INFRARED EVIDENCE OF DIOCTAHEDRAL-TRIOCTAHEDRAL SITE OCCUPANCY IN PALYGORSKITE

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Abstract—A Mg-rich palygorskite sample from phosphorite deposits of Ganntour (Morocco) with the structural formula $Si_8(Mg_{2.6}Al_{1.19}Fe^{III}_{0.33}\square_{0.88})Ca_{0.056}Na_{0.024}K_{0.104}O_{20}(OH)_2(OH_2)_4.4H_2O$, was studied by FTIR spectroscopy. In both OH-stretching and OH-bending regions, there is evidence of dioctahedral $Al_2\square OH$, $AlFe\square OH$ and trioctahedral Mg_3OH features, leading to a di-trioctahedral crystallochemical model of octahedral site occupancies in ribbons of Ganntour palygorskite.
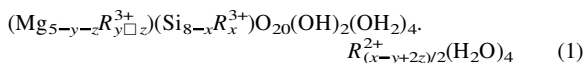
This model, established through the IR spectroscopy study of a Mg-rich palygorskite, seems to be appropriate for many other palygorskites with lower Mg content in the octahedral sheet.

Key Words—Cation Distribution, FTIR Spectroscopy, Octahedral Occupancy, Palygorskite.

INTRODUCTION

According to Bailey (1984), two main structural models were proposed for palygorskite, one by Bradley (1940) and the other one by Gard and Follet (1968). After X-ray diffraction (XRD) studies of palygorskite samples by Drits and Alexandrova (1966) and Drits and Sokolova (1971), Bradley's model is more generally accepted and used. Jeffers and Reynolds (1987) suggested that expandable palygorskite may have the Bradley structure.
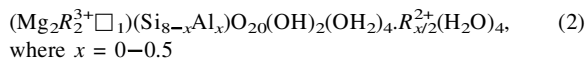
Because palygorskite is a fibrous Mg-clay containing generally large amounts of Al^{3+} and Fe^{3+} cations, their precise crystal chemistries (site occupancy, distribution of cations, di- or trioctahedral character) have often been studied. On the basis of Bradley's model, Drits and Alexandrova (1966) and Drits and Sokolova (1971) found that for many palygorskites only four of the five octahedral sites are occupied (dioctahedral) and that the vacant octahedral site is located in a *trans* site. They also showed that some palygorskites exhibit an octahedral occupancy >4. The structural formula they proposed, which is most often used for palygorskite, is:

$$(Mg_{5-y-z}R^{3+}_{y}\square_z)(Si_{8-x}R^{3+}_x)O_{20}(OH)_2(OH_2)_4.$$
$$R^{2+}_{(x-y+2z)/2}(H_2O)_4 \qquad (1)$$

(Bailey, 1984; Newman and Brown, 1987), where $\square$ is a vacant site, and R represents Mg, Al or Fe.

Recently Galán and Carretero (1999), using EDX chemical analyses, showed that palygorskite has octahedral chemistries located within the chemical gap between di- and trioctahedral phyllosilicates, taking into account the limits proposed by Foster (1960) and Weaver and Pollard (1973). According to them, the octahedral sheet of palygorskite contains mainly Mg, Al

and Fe with the R^{2+}/R^{3+} ratio close to 1, and with four of the five structural sites occupied. Considering that the variability of the published chemistries of palygorskite is mainly due to impurities and technical problems, Galán and Carretero (1999) proposed the following structural formula:

$$(Mg_2R^{3+}_2\square_1)(Si_{8-x}Al_x)O_{20}(OH)_2(OH_2)_4.R^{2+}_{x/2}(H_2O)_4, \qquad (2)$$
where $x = 0-0.5$

Russell and Fraser (1994) described palygorskite as 'similar to layer silicates intermediate between di and trioctahedral types', but underlined their dominant dioctahedral character on the basis of the occurrence of both 3615 and 913 cm^{-1} infrared (IR) absorption bands, clearly attributed to $Al_2\square OH$ vibrations.

After the IR study of the Georgia palygorskite (octahedral occupancy of 3.81 and R^{2+}/R^{3+} of 1.12), Serna *et al.* (1977) described this clay mineral as completely dioctahedral with octahedral edges of the ribbons occupied only by Mg cations.

By means of acid attack on two Australian palygorskites, from Mt. Grainer and Mt. Flinders (octahedral occupancies of 3.76 and 4.08, respectively, and R^{2+}/R^{3+} ratios of 0.84 and 1.95), Singer (1977) showed that the molar ratios of octahedral cations in equilibrium solutions are not identical to those of the solid phases, suggesting that the distribution of cations in octahedral sites is not random. As Mg and Fe cations were preferentially dissolved over Al, Singer (1977) suggested that Mg and Fe are situated in edge positions, and Al in more interior positions. After a Mössbauer spectroscopy study, Heller-Kallai and Rozenson (1981) concluded, on the basis of the Singer's (1977) model of palygorskite structure, that Fe ions occupy both edge sites and interior positions in silicate chains.

Using IR spectroscopy, Hayashi *et al.* (1969) studied Kuzu District palygorskite with octahedral site occupancy of 3.84 and an R^{2+}/R^{3+} ratio of 1.17. On the basis

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of the occurrence of a band at 3685 cm^{-1} in the IR spectra of both sepiolite and palygorskite, they concluded that these two clay minerals are trioctahedral.

From the IR study of two palygorskites (I and II) from Duero basin (Spain), with octahedral occupancies of 3.8 (I) and 4.5 (II), and R^{2+}/R^{3+} ratios of 0.8 (I) and 2.34 (II) respectively, Blanco *et al.* (1989) confirmed the dioctahedral character of the former and the trioctahedral character of the latter. The IR spectra of both samples exhibit a shoulder at 3680 cm^{-1}. A band at 685 cm^{-1} was observed for sample II and Blanco *et al.* (1989) suggested the occurrence of Mg in trioctahedral coordination.

From this literature review, it appears that there is no single model for palygorskite crystal chemistry which is accepted unanimously.

Palygorskite in sediments is often found mixed with salts, silicates and to a lesser degree with organic matter. This is attributed to the early diagenetic origin of palygorskite by transformation of previous Al clay minerals (smectite, illite...) (Decarreau *et al.*, 1975; Chahi *et al.*, 1993a). Chemical analyses of palygorskite available in the literature are often erroneous because the samples analyzed are admixtures of minerals (Galán and Carreto, 1999). The purification of palygorskite, by chemical techniques, whilst preserving its integrity is resolved partly by using cation exchange resins to extract carbonates, phosphates and sulfates (Chahi *et al.* 1993b), and using surfactants to separate palygorskite from organic matter-rich samples (Chahi *et al.* 1996). Because the particle sizes of palygorskite and associated silicates are small, silicate impurities are not easily separated by physical techniques such as ultracentrifugation, heavy liquid, or even with centrifugation and electro-magnetic separation, Thus, it is best to study samples of palygorskite associated with as few impurities as possible, with the impurities being well characterized independently.

The aim of this paper was to study an Mg-rich sample of palygorskite from Ganntour (Morocco) (Chahi *et al.*, 1993a), by IR spectroscopy, in both the OH-bending OH-and stretching regions.

MATERIAL AND METHODS

For this work, two types of clay fractions separated from samples of the phosphorite deposits of Ganntour (Morocco) were studied: (1) the palygorskite-rich clay fraction (PA-D) separated from dolomitic marl, containing minor amounts of smectite; and (2) the smectite-rich clay fraction (SM-Q) separated from sandy claystone. This smectite, which is similar to that mixed with palygorskite, is a montmorillonite having the following structural formula (Chahi *et al.*, 1999): $(Si_{3.96}Al_{0.04})(Al_{1.44}Fe^{III}_{0.30}Mg_{0.25})(Ca_{0.11}K_{0.10})O_{10}(OH)_2$.

The SM-Q and PA-D fractions were separated using cation exchange resin (amberlite IRC-50H eluted with

1.5 N HCl) to remove phosphate and carbonate phases (Chahi *et al.*, 1993b). X-ray diffraction patterns were obtained using a Philips diffractometer equipped with a Ni-filtered Cu tube. Chemical analyses were performed by arc emission spectrometry, the relative error being ~2% (Samuel and Rouault, 1990). Chemical analyses of individual palygorskite fibers were obtained by analytical electron microscopy (AEM), using a scanning transmission electron microscope (STEM) equipped with an X-ray spectrometer connected to a solid-state detector for energy dispersive analyses (EDAX 9900). The very thin individual fibers of palygorskite were easily destroyed under the beam, and therefore chemical analyses show an overstated silica content. Mössbauer spectra were recorded at 298 K over the range ±4.2 mm/s in 512 channels, with a spectrometer using a 1.85 Gbq ^{57}Co source (in Rh), and equipped with a WISEL MS1 vibrator, and a γ MICI-SEPH detector.

Fourier transform infrared (FTIR) spectra were recorded in the 4800−200 cm^{-1} range on a Nicolet 510-FTIR spectrometer. The spectrometer was continuously purged with dry air during scanning of the transmission spectra. The disks were prepared by mixing 3 mg of sample with 300 mg of KBr. The smectite spectrum was recorded after heating the pellet for 10 h at 100°C in order to evacuate the hygroscopic water. The IR spectra of palygorskite in the OH-stretching zone are somewhat complicated because bands due to structural OH are overlapped by the bands due to bound molecular water and zeolitic water within the channels (Russell and Fraser, 1994), and IR spectra are difficult to interpret if samples are not heated or deuterated. For this study, the IR spectra of palygorskite were recorded at room temperature, after heating the pellets in air for 10 h at 100°C, for 2 h at 200°C, and for 2 h at 500°C.

Serna *et al.* (1977) attributed the bands as being due to vibration of structural OH of palygorskite on the basis of dioctahedral mica data. However, palygorskite is a low-temperature clay mineral having low layer charge and few or no K^+ interlayer cations, like smectite. The wavenumber of νOH absorption bands due to precise chemical environments ($\nu M_1 M_2 \square OH$) differ from their equivalent in dioctahedral micas (Farmer, 1974). For this study, we preferred to attribute the bands due to vibration of structural OH in palygorskite on the basis of smectite data.

RESULTS

Chemical characterization of palygorskite

Taking into account that: (1) smectite associated with palygorskite in PA-D and the SM-Q smectite are genetically the same; (2) the bulk chemical compositions of samples PA-D and SM-Q are quite similar to the X-ray absorption coefficients of the two samples and can be assumed to be similar; and (3) the powder XRD patterns of both samples were performed using exactly

the same conditions, the percentage of smectite in PA-D can be estimated by using the ratio of the peak areas of smectite and palygorskite in PA-D and the peak area of smectite in SM-Q. The measurements suggested that PA-D contained ~17% of smectite.
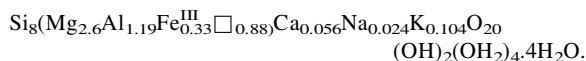
In Table 1 the bulk chemical composition and the mean chemical composition of isolated smectite particles ($Sm_{(PA-D)}$) in the PA-D sample, obtained by AEM, are given. The mean chemical composition of smectite particles in PA-D is similar to that of the smectite in SM-Q. Taking into account the proportion of smectite in sample PA-D from XRD data, the chemical composition of palygorskite ($Pal_{(PA-D)}$) in PA-D was calculated. From the XRD and IR data (see below), a small number of silica phases (chalcedony and/or quartz) is evident in PA-D; no sepiolite was detected.

The atomic ratio obtained by AEM chemical analyses of 16 individual palygorskite fibers of the PA-D sample plotted within an Al, Fe, Mg triangular diagram (Figure 1) indicate that Al, Fe and Mg cations are detected simultaneously within each fiber analyzed. The AEM data are consistent with the calculated chemical composition of palygorskite $Pal_{(PA-D)}$. The scattering of AEM data of clay minerals are often observed and are partly explained by analytical errors (Warren and Ransom, 1992). Nevertheless, AEM data (Figure 1) suggest that fibers of $Pal_{(PA-D)}$ palygorskite can contain different amounts of Mg and Al.

Mössbauer spectroscopy shows that all Fe occurs as Fe(III).

The mean structural formula of palygorskite $Pal_{(PA-D)}$ was established taking no tetrahedral substitution into account. This assumption is supported by the fact that in palygorskites described in the literature, tetrahedral substitutions are generally very low (Galán and

Carretero, 1999). The structural formula was established as follows:

$$Si_8(Mg_{2.6}Al_{1.19}Fe^{III}_{0.33}\square_{0.88})Ca_{0.056}Na_{0.024}K_{0.104}O_{20}$$
$$(OH)_2(OH_2)_4.4H_2O.$$

The sum of octahedral cations, Al/Mg and R^{2+}/R^{3+} ratios are 4.12, 0.42 and 1.7, respectively. These values are in the range of those reported for natural palygorskites (Weaver and Pollard, 1973; Paquet *et al.*, 1987; Galán and Carretero, 1999), and characterize a Mg-rich palygorskite.

The cation exchange capacity, deduced from the structural formula given above, is 31 $cmol_c/kg^{-1}$ and is similar to that of other natural palygorskites (Bakkasetter: 36 $cmol_c/kg^{-1}$; Hirsiger *et al.*, 1975; Georgian palygorskite: 25 $cmol_c/kg^{-1}$, Serna *et al.*, 1977; and Caceres palygorskite from Spain: 42.5 $cmol_c/kg^{-1}$; Blanco *et al.*, 1989). These data indicate the validity of the approach used to calculate the chemical composition of $Pal_{(PA-D)}$.

Infrared spectroscopy

OH-bending vibrations region. In the PA-D spectrum (Figure 2, spectrum b), bands at 911, 867, 834, 684 and 650 cm^{-1} are observed. Using previous attributions for smectite, the 911, 867 and 834 cm^{-1} bands can be attributed to $\delta Al_2\square OH$, $\delta AlFe\square OH$ and $\delta AlMg\square OH$, respectively (Farmer, 1974). The SM-Q smectite reveals the same bands (Figure 2, spectrum a). Considering the small amount of smectite in the PA-D sample (17%) and the Al content in $Pal_{(PA-D)}$, the $\delta Al_2\square OH$ band (Figure 2, spectrum b) is probably mainly due to palygorskite. Because the $\delta AlFe\square OH$ band is more intense in the PA-D spectrum than in the SM-Q one, $AlFe\square OH$ groups clearly occur in $Pal_{(PA-D)}$. As this is the reverse for the $\delta AlMg\square OH$ band, the occurrence of $AlMg\square OH$ groups in $Pal_{(PA-D)}$ is possible but cannot be demonstrated unambiguously.
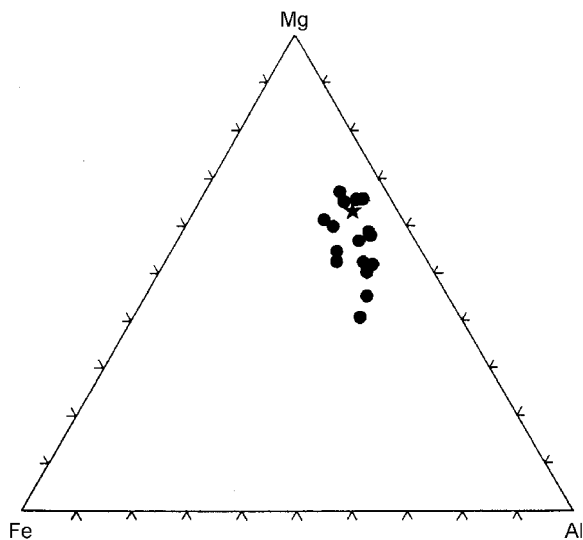

Figure 1. Distribution of Al, Mg and Fe in sample PA-D. ★: $Pal_{(PA-D)}$ chemical composition (Table 1); ●: AEM analyses of individual $Pal_{(PA-D)}$ palygorskite fibers.

Table 1. Chemical analyses (wt.%) of clay samples.

	$Sm_{(PA-D)}$	PA-D	$Pal_{(PA-D)}$
SiO_2	65.21	71.57	72.9
Al_2O_3	20.51	10.31	8.19
MgO	2.00	11.97	14.05
Fe_2O_3	7.73	4.26	3.54
K_2O	4.55	1.44	0.80
CaO	n.d.	0.35	0.43
Na_2O	n.d.	0.08	0.10

$Sm_{(PA-D)}$ = mean AEM chemical composition of smectite particles from sample PA-D (the relative analytical error for major elements is ~2%; n.d.: not determined); PA-D = bulk chemical composition by arc emission spectroscopy of sample PA-D (the relative analytical error is ~2%; the total is calculated to 100%; the loss after ignition at 1000°C is 13.74%, and the TiO_2 content is 0.47%); $Pal_{(PA-D)}$ = deduced chemical composition of pure palygorskite from sample PA-D (see text).
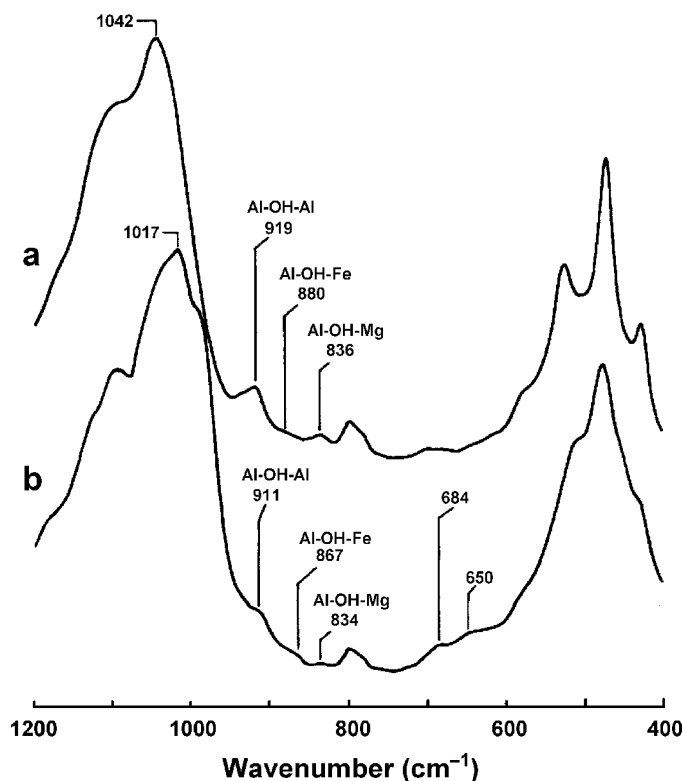
Figure 2. IR spectra in the 1200—400 cm^{-1} region at 100°C: (a) SM-Q sample, (b) PA-D sample.

The two bands at 650 and 684 cm^{-1} in PA-D spectrum are commonly observed in IR spectra of trioctahedral clays (Farmer, 1974) and correspond to the Si—O and δMg_3OH vibration bands, respectively, clearly giving evidence for the occurrence of tri-octahedral site occupancy.

The broad band at 790—785 cm^{-1} in SM-Q and PA-D spectra indicates the presence of silica phases (quartz and/or chalcedony) (Farmer, 1974), also detected by XRD. However, this band may overlap some weak δOH vibration bands due to palygorskite, such as $\delta FeMg\square OH$ and $\delta Mg_2\square OH$.

The vibration bands between 400 and 600 cm^{-1} and 1000 and 1200 cm^{-1} correspond to the framework of clay and silica phases (Farmer, 1974).

OH-stretching vibrations region. At room temperature, the FTIR spectrum of the PA-D sample reveals absorption bands at 3616, 3583, 3549 and 3408 cm^{-1} (Figure 3). This spectrum is similar to that obtained at room temperature by Khorami and Lemieux (1989). After heating at 100°C (Figure 3, spectrum b) and 200°C (Figure 3, spectrum c), the band at 3583 cm^{-1} is better resolved, whereas a new band appears at 3524 cm^{-1}. The band at 3616 cm^{-1} disappears while a new intense band appears at 3610 cm^{-1} with a shoulder at 3623 cm^{-1}. A band at 3720 cm^{-1} and a shoulder at 3680 cm^{-1} also appear.

The bands observed at 3549 and 3408 cm^{-1} at room temperature and their evolution upon heating (bands at 3549, 3524 and 3390 cm^{-1} at 100 and 200°C, and vanished at 500°C) are consistent with previous published data (Hayashi *et al.*, 1969; Mendelovici, 1973; Van Scoyoc *et al.*, 1979; Blanco *et al.*, 1988). They are mainly due to bound water.

As the shape of the 3583 cm^{-1} band is modified upon heating, another νOH is more likely to occur close to (or at) this wavenumber. Similarly, Serna *et al.* (1977) observed a band at 3595 cm^{-1} for the Georgia paly-gorskite. In the present study, the 3583 cm^{-1} band can be interpreted as the sum of two bands, one due to bound water, the other due to $\nu AlFe\square OH$ vibrations, by analogy with IR spectra of smectite (Farmer, 1974).

The band at 3623 cm^{-1} is well known in all palygorskite and is undoubtedly attributed to $\nu Al_2\square OH$ (Mendelovici, 1973; Mendelovici and Carroz Portillo, 1976; Serna *et al.*, 1977; Van Scoyoc *et al.*, 1979). As observed in previous IR studies of palygorskite upon heating, the 3623 and 3610 cm^{-1} bands observed above 100°C can be interpreted as a split of the 3616 cm^{-1} band observed at 25°C, all these bands being related to $\nu Al_2\square OH$ (Van Scoyoc *et al.*, 1979; Madejová and Komadel, 2001). The split of the $\nu Al_2\square OH$ band is connected with the structural modifications of the palygorskite fibers upon heating
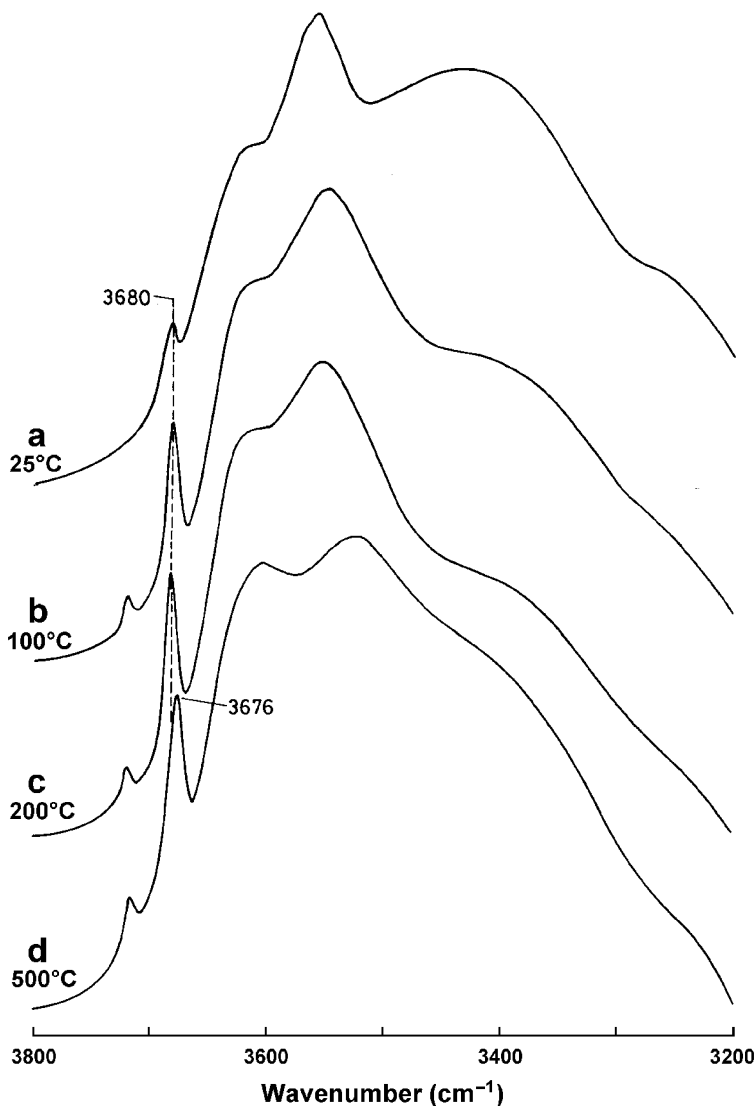
Figure 3. IR spectra of sample PA-D in the OH-stretching vibration zone: (a) under atmospheric conditions; (b) after heating the pellet at 100°C for 10 h; (c) after heating the pellet at 200°C for 2 h; and (d) after heating the pellet at 500°C for 2 h.

("folding structure") due to the loss of zeolitic and coordinated water (Preisinger, 1963).

In accordance with the δOH region, we conclude that $Al_2\square OH$ and $AlFe\square OH$ groups clearly occur in $Pal_{(PA-D)}$ palygorskite.

After heating a pellet at 500°C, a broad complex band with a maximum at 3630 cm^{-1} is also visible (Figure 3, spectrum d). Because at 500°C the dehydroxylation of Al_2OH groups is generally complete in palygorskite (Van Scoyoc *et al.*, 1979) while it is only partially complete in smectite (Serratosa, 1962), the 3630 cm^{-1} band should at least be partly attributed to $Al_2\square OH$ groups in the smectite impurity.

During heating, a shoulder at 3680 cm^{-1} appears. After heating the pellet at 500°C for 2 h, this shoulder

becomes a clear band at 3676 cm^{-1} (Figure 3, spectrum d). Such a band is commonly observed in IR spectra of all trioctahedral Mg clays and is attributed to νMg_3OH (*e.g.* Farmer, 1974). In the PA-D spectrum, this band can be attributed to Mg_3OH groups in the octahedral sheet of palygorskite. As is well known for sepiolite (Serna *et al.*, 1975), it is very convenient to study IR spectra of palygorskite after heating, because of the difference in dehydroxylation temperatures of dioctahedral, mainly $Al_2\square OH$ groups, and trioctahedral, mainly Mg_3OH groups.

The band at 3720 cm^{-1}, appearing upon heating (Figure 3), is attributed to an Si-OH group (Serna *et al.*, 1977).

Distribution of octahedral cations in the Pal$_{(PA-D)}$ palygorskite

The AEM chemical analyses of individual Pal$_{(PA-D)}$ palygorskite fibers (Figure 1) reveal that the three octahedral cations Mg, Al and Fe, occur in each isolated fiber in similar ratio. Infrared data reveal the occurrence of Al$_2\square$OH, AlFe$\square$OH and Mg$_3$OH groups, in both the OH-bending and OH-stretching regions, and do not exclude the occurrence of RMg$\square$OH groups (with R = Mg, Al or Fe) in Pal$_{(PA-D)}$ palygorskite. The Al$_2\square$OH, AlFe$\square$OH groups characterize dioctahedral occupancies, whereas the occurrence of Mg$_3$OH groups reveals trioctahedral occupancies. The dioctahedral and trioctahedral occupancies therefore exist together within each fiber of the Pal$_{(PA-D)}$ palygorskite.

From the results presented above, a qualitative octahedral cation distribution is proposed for Pal$_{(PA-D)}$ palygorskite (Figure 4). One must keep in mind that the palygorskite octahedral sheet is discontinuous and that only a part of the ribbon is represented.

Following Drits and Alexandrova (1966) and Drits and Sokolova (1971), we used the Bradley model of crystallographic palygorskite structure. Following Drits and Alexandrova (1966), Drits and Sokolova (1971) and Serna *et al.* (1977), we assume that the vacancies occur in *trans* octahedral sites, because this is a more realistic structure; a *cis* distribution of vacant sites would have led to a less stable structure.

We assume that edge positions are filled by Mg cations instead of Fe cations. This assumption is supported by: (1) the small amount of Fe in the chemical composition of Pal$_{(PA-D)}$; and (2) the link between Fe and Al in the inner octahedral sites as shown by IR spectra in the bending region.

From IR data, inner octahedra are filled either by Al and Fe in dioctahedral configuration or by remaining Mg in trioctahedral configuration.

Taking into account the mean cation ratio in the palygorskite Pal$_{(PA-D)}$ and the above constraints given by chemical and IR data, Mg, Al and Fe were distributed in fifty half unit-cells. The Mg occupies the edge positions.
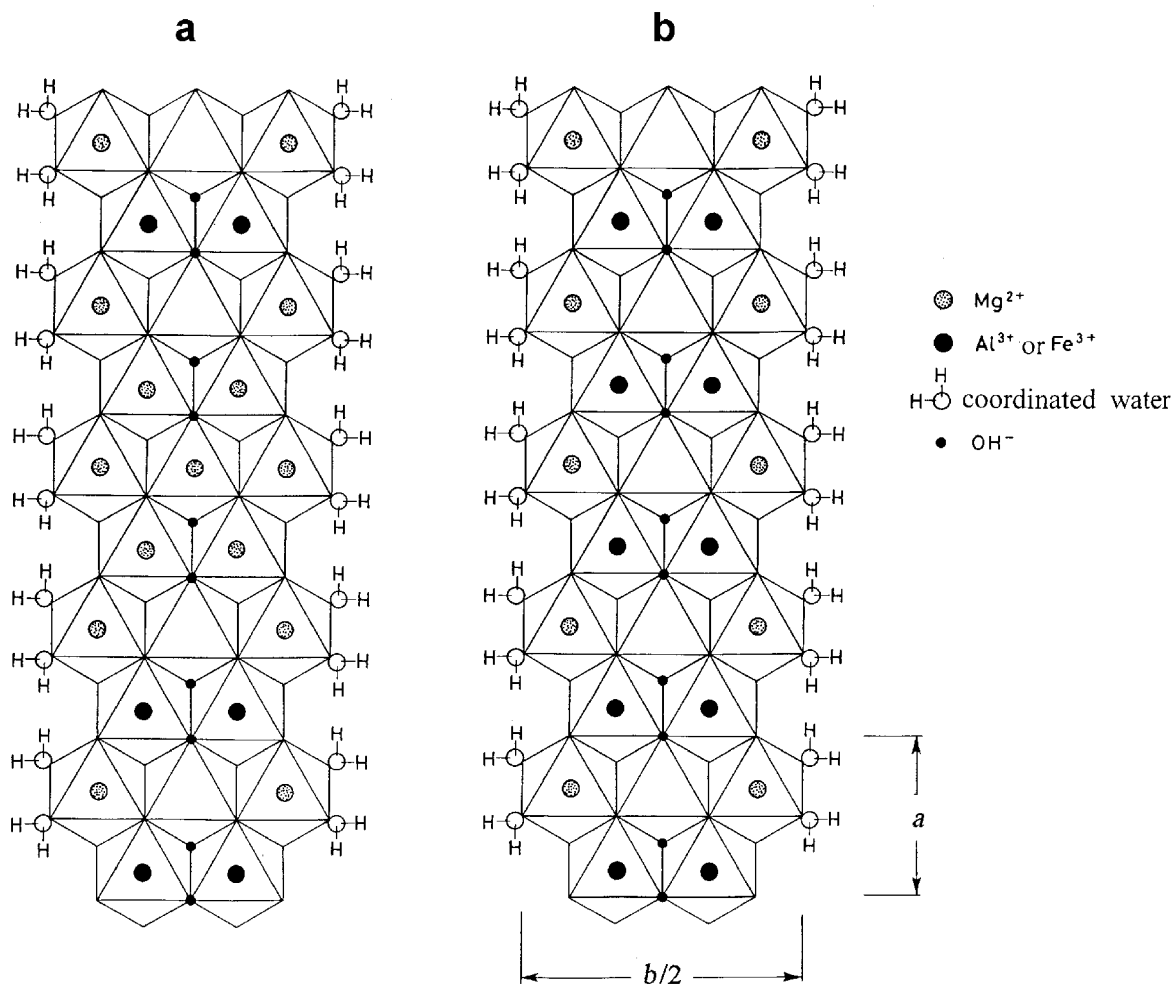

Figure 4. Schematic distribution of cations in the octahedral sheet of Pal$_{(PA-D)}$ palygorskite. (a) Part of ribbon with trioctahedral Mg clusters and dioctahedral Al-Fe zones; (b) part of ribbon with only dioctahedral Al-Fe zones.

The remaining Mg occupies the inner sites forming magnesian trioctahedral clusters. In Figure 4a, the cluster contains 5 Mg atoms, but it can be either more extended or duplicated. Aluminum and Fe occupy the remaining inner sites in dioctahedral regions (Figure 4b).

This proposed crystallochemical model for Ganntour palygorskite is simple and qualitative. The occurrence in the PA-D sample of impurities (smectite, silica phases) prevents the observation, in the δOH region of IR spectra, of other possible δOH bands due to palygorskite such as $\delta R Mg \square OH$ (with R = Mg, Al or Fe). It is also possible that some octahedra in edge positions are occupied by Al or Fe(III) instead of Mg, but with a low ratio. Even if it is so, it has no influence on the most important feature which is the occurrence of Mg_3OH absorption bands in IR spectra, proving the existence of trioctahedral clusters (or domains) within the ribbons of Ganntour palygorskite. The octahedral cation distribution described above is completely different to the previous one proposed by Serna *et al.* (1977) on the basis of a strictly dioctahedral model for palygorskite structure.

DISCUSSION

The palygorskite from phosphorite deposits of Ganntour (Morocco) is magnesian (2.6 Mg for 8 Si), and has an octahedral occupancy of 4.12 and a R^{2+}/R^{3+} ratio of 1.7.

As for many other palygorskites described in literature (Galán and Carretero, 1999), the Ganntour sample exhibits a chemistry intermediate between di- and trioctahedral clays. The IR study provides evidence, in both OH-bending and OH-stretching regions, of the occurrence of di- and trioctahedral site occupancies, proving crystallochemically the specific chemistry of Ganntour palygorskites by the juxtaposition within the ribbons of di- and trioctahedral domains, taking into account that the Mg and Al contents of each individual fiber are not always the same. This result is consistent with the high Mg content of the Ganntour palygorskite and its octahedral occupancy >4. Indeed, local tri-octahedral site occupancy can occur in palygorskite ribbons only if some *trans* sites are occupied. In this case, the octahedral occupancy must be >4, and the number of vacant sites <1 per half unit-cell. So, the structural formula (1) would appear to be more appropriate for describing all the possible chemistries of palygorskite than that of Galán and Carretero (1999) (formula 2).

Palygorskite samples, other than the Ganntour one, can present di-trioctahedral site occupancy in their ribbons. It would occur only if Mg_3OH features, which are indicative of at least local trioctahedral environments, are observed in IR spectra. It is the case for the PII sample studied by Blanco *et al.* (1989) which has an octahedral occupancy of 4.5 and has 3.18 Mg atoms per half unit-cell. It is also the case for the Cabrach sample (Scotland) (octahedral occupancy: 4.06, 1.7 Mg; Newman and Brown, 1987) for which Russell and Fraser (1994) observed on the IR spectrum an inflection at 3690 cm^{-1}. However, the di-trioctahedral site occupancy should not be generalized. For instance, after the study of the Georgia palygorskite (octahedral occupancy: 3.81, 1.36 Mg) by Serna *et al.* (1977), Mendelovici (1973) and Van Scoyoc *et al.* (1979), it seems that this sample is strictly dioctahedral without any local trioctahedral sites occupancy.

On the other hand, considering the structural formula (1) given above, if Mg_3OH features are observed in IR spectra of palygorskite samples, then it involves some complete site fillings within ribbons and an octahedral site occupancy >4. However, trioctahedral Mg_3OH features have been observed previously in IR spectra of palygorskite having an octahedral occupancy <4 by Hayashi *et al.* (1969) (octahedral occupancy: 3.84, 2.04 Mg) and Blanco *et al.* (1989) (sample PI; octahedral occupancy: 3.79, 1.69 Mg). These results are probably due to erroneous structural formulae. As stated by Galán and Carretero (1999), some of the chemical variability of palygorskite is caused by impurities, often difficult to eliminate. Taking into account the IR data, the octahedral occupancy of palygorskite samples studied by Hayashi *et al.* (1969) and Blanco *et al.* (1989) are probably underestimated. More generally, numerous published structural formulae of palygorskite have very low octahedral occupancies, clearly <4, and as low as 3.5 (Galán and Carretero, 1999; Weaver and Pollard, 1973). An octahedral occupancy <4 requires additional vacant sites within palygorskite ribbons, and thus two adjacent vacant octahedra are created locally (Figure 4). Such structural configuration would be highly unstable and would generate a major crystal defect.

CONCLUSIONS

As underlined by Galán and Carretero (1999), most palygorskites have chemistries intermediate between di- and trioctahedral phyllosilicates. For numerous samples, this specific chemistry is seen through the juxtaposition of ribbons of di- and trioctahedral domains or clusters which are more or less extended. This structural feature which occurs when the octahedral occupancy is >4 is not observed for all palygorskites, some being strictly dioctahedral.

Di-trioctahedral site occupancies can be detected easily by IR spectroscopy which appears to be very useful in constraining the structural formulae of palygorskite.

Lastly, the specific local crystallochemical structure described here for palygorskite is not restricted to fibrous clays. Such cation segregation within the octahedral sheets of 2:1 clays has already been described

for synthetic Al-Mg and Fe(III)-Mg smectites having octahedral occupancies >2 per half unit-cell (Grauby *et al.,* 1993, 1994).

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