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Hydroxyl groups and water in palygorskite[1]

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Abstract

Infrared spectra of the coordinated water in palygorskite were studied at different degrees of exchange of deuterons and protons. The single peaks observed for the bending fundamental of isotopically diluted H_2O and D_2O show that all the coordinated water molecules are equivalent, as suggested by Bradley's structure determination. The doublets observed for the three fundamentals of isotopically dilute HDO showed that the coordinated water molecules are asymmetric (C_s symmetry). Response of palygorskite films to the angle of orientation indicated one of the OH stretching modes to have its transition moment nearly perpendicular to the [100] plane. The orientation effect results from one of the protons on each of the coordinated water molecules forming a hydrogen bond directed towards the hexagonal holes of oxygens formed by the Si–O–Si connections between the amphibole chains, and it explains the distorted character of this water. Deuteration and orientation studies also verified that the two OH stretching bands of the distorted water are truly uncoupled.

Georgia palygorskite is shown to be completely dioctahedral, and a model is presented to explain its octahedral cation occupancy and the frequency of the structural hydroxyls. Infrared adsorption bands around 3700 cm^{-1} indicated the presence of some SiOH groups in the mineral. These groups are less abundant in palygorskite than in sepiolite, indicating that palygorskite has less exposed edges.

Introduction

A large number of infrared studies have been published on hydroxyl groups and water in layer silicates. However, little is known about these groups and molecules in fibrous silicates such as sepiolite and palygorskite. X-ray diffraction investigations have indicated that palygorskite belongs to the space group C^3_{2h}–$C2/m$, with two formula units per primitive cell (Bradley, 1940). In the structural scheme of Bradley, the eight oxygen atoms of water (O*w*) have been placed in equivalent positions, suggesting only one kind of coordinated water molecules. Recently, Prost (1975) has shown each coordinated water molecule to be distorted by means of hydrogen bonding through one of its protons. Our detailed study substantiates the presence of hydrogen bonding of the water and shows the orientation of the protons in the structure. Also, important conclusions about the uncoupled character of the HDO and H_2O molecules will be considered.

The presence of SiOH groups at sepiolite crystal edges was illustrated by Ahlrichs *et al.* (1975). Similar SiOH groups are found in palygorskite. An explanation of their relative abundance and of the orientation of the hydroxyl will be presented.

The original chemical analysis published by Bradley (1940) on palygorskite and later reviewed by Drits and Aleksandrova (1966) shows that an average of four of the five octahedral cation sites are occupied. Therefore, some dioctahedral character has been suggested for the mineral (Henin and Caillere, 1975). The intensity and position of the infrared vibrations of the structural OH in palygorskite, as well as the particular arrangement of the octahedral layer, have been considered in developing the postulates concerning the di-trioctahedral character.

Methods and materials

The Georgia palygorskite (attapulgite) was obtained from the Clay Mineral Respository, Department of Geology, University of Missouri, Columbia, Missouri. Characterization of the sample by X-ray diffraction and infrared analysis showed it to be of

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high purity. Only slight evidence of an expanded phase (montmorillonite) was observed after treatment of the sample with ethylene glycol. The C.E.C. of the sample as determined by summation of the cations on the exchange sites was 25.1 meq./100 grams with 16.1 meq. Ca, 4.8 meq. Mg, 0.6 meq. K, 0.2 meq. Na, and 2.4 meq. H. The chemical formula given by Bradley (1940) for Georgia palygorskite is $(Si_{7.83}Al_{0.17})$ $(Al_{1.36}Ti_{0.07}Fe^{3+}_{0.37}Fe^{2+}_{0.03}Mg_{1.98})$ $O_{20}Ca_{0.32}$ $(OH)_2(OH_2)_4 \cdot nH_2O$.

Powdered palygorskite samples were converted to a stable suspension in water by ultrasonic treatment. Self-supporting films (2 mg/cm^2) were prepared by drying suspensions on a flat mylar surface. This should have resulted in a portion of the crystal fibers having their [100] plane parallel to the film surface. The films were mounted in aluminum foil holders and placed in an evacuable infrared cell similar to that described by Angell and Schaffer (1965). Spectra were obtained using a Perkin-Elmer 421 spectrophotometer. Deuteron and proton exchange studies were made in a high vacuum system which gave a vacuum of less than 10^{-5} mm Hg.

Separation of the structural OH from the coordinated H_2O was achieved through deuteration of the coordinated H_2O by flushing the film repeatedly with D_2O vapor at room temperature. Separation of the structural OH and coordinated H_2O was also achieved by deuterating the structural OH. Samples with structural OD and coordinated H_2O were produced without altering the structure of the palygorskite by heating the sample to 300°C in an atmosphere of D_2O, cooling to 25°C, and then flushing several times with H_2O vapor. The important feature of this approach is that the sample can be studied in both the OH and OD stretching regions of the spectrum without overlap of the structural hydroxyl and coordinated water bands.

Study of the coordinated water was conducted by progressive proton or deuteron exchange in samples with structural OD or OH, respectively. The D_2O to H_2O ratio used for these isotopic dilution studies was adjusted to produce the amount of exchange desired. A 5 to 1 ratio was used to observe the uncoupled OH and a 0.2 to 1 ratio for the uncoupled OD.

Results and discussion

A. Infrared spectra of palygorskite

Under atmospheric conditions palygorskite contains loosely adsorbed water. It has been suggested that this water is hydrogen-bonded through the water coordinated to the edge cations of the octahedral sheet exposed on the external surface and in the channels (zeolitic water). This physically adsorbed water can be removed under vacuum (< 10^{-5} mm Hg) at room temperature, leaving the mineral with two water molecules coordinated to each external octahedral cation (Fig. 1).

Under this evacuated condition a nonsymmetric absorption band appears at 1624 cm^{-1} due to the bending mode of the coordinated water. However, a complex spectrum of stretching bands of the coordinated water and the structural hydroxyls still exists in the 3800–3300 cm^{-1} region (Fig. 2A). Because of the more accessible position of the coordinated water molecules, they were easily deuterated at room temperature, leaving three absorption bands at 3625, 3595, and 3560 cm^{-1} due to the structural hydroxyls (Fig. 2B). The assignment of these bands based on position and chemical composition will be considered later. Due to the isotopic exchange, an OD shoulder appears at 2745 cm^{-1} and two bands at 2700 and 2585 cm^{-1}. At the same time, a split (1220 and 1205 cm^{-1}) is observed in the nonsymmetric bending mode of the coordinated D_2O (Fig. 2B). Similar spectra have been presented by Mendelovici (1973) for Georgia pal-

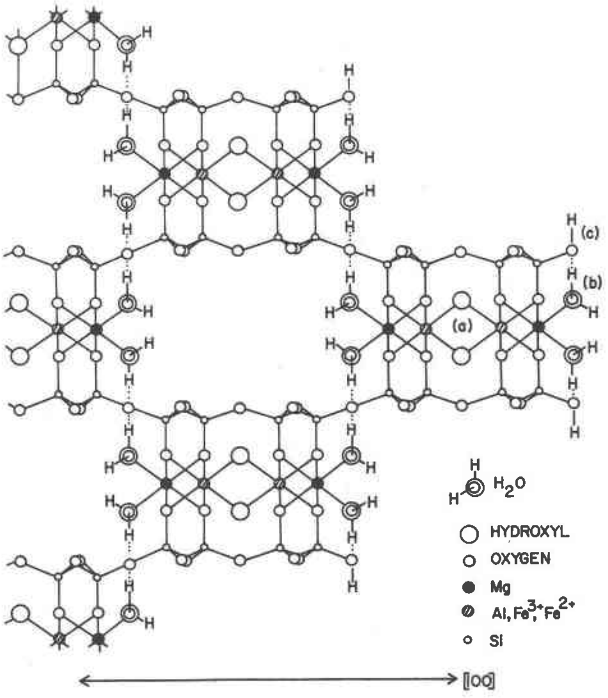

Fig. 1. Palygorskite model (Bradley, 1940) modified to show (a) the dioctahedral character, (b) the position of the protons in the coordinated water, and (c) in the SiOH.

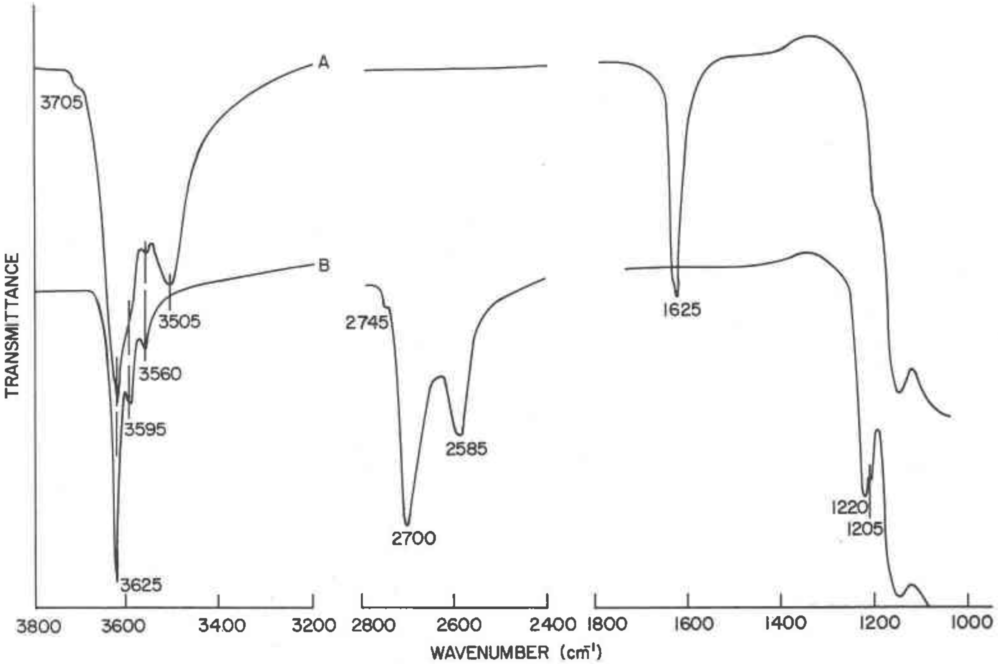

Fig. 2. Spectra of palygorskite under vacuum with structural hydroxyls as OH and coordinated water as (A) H_2O and (B) D_2O.

ygorskite and by Prost (1975) for palygorskite from Serradilla.

Samples with structural OD (Fig. 3A–B) show features analogous to those with structural OH. A comparison of the positions of the OH and OD absorptions is presented in Table 1 with the corresponding OH/OD frequency ratios.

B. Coordinated water

Numerous studies of the nature of water molecules in hydrated crystals have been made using the isotopic dilution technique. These studies have shown that the number and position of the infrared absorption bands of the water molecules in crystals are affected by inter- and intramolecular coupling. Slight isotopic exchange can eliminate these couplings, thus making it possible to observe the different number and kinds of uncoupled OH (or OD) vibrations that exist in the crystal (Falk and Knop, 1973).

Although both protonated and deuterated studies gave similar results, much better resolution was obtained when the spectra were studied in the OD stretching region (Fig. 4). This phenomenon has been previously reported in a study of water in copper chloride dihydrate by Fifer and Schiffer (1971). They suggested that the H_2O stretching bands are more difficult to discern than their D_2O counterparts due to the smaller ν_3–ν_1 separation for H_2O. Since an equal separation of 115 cm^{-1} was found in the H_2O and D_2O absorption bands of palygorskite (Table 1), their suggestion does not seem to provide a general explanation for their observation. Other examples of better resolution in deuterated specimens have been reported for adsorption of water on ZrO_2 (Agron *et al.*, 1975), and for deuterated molecules like H_2S (Forster and Schuldt, 1975).

(1) The bending fundamental of isotopically diluted H_2O and D_2O. The vibrations of equivalent water molecules in a crystal may engage in dynamic coupling. This phenomenon is often referred to as correlation field splitting (Khanna *et al.*, 1969). However, this coupling can be eliminated when the H_2O or D_2O is isotopically diluted. As the coordinated water molecules in palygorskite are isotopically diluted, a single absorption band appears for the bending fundamental at 1620 cm^{-1} for H_2O or 1215 cm^{-1} for D_2O (Fig. 5B). These data indicate that the four water molecules per half-unit cell of the palygorskite are crystallographically equivalent. The results are also in good agreement with the structural model of Bradley (1940), in which the eight O_w of the water per unit cell are placed in the same equipoint (Fig. 1).

From the correlation diagram for the site symmetry of water, C_1, in association with the group factor symmetry of palygorskite, C_{2h} (Bradley, 1940), one would postulate that correlation field-splitting should

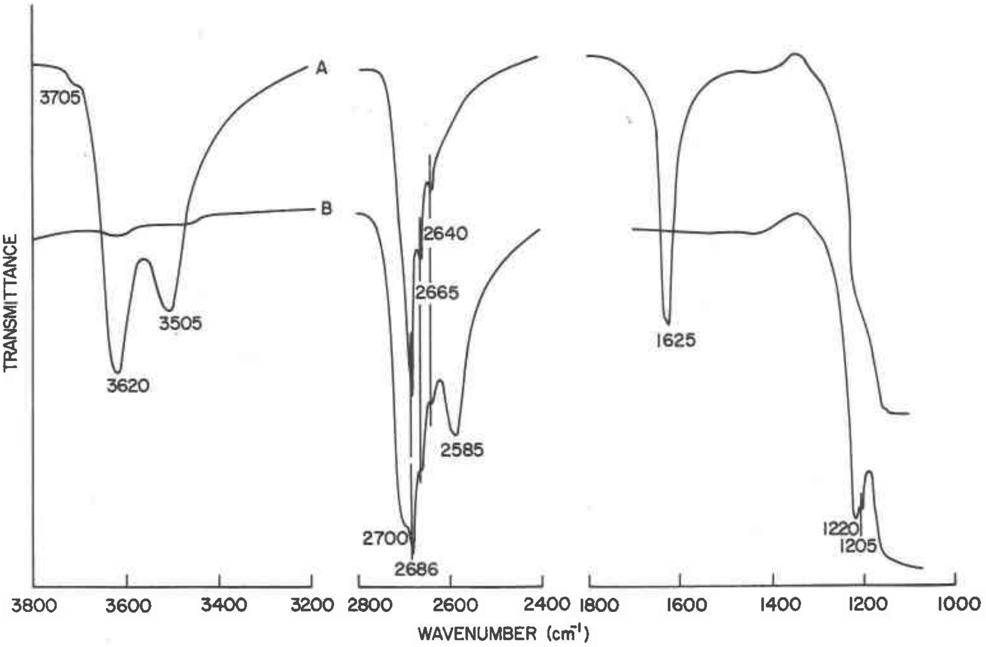

Fig. 3. Spectra of palygorskite under vacuum with structural hydroxyls as OD and coordinated water as (A) H_2O and (B) D_2O.

cause the internal vibrations of a water molecule to give rise to two coupled vibrations which are infrared active, *Au* and *Bu* (Table 1). Thus the nonsymmetrical character of the bending absorption of the H_2O (Fig. 5A) and the comparable doublet observed for the D_2O (Fig. 5C) could be considered due to the vibrational coupling of the water molecules present in the unit cell. Some previous examples of correlation field splitting have been found in water molecules of several crystal hydrates (Seidl *et al.*, 1969; Holzbecher *et al.*, 1971).

(2) The OH and OD fundamentals of HDO. Figure 4 shows the spectrum of the OH and OD stretching regions at various degrees of proton exchange. Exchange of a small fraction of the H_2O and D_2O (or vice versa) produced two stretching absorption bands due to uncoupled OD at 2670 and 2600 cm^{-1}. At the same time two bending HDO absorptions at 1445 and 1425 cm^{-1} appear (Fig. 5A). Vibrations isotopically isolated are considered to be uncoupled, since coupling between OD (OH) and surrounding OH (OD) vibrations is extremely weak compared to cou-

Table 1. Position of structural hydroxyl and coordinated water absorption bands in palygorskite

Structural Hydroxyl				Coordinated Water			
OH	OD	OH/OD	Assignment	H_2O	D_2O	OH/OD	Assignment
3705	2745	1.350	SiOH	3620	2700	1.341	Unperturbed OH
3625	2686	1.350	Al_2-OH	3505	2585	1.356	Hydrogen bonded OH
3595	2660	1.349	(Al,Fe^{2+})-OH (AL,Mg)-OH	1625*	1220 1205		Bending modes, Au and Bu
3560	2640	1.349	(Fe^{3+},Fe^{2+})-OH (Fe^{3+},Mg)-OH				

*a nonsymmetric peak

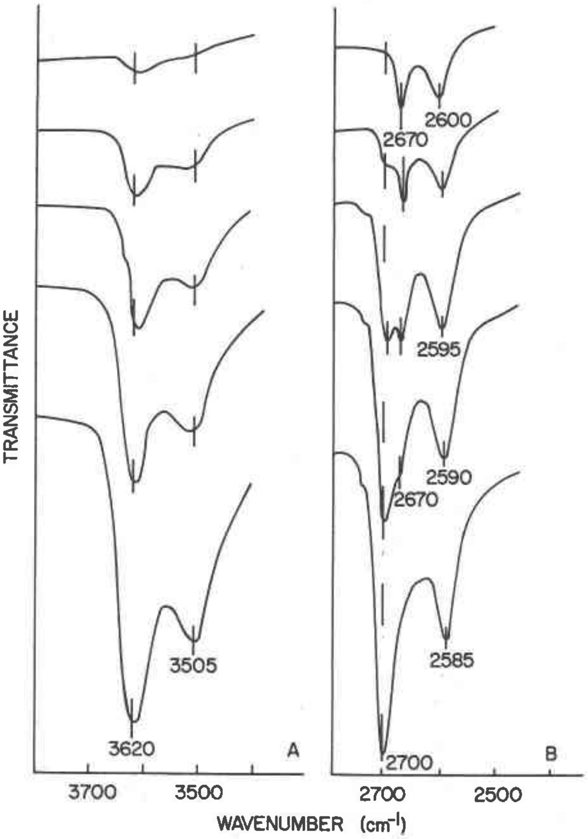

Fig. 4. Spectra of the progressive H–D exchange in coordinated water of palygorskite with (A) increasing H exchange in the coordinated D_2O, and (B) with increasing D exchange in coordinated H_2O. Initial states shown in Figs. 3B and 2A, respectively.

pling between like oscillators. Therefore, the doublets observed for the three fundamentals (OH and OD stretching, HDO bending) of isotopically-diluted HDO indicate that the water molecules in palygorskite are asymmetric (Seidl *et al.*, 1969).

The lack of a frequency shift during the progressive isotopic exchange in the uncoupled OD of the HDO (2670, 2600 cm^{-1}) and in the OD stretching of the D_2O (2700, 2585 cm^{-1}) is characteristic of water molecules without intermolecular coupling (Kling and Schiffer, 1971). The apparent change in frequency in the uncoupled OD at 2600 to 2585 cm^{-1} during the isotopic exchange is considered to be due to the lack of resolution of the different proportions of HDO and D_2O molecules.

(3) Uncoupled character of the HDO and D_2O. An important feature which appears when the partially deuterated film is oriented at 40° (Fig. 6A) is the significant increase in intensity of the lower frequency absorption band (2600 cm^{-1}) of uncoupled OD. This increase in intensity of 2600 cm^{-1} occurs while the uncoupled OD at 2670 cm^{-1} remains unchanged. A similar effect due to orientation is also noted for the lower-frequency coordinated water band in sepiolite, which is a trioctahedral fibrous silicate with a similar structure to palygorskite (Fig. 7B). This response to orientation shows that one of the OH groups of the coordinated water in the palygorskite has its axis directed essentially perpendicular to the [100] plane. This orientation leaves the proton in a favorable position to bond with the *p*-electron clouds which project from the surface oxygens into the hexagonal holes formed by the Si–O–Si connections between the silica chains of adjoining amphibole ribbons. Strong hydrogen bonding of water molecules into the hexagonal holes of saponite and vermiculite has previously been suggested (Farmer and Russell, 1971). The low frequency of the OH (OD at 2600 cm^{-1}) supports the presence of this hydrogen bond. Hydrogen bonding of one of the OH groups of the coordinated water in palygorskite has been previously sug-

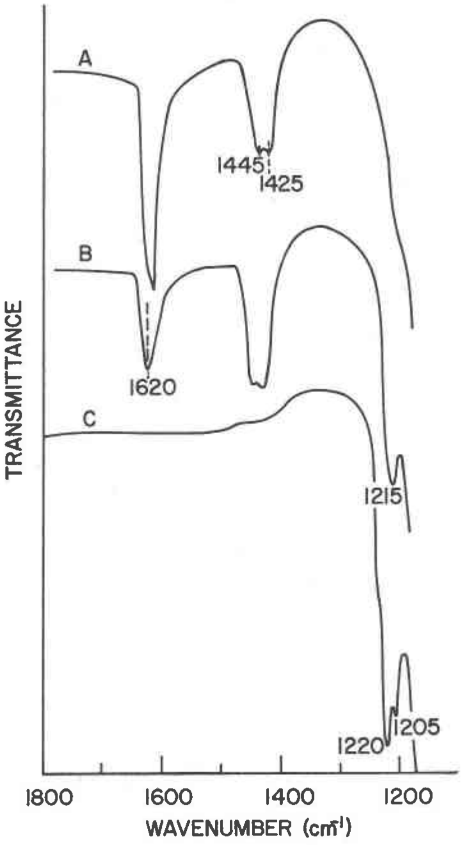

Fig. 5. Spectra of the bending mode of coordinated water in palygorskite with increasing deuteration.

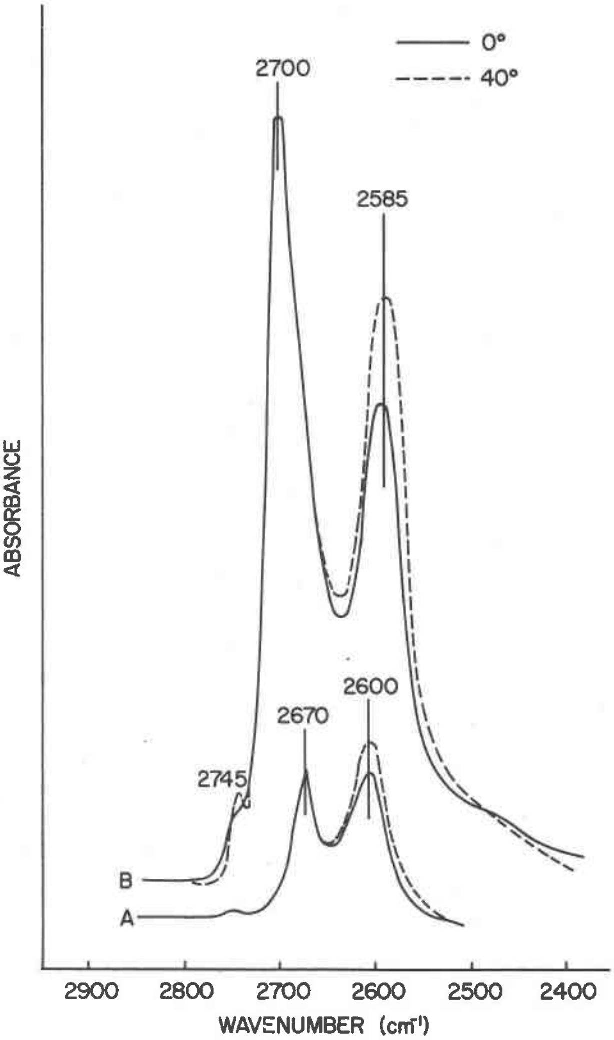

Fig. 6. Spectra of (A) uncoupled OD from HDO and (B) uncoupled OD from D_2O.

gested by Prost (1975). He assigned the hydrogen bond of the distorted water molecule inward toward one of the oxygen atoms of the octahedral sheet. This assignment is based on an appropriate O–O bond distance predicted from the frequency of the uncoupled OD applied to the Nakamoto *et al.* (1955) relationship. However, this bond orientation would place the proton in close proximity to both the Mg and Si atoms of the lattice, where repulsive forces on the proton would exist. The model we have presented in Figure 1 places the hydrogen-bonded proton in the hexagonal hole formed by adjoining amphibole ribbons, and places the other proton into the open channel. Both protons would thus be accessible to zeolitic water, and the hydrogen-bonded proton would show an orientation affect as noted. In addition, if the coordinated water in palygorskite is regarded to be a distorted water molecule (C_s symmetry), the fact that each OH or OD behaves independently shows its true uncoupled character. This is not unexpected, since coupling can be eliminated by partial deuteration (Bellamy and Pace, 1972).

The important feature observed following complete deuteration is that the coordinated water, as D_2O, has the same independent response to orientation (Fig. 6B) that was observed in the uncoupled OD. This shows that there is almost no intramolecular coupling present in the distorted water molecule in palygorskite. Therefore, the two absorption bands at 2700 and 2585 cm^{-1} correspond to the stretching motions of the two different OD (or OH) groups of each highly distorted water molecule.

The degree of vibrational distortion of a water molecule, *i.e.*, degree of coupling between both stretching vibrations, in molecules asymmetrically perturbed has been considered by the equation proposed by Kling and Schiffer (1971).

$$\theta = (\Delta\nu_{D_2O} + \Delta\nu_{HDO})/2\Delta\nu_{D_2O}$$

$\theta = 1/2$ in undistorted molecules (C_{2v} symmetry) and $\theta = 1$ for a highly distorted molecule (C_s symmetry), where $\Delta\nu_{HDO} \simeq \Delta\nu_{D_2O}$ and the intramolecular coupling is negligible.

Applying this equation to the coordinated water in palygorskite gives the value for the D_2O specimen of 0.80. This means that the water molecule is highly distorted, and substantiates the relative independent

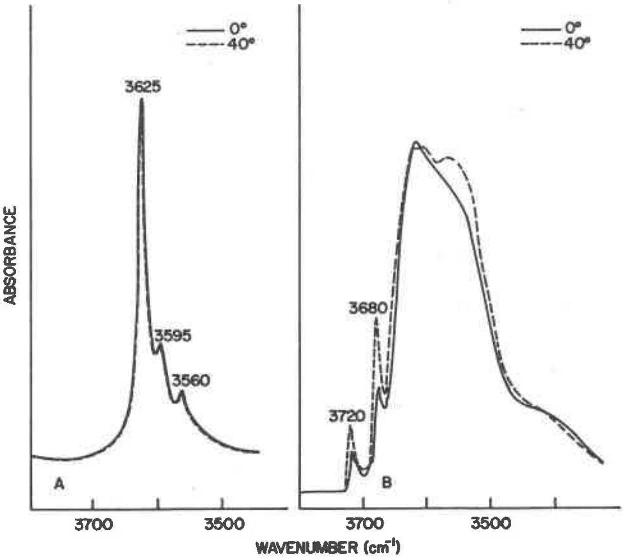

Fig. 7. Effect of orientation on evacuated films of (A) deuterated palygorskite and (B) non-deuterated sepiolite.

behavior of both OH groups as shown by the orientation effects. However, some slight coupling must exist, which is supported by the small difference in frequency between the uncoupled OD of the HOD, 2670 and 2600 cm^{-1}, and the uncoupled OD of the D_2O, 2700 and 2585 cm^{-1} (Bellamy and Pace, 1971). Kling and Schiffer (1971) found and discussed a similar distortion for the water molecules in calcium sulfate dihydrate.

C. *SiOH groups.*

The infrared study of hydroxyls in sepiolites has shown the presence of structural SiOH groups near 3700 cm^{-1} as a consequence of the large number of crystal edge sites (Ahlrichs *et al.*, 1975). The fibrous morphology of palygorskite (similar to sepiolite) would also predict a large number of SiOH groups to complete the coordination of the tetrahedra at the edge sites. Therefore, the shoulder observed at 3705 cm^{-1}, or at 2745 cm^{-1} following isotopic exchange, must be due to SiOH groups in the crystals (Table 1). The high frequency of SiOH and its ease of perturbation can be easily explained by its location at crystal edges, a very isolated site.

The relative abundance of these groups in sepiolite has been suggested as a measure of the degree of crystallinity of this mineral (Ahlrichs *et al.*, 1975). The low intensity of the SiOH band in palygorskite indicates less edge surface or fewer imperfections than was observed for the several sepiolites. The lower specific surface area of this mineral, 195 m^2/g, (Barrer and MacKenzie, 1954) in contrast to sepiolite, 320 m^2/g, (Fernandez Alvarez, 1971) also suggests it to have fewer imperfections or fewer exposed edges.

An increase in intensity of the SiOH groups is observed when the sample is oriented at 40°, showing that its OH axis is essentially perpendicular to the [100] plan (Fig. 6B). The position of the protons in the coordinated water produces a special orientation of the proton of the SiOH groups, due to repulsion effects (Fig. 1C). Similar behavior is shown by the SiOH (3720 cm^{-1}) in sepiolite minerals (Fig. 7B).

D. *Structural hydroxyls in the octahedral sheet*

Although Bradley's model for palygorskite is essentially correct, most of the chemical analyses show four cations per half-unit cell. Therefore, as has been pointed out, the mineral must have some dioctahedral character (Rautereau and Mifsud, 1975; Henin and Caillere, 1975).

Infrared studies of layer silicates have provided valuable information about the orientation of their OH groups. These studies have shown that in trioctahedral minerals the transition moment of the OH groups is essentially perpendicular to the plane of the layer, whereas in dioctahedral minerals it is tilted out of the cleavage plane (Serratosa and Bradley, 1958). Oriented self-supporting films permit a similar study of the OH groups in the fibrous silicates. Figure 7 shows the effect of orientation on the intensity of the structural hydroxyl bands in palygorskite and the structural hydroxyl and coordinated water bands in sepiolite. In agreement with its trioctahedral character, sepiolite shows an appreciable increase in intensity of its OH groups at 3680 cm^{-1}. However, no orientation effect is shown for the three OH absorption bands in palygorskite, which suggests a complete dioctahedral character for the mineral. This seems inconsistent with the chemical analysis, but as will be shown below this inconsistency is only apparent.

Figure 8 presents a scheme of the octahedral layer in palygorskite. If we consider that the two octahedra holding the coordinated water at the edge of the channel in each half-unit cell are always occupied by cations, then wherever the other two octahedral cations are placed the palygorskite will be a completely dioctahedral mineral, since only two out of the three octahedrons below the hexagonal hole will be occupied.

The cation ordering in the octahedral layers can be considered by taking into account the position and intensity of the structural OH. The chemical composition of the octahedral layer of Georgia palygorskite per three half-unit cells is $(Al_{4.08}Fe^{3+}_{1.11}Fe^{2+}_{0.09}Ti_{0.21}Mg_{5.94})$. In agreement with its dioctahedral character the mineral does not show an absorption at 3680 cm^{-1}, which is known to be due to 3 Mg in a trioctahedral mineral (Ahlrichs *et al.*, 1975). Therefore, most of the Mg cations must be placed at the edge of the channels holding the coordinated water (6 Mg per three half-unit cells). This model, with water all coordinated to the same cation (Mg), is in good agreement with the observation of only one kind of coordinated water molecule in palygorskite, and with the sharpness of the stretching absorption bands of this water. Ordering in the cation positions, as shown here for Mg, is now being commonly found in the layer silicates, as a consequence of the refinement of structures in subgroup symmetry (Bailey, 1975).

The remaining cations $(Al_{4.08}Fe^{3+}_{1.11}Fe^{2+}_{0.09}Ti_{0.21})$ must be placed in the 6 inner octahedral positions, and must be responsible for the infrared absorptions at 3625, 3595, and 3560 cm^{-1}. The absorption at 3625

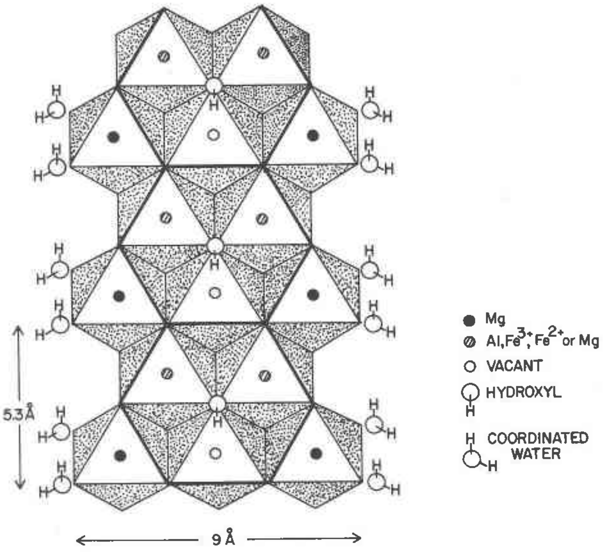

Fig. 8. Arrangement of cations in the octahedral layer of palygorskite illustrating its dioctahedral character (three half-unit cells).

cm^{-1} is well established as being due to Al_2–OH (Russell and Fraser, 1971). This would be in agreement with the high amount of Al present in the palygorskite. The less intense hydroxyl peaks at 3595 and 3560 cm^{-1} are not as well established, but are characteristic of dioctahedral minerals (Farmer *et al.*, 1971; Farmer, 1974). In analyzed biotites the absorption at 3600 cm^{-1} was considered (Al,Fe^{2+})–OH and the band at 3550 cm^{-1} was considered (Fe^{3+}, Fe^{2+})–OH. In celadonite, a dioctahedral mica, absorption bands at 3603 and 3557 cm^{-1} have been assigned to (Al,Mg)–OH and (Mg,Fe^{3+})–OH, respectively. Applications of these assignments to palygorskite are summarized in Table 1.

Conclusions

Interpretation of the infrared spectra of the coordinated water molecules and hydroxyl groups in palygorskite provides the following conclusions:

(1) There is only one kind of coordinated water molecule in palygorskite, according to isotopic dilution studies.

(2) This water has C_s symmetry and is coordinated mainly to Mg cations located in the channels at the edges of the octahedral sheets.

(3) The coordinated water is oriented with the transition moment of its hydrogen-bonded hydroxyl perpendicular to the [100] plane and its other hydroxyl directed toward the channels.

(4) The two stretching frequencies of the distorted water are not coupled and therefore are independent vibrators.

(5) The OH bond of the SiOH group at the crystal edges is oriented nearly perpendicular to the [100] plane, and it is less abundant than in sepiolite, indicating fewer crystal imperfections or edge surfaces.

(6) The Georgia palygorskite shows complete dioctahedal character, and its three stretching vibrations from structural OH can be assigned to (1) Al_2–OH, (2) (Al,Fe^{2+})–OH or (Al,Mg)–OH, and (3) (Fe^{3+},Mg)–OH or (Fe^{3+},Fe^{2+})–OH.

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