03}Na_{0.04})Mg_{0.42}Al_{0.58}Fe_{0.41}O_{20}(OH)_{4} \\
& (Si_{6.10}Al_{1.74}Fe_{0.13})O_{20}(OH)_{4} \\
& (Mg_{0.25}K_{0.26}Ca_{0.03}Na_{0.04})Mg_{0.42}Al_{0.58}Fe_{0.41}O_{20}(OH)_{4} \\
& (Si_{6.46}Al_{1.54})O_{20}(OH)_{4} \\
& (K_{1.15}Ca_{0.92}Na_{0.17})Mg_{4.43}Fe_{0.30}Ti_{0.12}O_{20}(OH)_{4} \\
& (Si_{6.88}Al_{0.16}Fe_{0.16})O_{20}(OH)_{4} \\
& (Mg_{0.10}K_{0.21}Ca_{0.18}Na_{0.26})Mg_{4.43}Al_{0.41}Fe_{0.41}O_{20}(OH)_{4} \\
& (Si_{6.22}Al_{1.40})O_{20}(OH)_{4}
\end{align*}
\]

Fig. 3. The range of the quadrupole splittings and isomer shifts reported for a variety of silicates (after Coey, 1984). The up triangles, squares, diamonds, circles, and down triangles refer to tetrahedral Fe\(^{3+}\), octahedral M1 and M2 Fe\(^{3+}\), and octahedral M1 and M2 Fe\(^{2+}\), respectively, in the eight samples studied herein.

\[
\begin{align*}
& (Mg_{1.38}K_{1.25}Ca_{0.07}Na_{0.03})(Mg_{4.41}Fe_{0.39}Fe_{0.23}Ti_{0.15}) \\
& (Si_{6.37}Al_{0.92}Fe_{0.16})O_{20}(OH)_{4} \\
& (K_{0.99}Ca_{0.15}Na_{0.14})(Mg_{2.75}Fe_{0.17}Fe_{0.20}Ti_{0.11}Mn_{0.01})(Si_{6.69}Al_{1.46})O_{20}(OH)_{4} \\
\end{align*}
\]

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter Fe(^{3+})</th>
<th>Fe(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M1)</td>
<td>(M2)</td>
</tr>
<tr>
<td>Sta. Olalla</td>
<td>1.03(4)</td>
<td>1.06(3)</td>
</tr>
<tr>
<td>Benahavis</td>
<td>1.14(2)</td>
<td>1.15(1)</td>
</tr>
<tr>
<td>Piauí</td>
<td>0.98(2)</td>
<td>1.16(1)</td>
</tr>
<tr>
<td>Goiás</td>
<td>0.96(1)</td>
<td>1.01(1)</td>
</tr>
<tr>
<td>Palabora</td>
<td>0.99(3)</td>
<td>1.22(1)</td>
</tr>
<tr>
<td>China W</td>
<td>1.13(1)</td>
<td>1.14(1)</td>
</tr>
<tr>
<td>China G</td>
<td>1.27(1)</td>
<td>1.27(1)</td>
</tr>
<tr>
<td>Palabora</td>
<td>0.99(3)</td>
<td>1.22(1)</td>
</tr>
<tr>
<td>China E</td>
<td>1.09(3)</td>
<td>1.15(5)</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Cationic distribution of the studied vermiculites.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sta. Olalla</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>∑interstices</td>
</tr>
<tr>
<td>Si/AlIV</td>
</tr>
</tbody>
</table>
According to the division by (Marcos et al., 2009) of commercial vermiculites in two types based on interlayer cationic composition, Sta. Olalla, Benahavis, Piauí and Goiás would belong to type-1 and China W, China G, Palabora and China E to type-2.

The composition in $\text{Al}^{3+}$, $\text{Mg}^{2+}$, and $\text{Fe}^\text{tot}$, of the octahedral sheet was plotted in a ternary diagram for the studied samples (see Fig. 4). The eight samples formed a group in which the Piauí, China W and China E samples had lower aluminium content in the octahedral sheet and the China E sample had higher magnesium and lower aluminium content than the rest of samples.

The triangular diagram of Fig. 5 concerns to octahedral composition of vermiculites related to trioctahedral micas. The points representing samples from Santa Olalla, Piauí, China W and China G fell in or to the left of the phlogopite zone; the points corresponding to Benahavis and China E fell in the top left of the Mg–biotite zone and the points representing the samples of Palabora and Goiás are in a zone between the biotite and phlogopite, but none fell below the Mg–biotite area into or to the left of the Fe–biotite area. Thus the octahedral composition of most of these vermiculites should be similar to that of phlogopite, except for a higher proportion of $\text{R}^2+$ with respect to $\text{R}^3+$ in some that the causes the points representing them to fall to the left of the phlogopite or Mg–biotite area. This proposition is in agreement with the previous results on the Sta. Olalla (de la Calle and Suquet, 1988; de la Calle et al., 1988), Benahavis (Justo Erbez et al., 1983) Piauí (Hennies and Stellin, 1978) and Palabora vermiculites (Badreddine, 1988).

Although the parent mineral is practically the same, the genetical process was different as revealed for the composition and the distribution of their iron content in the crystallographic sites of the tetrahedral and octahedral sheet.

The distribution of the cationic charges of Table 4 was calculated from the cation distribution in Table 3. Except for the China E and China W samples, the distribution of charge in octahedral (13–14) and in tetrahedral (30) sites agreed with the proposition of Köster (1982) for vermiculite. The charge in the interlayer space was generated by the charge imbalance in the structure and was larger in the China G and Palabora samples, which also had higher content of potassium plus magnesium.

Applying the empiric relation observed for Förster (1963) between the positive interlayer charges with determined cation exchange capacities (CEC) to the formulas calculated from the analyses in Table 1, considering the interlayer $\text{K}^+$ as non-exchangeable, the estimated CEC of the commercial vermiculites were obtained (see Table 5). The CEC values, for the half-layer formula, varied from about 27 to 400 meq/100 g, as the interlayer charge varied from 0.14 to 2.00. These vermiculites were formed from phlogopite basically and if the formation process was by simple replacement of $\text{K}^+$ by $\text{Mg}^{2+}$, and in

which there was no oxidation of iron, should have layer unit and interlayer charges comparable with those of phlogopite, which would be close to 1.00 in a half-layer formula and they would have a cation exchange of about 200 meq/100 g (Förster, 1963). In some of the samples the cation exchange capacity was very lower, particularly in those containing much $\text{K}^+$ and no magnesium as China W and China E or very little potassium as Goiás. The reason might be due to the oxidation of iron or erroneous allotment of $\text{Mg}^{2+}$ in the octahedral positions, or both (Förster, 1963). The China G and Palabora samples with higher charge imbalance in the interlayer space than the proposed by Köster (1982) also provided the highest CEC values.

On the other way, it is known that: a) Structural $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ both significantly impact the smectite–water interaction (Stucki, 1988); b) The swellability of sheet-silicates as vermiculite is affected by the cationic composition of the interlayer space (Mathieson and Walker, 1954; Shirozu and Bailey, 1966; Grim, 1968; Brown and Brindley, 1980; de la Calle and Suquet, 1988); and c) the presence of reduced structural iron has a depressing effect on water retention capacity in smectites (Yan and Stucki, 1999, 2000). Two observations provided understanding how structural $\text{Fe}^{2+}$ has a great effect on surface hydration and other surface properties. The first observation was by Yan and Stucki (1999, 2000) about the increase of the vibrational energy of the $\text{H}–\text{O}–\text{H}$ bending mode for the interlayer $\text{H}_2\text{O}$ with increasing of $\text{Fe}^{2+}$ content of the clay. The second observation was by Yan et al. (1996a,b,c,d) and Yan and Stucki (1999, 2000) about the coupling of the mentioned energy with the vibrational energy of the structural $\text{Si}–\text{O}$ stretching bands.

Vermiculites of type-2 gave lower molar ratio $\text{H}_2\text{O}$/interlayer ion, lower dehydration and restricted to one or one/zero-water layer in the interlayer space, higher expansive capacity and higher specific surface than vermiculites of type-1 (Marcos et al., 2009). These vermiculites also gave contents of $\text{Fe}^{2+}$ and $\text{K}^+$ ions (Table 3) higher than vermiculites of type-1, except the China E vermiculite, which has suffered less oxidation. It seemed that structural $\text{Fe}^{2+}$ had a great effect on surface hydration and other surface properties. Since structural $\text{Fe}^{2+}$ increases the interaction between $\text{H}_2\text{O}$ and the clay surface (Stucki, 2006) the hydration in vermiculites type-2 should be greater than in vermiculites type-1. However, it was contrary as it was also observed by other authors (Förster, 1953, 1955; Egashira and Ohta, 1983; Stucki et al., 1984; Lear and Stucki, 1985; Gates et al., 1993; Stucki et al., 2000) in smectite and other clays. The explanation in the last minerals established that two types of interlayer spaces were possible in swelling smectites: fully expanded and fully or partially collapsed (Viani et al., 1983; Wu et al., 1989) and the increase

![Fig. 4. The partial Mg–Al–Fe$_{\text{tot}}$ ternary phase diagram for the studied samples.](image-url)
of octahedral Fe$^{2+}$ caused more of the clay layers to collapse compared to the oxidized state, thereby removing those layers from the pool of fully expanded layers. The overall capacity of the clay to adsorb water on a mass basis was thus diminished. The explanation for the vermiculites may consist in a higher cation fixation, as potassium, with a higher content of Fe$^{3+}$, indicating that layers are indeed collapsing around this cation (Lear and Stucki, 1987; Khaled and Stucki, 1991; Shen and Stucki, 1994).

4. Conclusions

The tetrahedral Fe$^{3+}$ and octahedral Fe$^{3+}$ and Fe$^{2+}$ contents of the commercial vermiculites investigated were estimated using Mössbauer spectroscopy and the structural formulas were recalculated, allowing corroborate their origin.

Type-2 vermiculites suffered a larger expansion than type-1 ones after abrupt heating at 1000 °C during 1 min, due to its higher Fe$^{2+}$ content, which seemed to facilitate the fixation of the potassium in the interlayer space. This fact does of these commercial samples materials very suitable to retain contaminating substances.

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References


