FTIR spectroscopic study of palygorskite: Influence of the composition of the octahedral sheet

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Abstract

The influence of chemical composition to position and intensity of the absorption bands observed in the FTIR spectra of palygorskite has been studied by a detailed comparative study of six samples. Palygorskites studied have high purity and different chemical composition. At one extreme, there are two samples that correspond to Mg-rich palygorskites, at the other extreme a sample with a composition very close to the theoretical formula of this mineral, and there are three further samples whose structural formulae lie between these extremes. The position of the bands identified in the FTIR spectra of the palygorskites studied is similar for all samples, but there are some differences in their intensity, which are significant. Analysing these intensities, valuable information about the distribution of cations along the octahedral sheet has been obtained. Isomorphic substitution in octahedral sheet occurs only in M2 position. Al, and Fe may occupy M2 position whereas Mg can occupy all possible sites: M1, M2 and M3.

Keywords: Palygorskite; FTIR spectroscopy; Structural formulae; Octahedral sheet

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1. Introduction

Palygorskite is a clay mineral with a wide variety of industrial applications. This mineral has some particularly desirable sorptive, colloidal-rheological, and catalytic properties, in comparison with other clay minerals (Jones and Galán, 1988). Technological applications are based on its physicochemical properties, principally on composition, surface area, porosity, among others, and especially in its fibrous structure. Bradley (1940) described the structure of palygorskite, then referred to as attapulgite, a term now used in mining terminology. It is a 2:1 phyllosilicate in which the sheets of silica tetrahedra are periodically inverted with respect to the tetrahedral bases. As a result of this inversion, the octahedral sheets are periodically interrupted and terminal cations must complete their coordination sphere with water molecules. As only four of five octahedral positions available (as an average) are filled, palygorskite appears to be intermediate between dioctahedral and trioctahedral minerals (Martín Vivaldi and Fenoll, 1970). When compared to others phyllosilicates, even to sepiolite, palygorskite is very different because it does not have an "actual octahedral sheet", the octahedral ribbon is very sharp, more similar to a chain, and there are three different types of water molecules.

Considering the structure of palygorskite, there are several bonds that can give absorption effects in IR region. As in other clay minerals, the most intense absorptions are related to water and hydroxyl stretching

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and bending vibrations. This mineral has three types of water in its structure (Fig. 1), the first of which, named structural water, corresponds to OH of the octahedron placed in the central positions of the octahedral sheet. In the theoretical model (with Mg/Al = 1 and four octahedral positions occupied) 2M2–OH bonds are present because the central octahedron is vacant, as corresponds to a dioctahedral model (Fig. 1). But in a trioctahedral model, which M1 position is occupied, M1–2M2–OH bonds also occur. The cations that occupy the most external positions (M3 in Fig. 1) complete their coordination sphere with two molecules of water; this second type of water is named coordinated water or bonded water, as mentioned above. The last type is named zeolitic water, which is found inside the palygorskite channels.

Güven et al. (1992), for a dioctahedral palygorskite with a theoretical formula $Si_8O_{20}(Al_2Mg_2)(OH)_4(OH_2)_4 \cdot 4H_2O$, proposed that Al occupies the M2 position, Mg the M3 and M1 is vacant (Fig. 1). Considering this structural formula, Mg–OH_2 and Al–Al–OH bonds are present, and their corresponding absorptions may be found in the spectra. But in all palygorskites there can be certain differences between this ideal formula and their actual composition. The Mg/Al ratio is higher than 1, the number of octahedral positions occupied can be greater than 4, and substitution of octahedral Al by Fe^{3+} is present in all palygorskites (García-Romero et al., 2004).

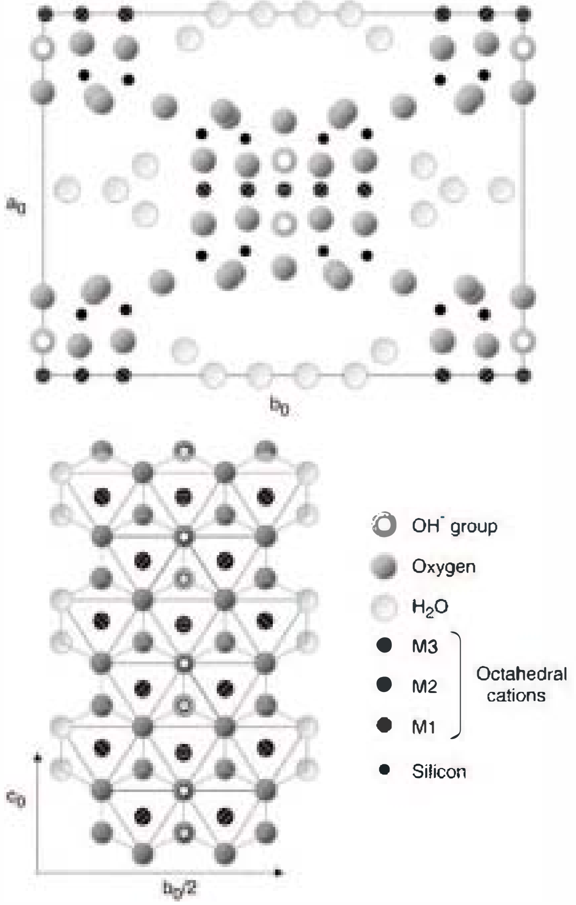

Fig. 1. Structural scheme of palygorskite projected on (001) according to Bradley (1940), and octahedral ribbon according to Güven et al. (1992).

These differences between the theoretical and actual composition must be taken into account when the FTIR spectra are interpreted. If the number of octahedral positions occupied is greater than 4, then M1 may be partially occupied and it is possible to find a new type of bond (trioctahedral model): M1–2M2–OH. In this case the three cations, Al, Mg and Fe, would occupy the M1 position, depending on the composition of the sample. Also, the number of octahedral cations can be greater than 4 and this is only possible with more than 2 R^{2+} cations (Mg in palygorskite) in order to have a charge of 10 per half-cell, and then the most probable bonds are 3Mg–OH or (Al, Fe)–2Mg–OH.

In addition to these considerations, the modification of the spectra after heating, and the consequent dehydration of the palygorskite, is very helpful for a correct interpretation. Loss of both zeolitic and coordinated water molecules after heating, as it can be seen by thermal techniques such as DTA and TGA, occurs in a reversible process up to 350 °C (Hayashi et al., 1969; Singer, 1989; Cases et al., 1991 and Khorami and Lemieux, 1989, among others). Above 350 °C, hemihydrated palygorskite is formed and the process is irreversible. After heating below 350 °C, the M3–OH_2 bonds are modified whereas the 2M2–OH bonds remain unmodified.

Most studies on FTIR of palygorskites interpret the absorptions observed in spectra either according to the theoretical formula, or either according to the formula obtained from bulk analyses of raw sample, which may contain some impurities. Taking into account that there is certain variability in the structural formulae of palygorskite, the aim of this work is to study how chemical composition influences the position and intensity of the vibrations in the FTIR spectra. Therefore, an FTIR spectroscopy study has been carried out, on several palygorskites, which have a well-known chemical composition, and the absorptions observed in the spectra have been related to structural formulae. By this means, valuable information about the distribution of cations along the octahedral sheet can be obtained.

2. Experimental

2.1. Materials

The following six palygorskites selected for their high purity have been used in this work, the first three collected by the authors:

1. ESQ sample proceeds from Esquivias, Toledo (Spain). Characterized by García-Romero et al. (2004).
2. LIS palygorskite proceeds from Volcanic Complex from Lisbom (Portugal).
3. TRA palygorskite proceeds from Cabo de Gata, Almería (Spain).
4. Palygorskite from Florida, (USA) supplied by Source Clays as PF1-1 and referred to as ATT in this work. This palygorskite has been widely reported in literature and has been used as a reference sample in numerous works including the "Baseline studies of the Clay Minerals Society Source Clays" (Costazo and Guggenheim, 2001).
5. TOR palygorskite was supplied by TOLSA Company and comes from the ore of Torrejón el Rubio, Cáceres (Spain). It was studied by Galán et al. (1973) and Fernández Macarro and Blanco Sánchez (1990).
6. YUC palygorskite from Ticul, Yucatán (Mexico), supplied by Dr. Manuel Sanchez del Rio, was reported by Isphording (1984).

These palygorskites have been selected not only for their high purity but also for their different chemical composition. At one extreme, there are two samples that correspond to Mg-rich palygorskites: ESQ and TRA. At the other extreme, LIS sample has a composition very close to theoretic formula of this mineral, and there are three further samples whose structural formulae are between these extremes (ATT, TOR and YUC).

2.2. Techniques

Chemical composition was obtained by analytical electron microscopy (AEM) of isolated particles with transmission electron microscopy (TEM), in samples of great purity using a JEOL 2000 FX microscope equipped with a double-tilt sample holder (up to a maximum of ±45°) at an acceleration voltage of 200 kV, with 0.5 mm zeta-axis displacement and 0.31 nm point-to-point resolution. The microscope incorporates an OXFORD ISIS energy dispersive X-ray spectrometer (136 eV resolution at 5.39 keV) and has its own software for quantitative analysis. Structural formulae of palygorskites were calculated on the basis of 21 oxygens per unit cell. All the Fe present was considered as Fe^{3+} (owing to the limitation of the technique), but the possible existence of Fe^{2+} should be taken into account.

Mineralogical characterization was performed by X-ray diffraction (XRD) using a Siemens D500 XRD diffractometer with Cu Kα radiation and a graphite monochromator. The samples used were random-powder specimens. Powders were scanned from 2° to 65° 2θ at a 0.02° 2θ/3 s scan speed.

The Fourier transformed infrared spectrometry (FTIR) was recorded in the 4000 to 400 cm^{-1} range on a BRUKER EQUINOX 55 spectrometer. The samples were prepared using the KBr pellet technique. All samples were studied under the same hydration conditions, kept over H_2SO_4 solutions (R.H. = 45%). The mixtures of the clays, and dried KBr (ratio 1:200) were subjected to a pressure of 8 ton cm^{-2}.

The statistic treatment of data was carried out using the SPSS 10.0 program.

3. Results and discussion

3.1. X-ray diffraction

Fig. 2 shows the X-ray diffractograms of the whole sample of the palygorskites studied. The high purity

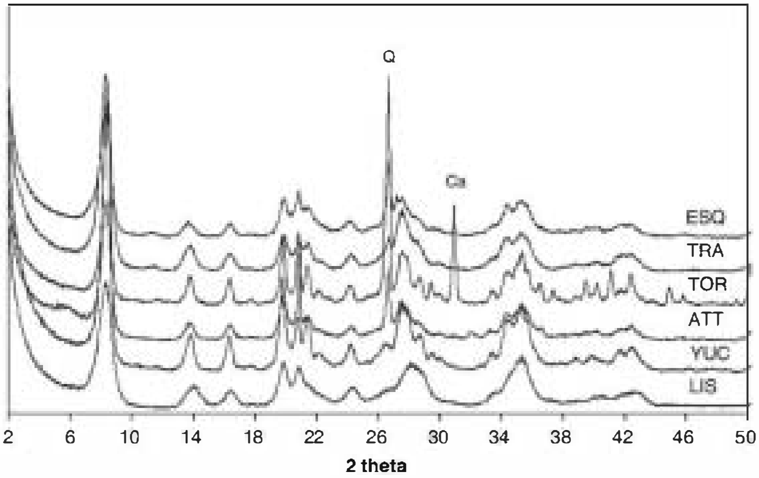

Fig. 2. XRD patterns of whole sample of the palygorskites studied. Q: quartz and Ca: calcite.

Table 1
Structural formulae for the six palygorskites studied, obtained from AEM analyses of isolated particles on the basis of 21 oxygen atoms

Sample	Si	Al^{IV}	Al^{VI}	Fe^{3+}	Mg	∑Oct. C.	R^{3+}	R^{3+}/R^{2+}
ESQ	7.87	0.13	1.04	0.20	3.11	4.35	1.24	0.40
TRA	8.02	–	1.2	0.16	2.89	4.25	1.36	0.47
TOR	7.91	0.09	1.48	0.37	2.25	4.10	1.85	0.82
ATT	7.85	0.15	1.47	0.25	2.30	4.02	1.72	0.75
YUC	7.85	0.15	1.57	0.24	2.21	4.02	1.81	0.82
LIS	8.02	–	1.91	0.04	2.01	3.96	1.95	0.97

of the samples has been confirmed from the diffractograms. Only small amounts of quartz in the ATT and the ESQ sample and calcite in the TOR sample have been found. The high crystallinity of the YUC and TOR samples can be deduced from the higher narrowness of the principal peaks. It is very important to take into account the purity of each sample, given that the impurities have their own absorption features. It must be pointed that in all the samples studied, except the very small amounts of smectite in the ATT sample, there are no impurities of other clay minerals, which have some absorption features similar to palygorskite.

3.2. Chemical composition

Table 1 shows the average structural formulae for the six palygorskites studied, the data were obtained from AEM analyses of isolated particles. It can be observed that there are some significant differences. The Al that occupies tetrahedral positions ranges between 0.15 (for the ESQ and YUC samples) and 0 (for the LIS and TRA samples). The most important differences were found in the octahedral cations content. Al, Mg and Fe are present in all the palygorskites studied, but the ratio among them strongly varies among the different samples. At one extreme there is an R^{3+}/R^{2+} ratio close to 1 without Fe^{3+} for the LIS sample, as corresponds to theoretical palygorskite, at the other there is a ratio $R^{3+}/R^{2+}=0.4$ for the ESQ sample, the most Mg-rich palygorskite. Fe^{3+} content varies between 0.04 (LIS) and 0.37 (TOR) and it is very similar to the other samples studied, approximately 0.2 cations per half-cell.

Therefore, the samples studied range between an Al-rich palygorskite and a very Mg-rich palygorskite and with respect to Al/Mg content they can be ordered thus: LIS–YUC–TOR–ATT–TRA–ESQ.

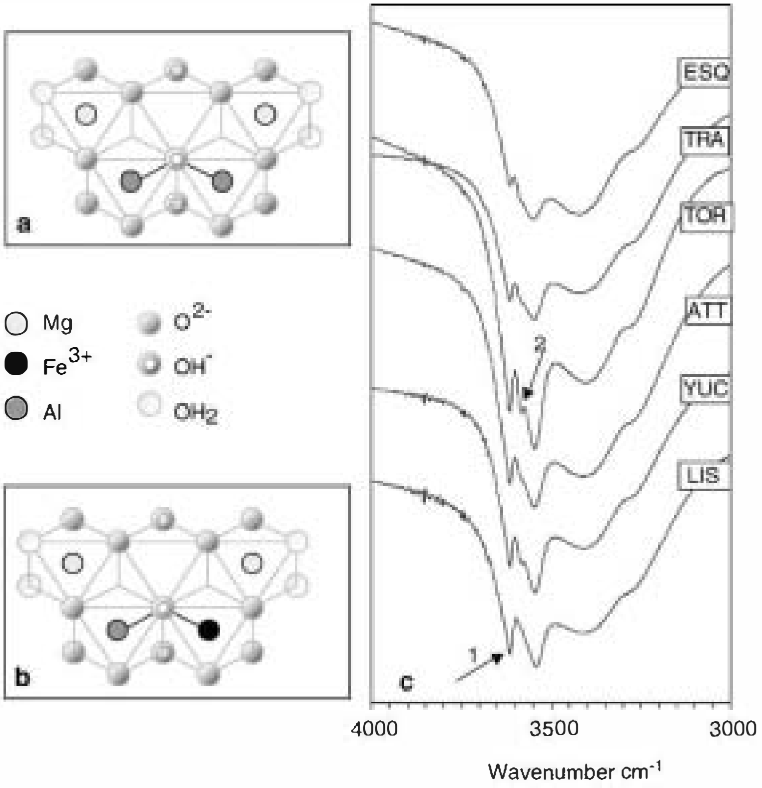

Fig. 3. Structural scheme of octahedral sheet for a half-cell of palygorskite showing different
(c) FTIR spectra in the region of high wavenumber of the palygorskites studied.

3.3. FTIR spectroscopy

The position of the bands identified in the FTIR spectra of the palygorskites studied is similar for all samples because all of them are very pure palygorskites, but there are some differences in their intensity, which are significant. The presence of small quantities of impurities can easily be detected in the FTIR spectra. Calcite is detected in the TOR sample by its characteristic band at 1430 cm^{-1} and a shoulder at 876 cm^{-1} (typical from carbonate anions) while quartz produces bands at 798 and 778 cm^{-1} in the ATT sample.

The spectra can be divided into two regions in order to make easier their study, the OH-stretching vibration region and the water bending vibration.

3.3.1. OH-stretching vibration region

In the higher wavenumber region of the samples studied the following can be observed (Fig. 3):

1. A sharp peak at 3616 cm^{-1}.
2. A peak or shoulder at 3580 cm^{-1}, which appears only in some samples.
3. Three bands centred at 3550, 3400 and 3350 cm^{-1}.

The first effect, at 3616 cm^{-1}, is described in all bibliographic references on FTIR of palygorskite (Mendelovici, 1973; Prost, 1973; Blanco et al., 1988; Frost et al., 1998, 2001; Shuali et al., 1987; McKeown et al., 2002; Chahi et al., 2002, among others) and it seems to be characteristic of this mineral. From heating and deuteration Mendelovici (op. cit.) concluded that this peak must be adscribed to bonds located in "inaccessible positions" in palygorskite, and therefore must be related to 2M2–OH bonds. It is well established in the literature that this is due to the OH-stretching mode in Al_2–OH groups (Fig. 3a). This band has been found in all the samples here studied, but with different intensities. In Fig. 3c, it will be noted that the highest intensities for this peak (labelled as 1) correspond to the LIS and TOR samples, and the lowest to the ESQ and TRA samples. As it is not possible to measure the area of the peak, the difference of transmittance between 3602 and 3616 cm^{-1} for each sample was measured with the aim of obtaining objective information about the intensity of this peak. The existence of a possible correlation between the octahedral content and the intensity of the peak ($I_{3616\ \mathrm{cm}^{-1}}$ in Table 2) has been investigated. The corresponding matrix of correlation is shown in Table 2. As can be seen, the peak of 3616 cm^{-1} is related with the content of R^{3+} and not only with the Al, that is to say, with the dioctahedral character of the mineral. While the coefficient of correlation (Pearson's correlation) for Al is 0.922, the R^{3+}/R^{2+} presents a higher correlation: 0.982. Therefore, the intensity of this peak indicates the highest dioctahedral character of the palygorskite, which is clearly related to the highest Al octahedral content and to the lowest Mg content (−0.990). A peak at similar wavenumber, also related to Al–Al–OH stretching vibration, can also be found in other dioctahedral and aluminic clay minerals such as

Table 2
Correlation matrix of crystallochemical data and peak intensities in the FTIR spectra

		Al	Mg	Fe	Oct. Cat.	R^{3+}	R^{3+}/R^{2+}	$I_{3616\ \mathrm{cm}^{-1}}$	$I_{912\ \mathrm{cm}^{-1}}$	$I_{510\ \mathrm{cm}^{-1}}$
Al	C.C.	1.000	−0.945	−0.317	−0.935	0.933	0.963	0.922	0.918	0.924
	B.S.		0.004	0.540	0.006	0.007	0.002	0.009	0.010	0.008
Mg	C.C.	−0.945	1.000	0.004	0.977	−0.994	−0.992	−0.990	−0.744	−0.797
	B.S.	0.004		0.994	0.001	0.000	0.000	0.000	0.090	0.058
Fe	C.C.	−0.317	0.004	1.000	0.099	0.046	−0.054	0.030	−0.647	−0.490
	B.S.	0.540	0.994		0.852	0.931	0.918	0.955	0.165	0.324
Oct. Cat.	C.C.	−0.935	0.977	0.099	1.000	−0.947	−0.955	−0.971	−0.759	−0.787
	B.S.	0.006	0.001	0.852		0.004	0.003	0.001	0.080	0.063
R^{3+}	C.C.	0.933	−0.994	0.046	−0.947	1.000	0.994	0.982	0.722	0.788
	B.S.	0.007	0.000	0.931	0.004		0.000	0.000	0.105	0.063
R^{3+}/R^{2+}	C.C.	0.963	−0.992	−0.054	−0.955	0.994	1.000	0.982	0.789	0.844
	B.S.	0.002	0.000	0.918	0.003	0.000		0.000	0.062	0.035
$I_{3616\ \mathrm{cm}^{-1}}$	C.C.	0.922	−0.990	0.030	−0.971	0.982	0.982	1.000	0.722	0.803
	B.S.	0.009	0.000	0.955	0.001	0.000	0.000		0.105	0.055
$I_{912\ \mathrm{cm}^{-1}}$	C.C.	0.918	−0.744	−0.647	−0.759	0.722	0.789	0.722	1.000	0.966
	B.S.	0.010	0.090	0.165	0.080	0.105	0.062	0.105		0.002
$I_{510\ \mathrm{cm}^{-1}}$	C.C.	0.924	−0.797	−0.490	−0.787	0.788	0.844	0.803	0.966	1.000
	B.S.	0.008	0.058	0.324	0.063	0.063	0.035	0.055	0.002	

C.C.: correlation coefficients of Pearson. B.S.: bilateral signification.

kaolinite and montmorillonite (Madejová and Komadel, 2001).

The second effect observed in this region in the samples studied is a peak or shoulder at 3580 cm^{-1} (labelled as 2 in Fig. 3c). This peak is not present in the LIS sample, while in the TOR sample it appears with the highest intensity. Mendelovici (1973) found a peak at 3590 cm^{-1} which shifts to 3570 cm^{-1} on heating, and Shuali et al. (1987) and Augsburger et al. (1998) assigned the weak band at 3580 cm^{-1} to coordinated water molecules in the channels. Serna et al. (1977) attributed this band to Al–Fe^{3+}–OH or Al–Mg–OH bonds, while Chahi et al. (2002), based on comparison with smectite, attributed it to Al–Fe–OH stretching. In the samples here studied there is a good correlation between the intensity of this peak and the Fe content. The LIS sample is the only sample that does not have Fe^{3+} (0.04), while the TOR sample is the one which presents the greatest content in Fe^{3+} of the samples studied (0.37). The YUC and ATT samples both present similar Fe^{3+} content ($\approx$0.24) and as can be observed in the spectra, they have similar intensity for the 3580 cm^{-1} shoulder. In the ESQ and TRA samples the content is lower than in the other samples, 0.20% and 0.16%, respectively, and the absorption feature also appears as a smaller shoulder. If the correlation with the Fe^{3+} content is taken into account, the possibility that the Fe^{3+} is located in M2 position may be considered (Fig. 3b). This is in agreement with Delineau et al. (1994) in their study on the iron content of kaolinite and, with Besson and Drits' (1997a,b) study of the relationships between chemical composition of dioctahedral mica minerals and their IR spectra. They found that the wavenumber of the band corresponding to OH groups increased with the sum of the valences of the cations in M–M–OH bonds, but for the same sum of valences the increase of mass of the cations leads to a decrease in wavenumber of the corresponding band. Thus, in mica the Al–Al–OH stretching vibration appears at 3621 cm^{-1} and that corresponding to Al–Fe^{3+}–OH at 3573 cm^{-1}.

With respect to the three bands centred at 3550, 3400 and 3350 cm^{-1}, as can be seen in Fig. 3c, the samples studied are similar in position but not in intensity. There is good agreement in the literature recording the assignation at water molecules (coordinated and zeolitic water), but according to Ausburger et al. (1998) "the band at 3543 cm^{-1} is excessively strong

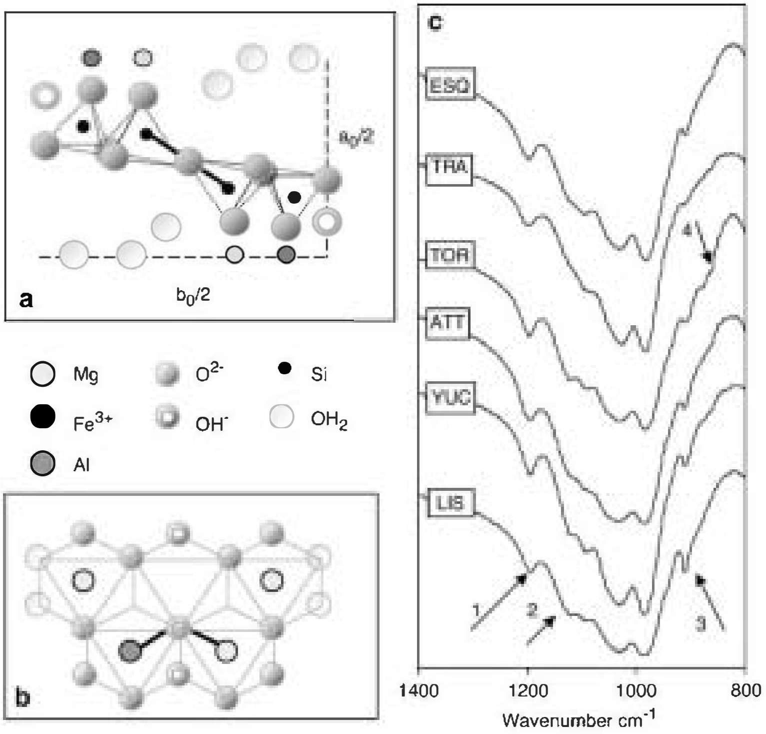

Fig. 4. (a) Structural scheme of bonds between alternative ribbons in palygorskite showing the Si–O–Si bond. (b) Structural scheme of octahedral sheet for a half-cell of palygorskite showing Al–Mg–OH bond. (c) FTIR spectra in the region between 800 and 1400 cm^{-1} of the palygorskites studied.

and sharp to be assigned only to coordinated water; a contribution of the OH-stretching mode in Al–Mg–OH, Fe–Mg–OH and Fe_2–OH groups is also considered". The peak intensities observed in the samples studied seem to be in agreement with this observation because the richest in Mg palygorskites present the lowest intensity due to the fact that they have the greatest trioctahedral character.

It is important to note that, even in the richest in Mg palygorskites (the ESQ and TRA samples), there is no absorption at 3680 cm^{-1} which corresponds to 3Mg–OH, that it is to say, Mg in trioctahedral coordination. According to Besson and Drits (1997a,b) a possible Mg–Mg–OH bond must produce an absorption at higher wavenumber than 3616 cm^{-1} (that corresponds to Al–Al–OH) because the sum of the valencies is lower. None of the samples now studied presents a peak at higher wavenumbers, and this means that there is no Mg occupying two contiguous M2 positions. There are other references to Mg-rich palygorskites (Blanco et al., 1989; Chahi et al., 2002; Cai and Xue, 2004) but in all cases they have trioctahedral Mg, and thus a peak at 3680 cm^{-1} is found. In our samples, although the trioctahedral character is very high, the distribution of Mg, Al and Fe must be without 3Mg–OH bonds, as proposed for the ESQ sample (García-Romero et al., 2004).

3.3.2. *Water-bending vibration region*

An asymmetric band, centred at 1650 cm^{-1}, appears in all samples studied. Mendelovici (1973) and Mendelovici and Portillo (1976) reported the presence of two partially resolved peaks at 1655 and 1630 cm^{-1}. It is well known that this effect corresponds to bending modes of absorbed and zeolitic water.

In Figs. 4 and 5, the region of the lowest wavenumbers can be seen. Between 1200 and 400 cm^{-1} characteristic bands of silicate can be observed, mainly those corresponding to Si–O bonds in the tetrahedral sheet, and also to M–O stretching vibrational bonds. This interval of wavenumber is very complex because the lattice modes also have an influence in this region of the spectra. For this reason there are few interpretations published about this region in palygorskite spectra. However, it is especially interesting because it provides information about the nature of the octahedral sheet.

Frost et al. (2001) assigned the absorption found between 1160 and 1115 cm^{-1} to Si–O stretching modes and those between 986 and 655 cm^{-1} to M–OH deformation. When the spectra of the samples are compared, some important differences are found. The first peak that appears in this region in all samples studied is located at 1190 cm^{-1} (labelled as 1 in Fig. 4c). Mendelovici (1973) reported this peak as characteristic of palygorskite. It is important to note that it does not appear in other clay silicates, except in sepiolite. Vicente Rodríguez et al. (1996), in the study of several phyllosilicates and their structural modifications during acid treatment by FTIR, found the peak at 1190 cm^{-1} in sepiolite and palygorskite, but not in lamellar clay minerals. The structure of palygorskite and sepiolite, with periodical inversion of apical oxygen in tetrahedra, presents an Si–O–Si bond between alternative ribbons (Fig. 4a). This bond is particularly noticeable in FTIR spectra with the absorption at 1190 cm^{-1} (Yariv, 1986).

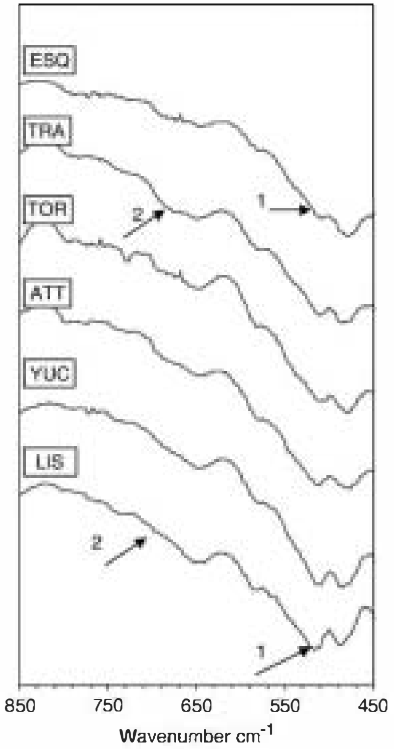

Fig. 5. FTIR spectra in the region between 450 and 900 cm^{-1} of the palygorskites studied.

At lower wavenumber there is a doublet placed at around 1100 cm^{-1} (labelled as 2 in Fig. 4c) that may correspond to M–O stretching vibrations (Blanco et al., 1989) or Si–O (Ausgburger et al. 1998; Frost et al., 2001). The first peak, at 1084 cm^{-1}, appears in all samples, with the best definition in the YUC sample (the most crystalline sample). The second peak, at 1116 cm^{-1}, appears as a shoulder in the ESQ sample, and its intensity may be related to the dioctahedral character.

The most intense peaks at 980 and 1024 cm^{-1} are those corresponding to stretching of the Si–O bond

(Blanco et al., 1989). In all samples studied, the position and intensity of both peaks are similar.

With respect to the peak that appears at 910 cm^{-1}, as can be seen in Fig. 4c (labelled as 3), this sharp peak is present in all spectra but with different intensity, the most intense peak corresponds to the LIS sample. There is good coincidence in bibliography with respect to the assignation of this peak (sometimes reported at 912 cm^{-1}). This peak corresponds to Al–Al–OH deformation, and it is a consequence of the dominantly dioctahedral character of palygorskite (Madejová and Komadel, 2001). For Augsburger et al. (1998) this band also encloses the symmetric stretching mode O′–SiO$_3$. If the intensity of the peak (measured by difference of the intensity at 918 cm^{-1}) is taken into account and is correlated with crystallochemical parameters, it will be noted ($I_{912\ \mathrm{cm}^{-1}}$ in Table 2) that this peak is directly related to the Al content (coefficient of correlation 0.918).

There is a small shoulder centred at 860 cm^{-1} (Fig. 4c, labelled as 4). This shoulder has been adscribed to the bending vibration mode of Al–Fe–OH bond (Fig. 3b), by Farmer (1974) for smectite and Chahi et al. (2002) for palygorskite. This assignation is in agreement with the intensity observed in the spectra of the samples studied, because the highest intensity corresponds to the TOR sample (labelled as 3 in Fig. 4c), the richest in Fe of the palygorskites studied. Madejová and Komadel (2001) interpreted the shoulder at 860 cm^{-1} as due to the Al–Mg–OH bond, in which case the sample with the greatest intensity for this effect must be the ATT sample, the most dioctahedral sample with lowest R^{3+} value (Table 1), but this is not experimentally found.

For Farmer (op. cit.) and Chahi et al. (2002), the presence of Al–Mg–OH bonds produces an absorption at 834 cm^{-1}. This effect is not observed in the palygorskites here studied, neither in the most dioctahedral ones (LIS, YUC and ATT samples). If the assignation at the Al–Mg–OH bond is taken into account, this means that in these samples the Mg occupy the M2 position. If only Al and Fe^{3+} occupy M2 position, then there may be a percentage of vacancies in this position for dioctahedral samples, because R^{3+} ranges between 1.95 and 1.72, but this does not seem possible. However, bearing in mind that there are Mg in excess for M3 position, it is possible to assume that this cation also occupies a small percentage of M2 position (as in Fig. 4b). The Mg content occupying the M2 position ranges between 1/10 and 1/7 per half-cell in the LIS and ATT samples respectively, but this is too small to give a clear spectral response.

The interpretation of the lowest wavenumber region, that corresponds to 450–700 cm^{-1}, is very problematic because “this part of the spectrum is of complex origin, with contribution from Si–O–Si and O′–SiO$_3$ bending vibrations and lattice modes” (Augsburger et al., 1998). For this reason, and because the spectrometers have lower capacity of resolution in this region, there are very few references to this IR region in palygorskite. Moreover, this region is important because in the sequence of Si–O–M–O–Si bonds, a very important factor is the nature of M (Mg, Al, Fe...) while the trioctahedral or dioctahedral surrounding has less influence. When the samples are compared (Fig. 5) it is possible to observe important differences and similarities, which can be related to chemical composition of the octahedral layer. There are three bands placed at 480, 578 and 647 cm^{-1} that appear almost with the same intensity in all samples. It is possible to assume that they are not influenced by the octahedral composition and therefore, they are related to bonds corresponding to tetrahedral sheet. On the contrary, the bands that appear at 510 cm^{-1} and the shoulder at 676 cm^{-1} (labelled as 1 and 2 in Fig. 5, respectively) vary in intensity for different palygorskites and thus permit, for the first time, the assignation of both bands. As with the 3616 and 912 cm^{-1} peaks, the intensity of the 510 cm^{-1} peak was correlated with crystallochemical parameters and, as can be seen ($I_{510\ \mathrm{cm}^{-1}}$ in Table 2), this peak is directly correlated with the Al octahedral content (correlation coefficient=0.924) and by analogy with smectite, this band is probably due to Si–O–Al(IV). The shoulder at 676 cm^{-1} is related to the Mg content, and for Chahi et al. (2002) this band is probably due to bending Mg$_3$–OH, but the effect due to the stretching mode of this bond does not appear in the samples here studied.

While it is observed that the lower is the content in Al, the lower is the intensity of the related FTIR effects, the increase in the Mg content is not reflected as a parallel increase in the intensity of the effects involving this element. Only the higher intensity in the shoulder at 670 cm^{-1} runs parallel to the increase if Mg content. On the contrary, the substitution in tetrahedral sheet is not easily detectable.

4. Conclusions

Several palygorskites with different chemical composition have been studied: four dioctahedral samples and two with higher trioctahedral character. Differences in composition of the octahedral sheet only seem to affect the M2 positions. All palygorskites here studied and those reported in bibliography contain more than 2 atoms of Mg per half-cell, therefore there is always enough Mg to complete M3 positions. Al occupies M2 positions in all samples studied, and if there is isomorphic substitution of Al by Fe this element also occupies M2 positions. If the sum of Al^{VI} and Fe^{3+} is less than 2 then Mg may also occupy this position.

In the spectra, the vibrations corresponding to M3–OH_2 bonds are similar because there is always enough Mg to complete M3 position. Since the M2 position is that which reflects the chemical variations, 2M2–OH bonds have the greatest influence in spectra and reflect these differences. If several palygorskites are compared it is possible to identify those which present the highest Al content (most intense, 912 and 510 cm^{-1} peaks), the highest Fe content (3590 cm^{-1} and 880 cm^{-1} shoulders), and the highest dioctahedral character (most intense 3616 cm^{-1} peak).

The decrease of the intensity of the most characteristic peaks in the spectra of palygorskite is clearly related to the increase in Mg content. In the most trioctahedral samples it is also possible to determine whether there are Mg-rich clusters (with two contiguous M2 positions, and the corresponding M1, occupied by Mg) or whether the distribution of the "excess" of Mg is along the octahedral ribbon, but without 3Mg–OH trioctahedral bonds. The two Mg-palygorskites here studied have no trioctahedral Mg bonds because the 3680 cm^{-1} peak is not found.

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