Structural changes in palygorskite during dehydration and dehydroxylation[1]

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Abstract

Infrared spectra and X-ray diffractograms were obtained for Georgia palygorskite with different contents of coordinated water. Interpretation of these results show that palygorskite starts to lose coordinated water at relatively low temperatures, causing the structure of the mineral to fold. Although the mineral is folded when 50 percent of the coordinated water is lost, the folding does not appear to be uniform. An ordered folded state is not reached until 65 percent of the water is lost. Rehydration from the folded state containing coordinated water is rapid. Removal of the last half of coordinated water is accompanied by loss of the structural hydroxyls.

Flushing palygorskite with ammonia removes the coordinated water and replaces it with ammonia coordinated to the Mg located at the channel edge. However, almost no ammonium is produced, indicating that the mineral contains few exchangeable cations. In the ammoniated palygorskite, folding of the mineral occurs readily upon evacuation of the sample at ambient temperature. This suggests that six-fold coordination of each edge Mg is an important factor in keeping palygorskite in the unfolded state.

Comparison of palygorskite to the analogous fibrous mineral sepiolite shows palygorskite to fold and dehydroxylate at lower temperatures. These characteristics parallel similar observations for other layer silicates, and have been attributed to differences between dioctahedral and trioctahedral minerals.

Introduction

Much of the commercial value of palygorskite to the pharmaceutical, fertilizer, and pesticide industries results from its surface area. The total surface area of palygorskite is dependent on both the external surface and the amount of surface available in its molecular-size channels. The structural arrangement of the mineral under different environmental conditions will dictate the total area available for physical and chemical interactions.

Both palygorskite and sepiolite (a fibrous mineral similar to palygorskite) have been shown to fold by rotation of their fibers on the axis through the Si–O–Si bonds that join the fiber units along the length of their edges (Preisinger, 1963). Folding closes the channels and thus eliminates this portion of the surfaces. Palygorskite, as characterized by X-ray diffraction, has an intense [110] reflection between 10.2 and 10.5A that is affected by the state of the channel.

Upon complete dehydration of the mineral, the 10.5A spacing has been shown to greatly decrease in intensity and a new peak (8.6 to 9.2A) of low intensity occurs as a consequence of the folded structure (Hayashi *et al.*, 1969; Hirsiger *et al.*, 1975). Preisinger (1959, 1963) concluded that the folding occurred following the loss of both the zeolitic and coordinated water, and therefore constituted the "anhydride" form. X-ray data by Hayashi *et al.* (1969) indicate that the folding occurs prior to complete dehydration.

Thermal analysis curves for several of the palygorskites have been reported (Caillere and Henin, 1961; Hayashi *et al.*, 1969; Nathan, 1969; Prost, 1975; Rautureau and Mifsud, 1975). All studies indicate that water in palygorskite exists in several states. The specific number, as well as temperature ranges for each state, is debated.

Caillere and Henin (1961) have listed three states for the water loss as seen from thermogravimetric curves: zeolitic water is lost below 200°, bound (or coordinated) water is lost between 250 and 400°, and

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hydroxyl water is lost above 400°C. According to both Prost (1975) and Hayashi *et al.* (1969), the loss of coordinated water in palygorskite occurs in two steps, as has been shown for sepiolite (Serna *et al.*, 1975). Prost (1975) indicates that under vacuum the first half of the coordinated water is removed between 150 and 300° and the last half, along with the structural hydroxyls, is removed at temperatures above 300°C.

Rehydration of palygorskite has been followed after heat treatments at 210, 350, 540, 600, and 800°C, using X-ray diffraction and infrared spectroscopy (Hayashi *et al.*, 1969). Rehydration was observed to occur after heating to 350° where approximately one half of the bound water was removed, but rehydration was not observed after heating to 540°C when all of the bound water was removed.

Thus the exact conditions under which the structure of palygorskite changes during heating are in dispute. This is due, in part, to incomplete studies and inadequate control of the experimental conditions. The objective of our investigation is to show the structural changes that occur in palygorskite as related to the coordinated water content of the mineral.

Methods and materials

The Georgia palygorskite used and the method for preparation of the self-supporting films for infrared analysis have previously been described (Serna *et al.*, 1977). The films were mounted in aluminum foil holders and placed in an evacuable infrared cell similar to that described by Angell and Schaffer (1965). Vacuum studies were conducted at less than 10^{-5} mm Hg, and infrared spectra were obtained using a Perkin–Elmer 421 spectrophotometer.

The dehydration and dehydroxylation studies were conducted by heating the samples stepwise under continuous vacuum for 5 to 90 minute periods at each temperature. After each heating period the sample was cooled under continuous vacuum before running the spectrum.

Samples for X-ray analysis were prepared by placing several milliliters of a dispersed palygorskite suspension on a glass slide. The slides were then subjected to specific thermal treatments in vacuum to remove portions of the coordinated water. X-ray diffractograms were obtained by placing the evacuated cell containing the sample into a glovebag, and removing the slide and scanning it in a dry N_2 atmosphere. The infrared spectra were taken in vacuum prior to the X-ray analysis and repeated in the N_2

atmosphere after the X-ray scan to be sure little or no water had been absorbed by the sample.

During this study we found that NH_3 could replace the coordinated water of palygorskite and produce a spectrum with distinct separation of the infrared absorption bands for structural OH and the stretching and bending modes of the coordinated NH_3. Ammoniation was accomplished at room temperature in the infrared cell. Self-supporting films were alternately flushed with anhydrous ammonia and evacuated several times. A detailed infrared study of the folding and dehydroxylation of ammoniated palygorskite was then conducted.

Results and discussion

X-ray analysis of palygorskite at various contents of coordinated water

The thermal data for various investigators show that the exact temperature at which palygorskite loses its zeolitic and coordinated water and hydroxyls will depend upon the environmental conditions under which the sample is heated. Therefore, the X-ray data presented here for palygorskite have been accompanied by infrared spectra of films which have been in similar environmental conditions. The area under the infrared peak for the bending mode of coordinated water was used to indicate the relative amount of coordinated water present at the time of X-ray analysis. This parameter can be used as a measurement of the amount of coordinated water, since palygorskite has been shown to contain only coordinated water under evacuated conditions (Prost, 1975; Serna *et al.*, 1977). Similarly, the presence or absence of hydroxyl groups was determined by the occurrence of their stretching vibrations in infrared spectra. Since the water content of this mineral greatly influences the structure, the coordinated water content is a much better reference for following structural change than the temperature and pressure conditions which are usually reported.

Figure 1 shows the X-ray diffractograms of palygorskite at four different contents of coordinated water. Considering the intensity of the reflection at 10.3A as a measurement for the amount of normal unit cells present in the crystal, Figure 1 shows that as the coordinated water present decreases from 65 to 35 percent, the mineral becomes almost completely folded. Folding of the mineral is supported by the appearance of a reflection at 9.2A in the sample with 35 percent coordinated water. This reflection is also present in the data of Hayashi *et al.* (1969) for paly-
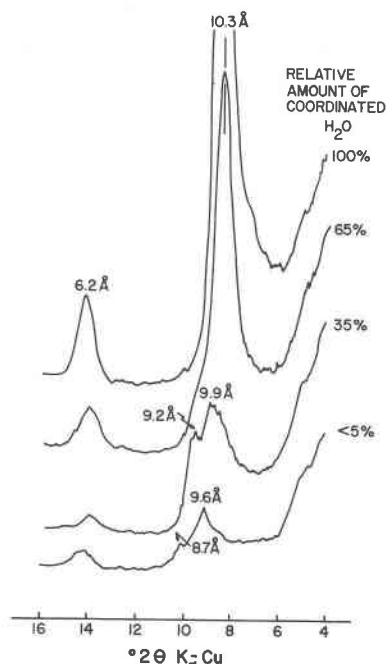
Fig. 1. X-ray diffraction patterns of palygorskite with varying proportions of coordinated water.

three different forms: (1) structural OH and coordinated D_2O (Fig. 2); (2) structural OD and coordinated H_2O (Fig. 3); and (3) structural OH and coordinated H_2O (Fig. 4). These first two systems permit interpretation of the dehydration process without overlap between water and structural hydroxyl absorption bands.

Structural hydroxyls. Figures 2 and 3 show the changes in the infrared spectrum of structural hydroxyls that occur upon heating. Thus stretching vibrations are seen as OH in the 3700–3500 cm^{-1} region and as OD in the 2800–2600 cm^{-1} region. Since these changes can be most clearly seen for the effect on vibrations of OH coordinated to the octahedral ion pair Al,Al at 3625 cm^{-1} (2686 cm^{-1} in the OD), the discussion will be centered around this absorption band (Serna *et al.*, 1977). As palygorskite is heated

gorskite with approximately half of its coordinated water removed. These data indicate that a large number of the unit cells have folded following the loss of the first half of the coordinated water.

The position for the characteristic [110] spacing for palygorskite was observed to change as the content of adsorbed water was varied. The 10.3 spacing shifted gradually to 9.6A as the sample was dehydrated, and the 9.2 spacing at 35 percent decreased to 8.7A at 5 percent of coordinated water. Similar influence of adsorbed water on the [110] spacing has been previously reported (Nathan, 1969; Hirsiger *et al.*, 1975). It is assumed to be due to the effect of the water molecules on the channel dimensions.

Infrared spectra of the folding of palygorskite

Hayashi *et al.* (1969) have previously presented infrared spectra of palygorskite heated to temperatures ranging from 25 to 1000°C. However, all of the samples contained adsorbed water, and the infrared spectra are difficult to interpret since overlapping of the absorption bands for different kinds of water and structural hydroxyl occurs. Since both the coordinated water and the structural hydroxyls of palygorskite could be deuterated (Serna *et al.*, 1977), the folding, dehydration and dehydroxylation process was studied when the evacuated sample was in
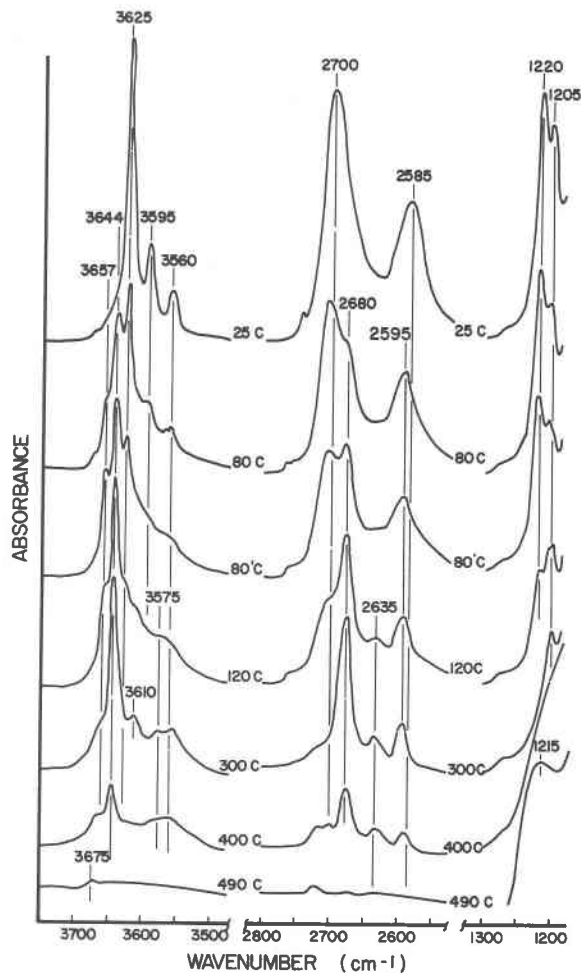

Fig. 2. Spectra of a single film of palygorskite with structural hydroxyls as OH and coordinated water as D_2O, as it alters to palygorskite anhydride during heating.
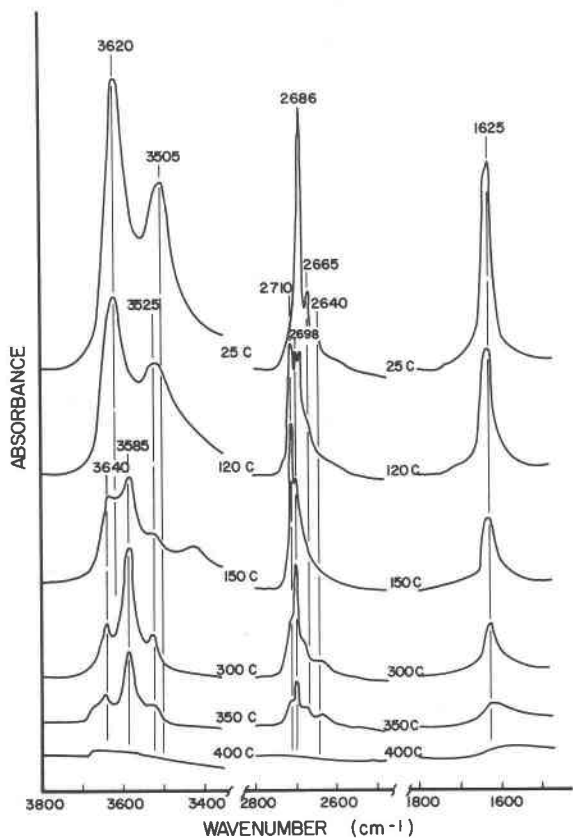
Fig. 3. Spectra of a single film of palygorskite with structural hydroxyls as OD and coordinated water as H_2O as it alters to palygorskite anhydride during heating.

cm^{-1} in the OD region (Table 1). At this point all of the structural hydroxyls appear again to be in a common environment.

The coordinated water. As palygorskite is heated, the loss of the coordinated water was observed by the decrease in intensity of the stretching absorption band at 3620 and 3505 cm^{-1} in the OH region (Fig. 3), or 2700 and 2585 cm^{-1} in the OD region (Fig. 2). At the same time, new absorption bands begin to appear at 3640, 3585 and 3525 cm^{-1} (Fig. 3) or 2680, 2635 and 2595 cm^{-1} (Fig. 2). All these absorption bands, however, may not be caused by the new environment of the coordinated water, since mixing of OH and OD occurs at elevated temperatures because of increased proton mobility. Therefore, in the OH region, part of the absorption at 3640 cm^{-1} (Fig. 3) would be due to the protonated structural OD vibration at 2686 cm^{-1}, and in the OD region (Fig. 2) the band at 2635 cm^{-1} would be due to the deuterated structural OH vibration at 3575 cm^{-1}. If this is assumed, then it would appear that in the OH stretch-

and some of the coordinated water is lost (as measured by the decreased intensity of the 1625 cm^{-1} band), two new higher-frequency stretching bands appear at 3657 and 3644 cm^{-1} in the OH region (Fig. 2) or at 2710 and 2698 cm^{-1} in the OD region (Fig. 3). This is accompanied by a decrease in intensity of the original vibration (2686 cm^{-1} OD or 3625 cm^{-1} OH). In Figure 3, the original absorption at 2686 cm^{-1} is almost completely gone at 150°C, when approximately 50 percent of the coordinated water has been lost as determined by the area under its bending fundamental. In Figure 2 the spectrum at 120°C shows only a small shoulder remaining for the original absorption at 3625 cm^{-1}, indicating that the environment for this hydroxyl has been completely altered.

As heating of each sample is continued up to 300°C, where only about 35 percent of the coordinated water remained, the highest frequency absorption band (3657 cm^{-1} in the OH region or 2710 cm^{-1} in the OD region) disappears, leaving only one intense band at 3644 cm^{-1} in the OH region or 2698
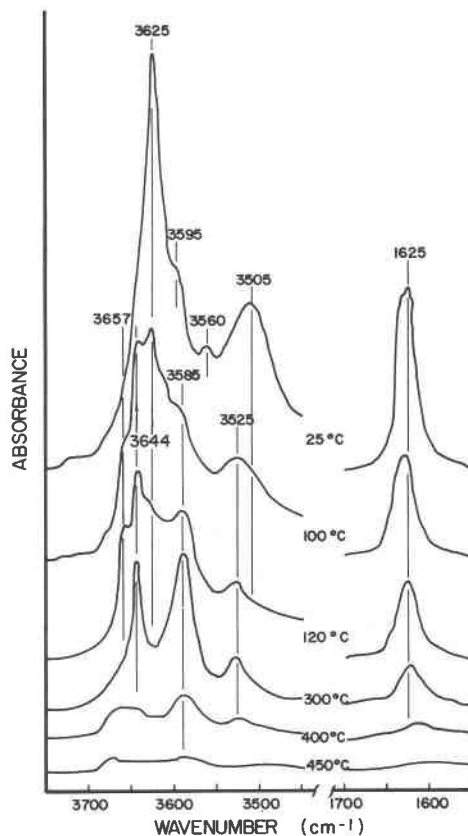

Fig. 4. Spectra of a single film of palygorskite with structural hydroxyls as OH and coordinated water as H_2O, as it alters to palygorskite anhydride during heating.

Table 1. Assignment of absorption bands due to Al,Al–OH and coordinated water in palygorskite (p) and in folded palygorskite (f)

Structural Hydroxyl		Coordinated H_2O – Stretching Bands			
Al, Al–OH		High Frequency OH		Low Frequency OH	
OH	OD	OH	OD	OH	OD
3625 p	2686 p	3620 p	2700 p	3505 p	2585 p
3657 f*	2710 f*				
3644 f	2698 f	3585 f	2680 f	3525 f	2595 f

*present during early stages of folding in addition to those present in the final folded state (f).

ing region of the spectra, the absorption bands for coordinated water at 3620 and 3505 cm^{-1} have shifted to 3585 and 3525 cm^{-1}, respectively. Similarly, in the OD region, the bands at 2700 and 2585 cm^{-1} have shifted to 2680 and 2595 cm^{-1}, respectively (Table 1).

Folding of palygorskite with structural OH and coordinated H_2O. Interpretation of structural changes in palygorskite by infrared spectroscopy during folding is greatly facilitated by separation of the structural OH and coordinated H_2O absorption bands (Figs. 2 and 3). However, since some proton–deuteron exchange does occur at elevated temperatures, it is important to verify the observations in a completely protonated system (Fig. 4).

At 120°C, when half of the coordinated water has been lost (according to the area determination under the 1625 cm^{-1} absorption band), the absorption band at 3625 cm^{-1} disappears and two new bands at 3644 and 3657 cm^{-1} appear, due to the new environment created for the Al,Al–OH during folding (Fig. 4 and Table 1). Absorption bands also appear at 3585 and 3525 cm^{-1}, due to the coordinated water.

After heating the sample to 300°C, thus removing approximately 65 percent of the coordinated water, three distinct bands appear: the 3644 cm^{-1} absorption band caused by Al,Al–OH, the nonsymmetrical band at 3585 cm^{-1} caused primarily by the coordinated water (and the two perturbed lower-frequency structural OH bands), and the band at 3525 cm^{-1} caused by coordinated water (Fig. 4 and Table 1). Therefore, the absorption bands at 2635 cm^{-1} (Fig. 2) and 3640 cm^{-1} (Fig. 3) were due to proton–deuteron exchange, as previously suggested.

Interpretation of the folding mechanism in palygorskite

A model. Infrared spectroscopy and X-ray diffraction have shown that drastic structural changes occur

in palygorskite during dehydration. However, most of these changes occur prior to complete dehydration. X-ray diffraction indicates that the structure folds when 50 to 65 percent of the coordinated water is lost (Fig. 1). Infrared spectroscopy shows that during dehydration all the structural hydroxyls and coordinated water have shifted to a new environment. With 50 percent coordinated water left, most of the frequencies have already shifted; however, some evidence of the original vibrations remain until 65 percent of the coordinated water is lost.

Prost (1975) presented an illustration showing folded palygorskite, based on his studies of the symmetry of water in the mineral. This diagram indicated that palygorskite contained half of its coordinated water in the folded state. However, an explanation for the mechanism of folding such as has been reported for sepiolite was not discussed (Serna *et al.*, 1975). Therefore, to clarify the structural changes we have observed by X-ray diffraction and infrared spectroscopy, a modified version of Prost's diagram is presented in Figure 5 as a model for discussion.

This model shows the orientation of each of the coordinated water protons and the proton of the structural hydroxyls. Since palygorskite is a dioctahedral mineral, the structural OH will not be oriented perpendicular to the [100] plane as found in sepiolite but will be tilted out of the cleavage plane (Serratosa and Bradley, 1958). Since the oxygens of the octahedral layer of palygorskite may be assumed to be in a

H–O H_2O
O^H HYDROXYL
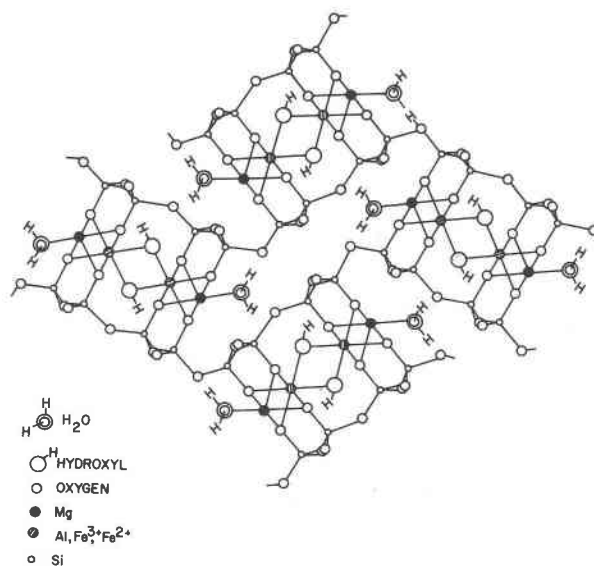○ OXYGEN
● Mg
◉ Al, Fe^{3+}, Fe^{2+}
○ Si

Fig. 5. View of the [001] plane of a palygorskite model which folded after losing half of its coordinated water. Orientation of the water and hydroxyl protons is depicted.

sp^3 hybridization with tetrahedral bond arrangement, this proton could be either tilted toward the hexagonal hole or toward the vacant octahedral position of the mineral (Ledoux, 1964). For the model shown, the proton has been oriented toward the hexagonal hole formed in the tetrahedral layer. This orientation was selected for two reasons: (1) if each hydroxyl proton was tilted toward the vacant octahedron, each would contain two protons, one from each side of the octahedral layer; and (2) Vedder and McDonald (1963) have indicated from studies of the dioctahedral mineral muscovite that the OH transition moment is tilted 16° out of the cleavage plane. These authors concluded from indirect evidence that the hydroxyl groups are tilted towards the surface of the unit layers, and this orientation has been confirmed by Rothbauer (1971), using neutron diffraction.

In the unfolded state, the low-frequency band of the coordinated water for palygorskite has been shown to increase in intensity as the film was oriented at 40° (Serna *et al.*, 1977). However, as would be expected from looking at the model of folded palygorskite (Fig. 5), no orientation effect was observed for the coordinated water bands after folding.

Discussion of the folding mechanism. As one of the coordinating water molecules is removed from each of the octahedral magnesiums, the structure folds. The remaining coordinated water is then forced closer to the hexagonal hole of the amphibole chain. As the water approaches the hydroxyl group, a perturbation occurs which shifts the frequency of the structural hydroxyl to a higher value. The model of folded palygorskite in Figure 5 shows that all of the hydroxyls (except for a few at the edge of each fiber) should be in a similar perturbed environment. When one looks at the infrared spectra of folded palygorskite at 300°C (Fig. 4), with 35 percent of the coordinated water left, only one band at 3644 cm^{-1} exists for the Al,Al–OH stretching vibration, indicating that only one environment exists for these hydroxyl groups.

However, prior to reaching this ordered state, disordered forms of the mineral are observed. This is supported by the presence of two different perturbed frequencies (3657 and 3644 cm^{-1}) for the Al,Al–OH during several states of dehydration, rather than one perturbed frequency as would be expected from the model proposed. One interpretation is that the chains near the edge of the structure fold, placing a strain on the internal channels, where two coordinated waters may remain coordinated to each edge Mg or where trapped water exists due to slow diffusion out of the folded crystal. Thus folding would begin to occur at a state where two water molecules were still coordinated to edge Mg. The presence of the two waters at many of these sites would cause greater perturbation of those structural hydroxyls and produce the 3657 cm^{-1} band. Therefore, the rate of heating and time of evacuation could affect the relative intensity of this peak. This is observed in Figures 2, 3 and 4, where the intensity of the band at 3657 cm^{-1} (2710 cm^{-1} in the OD) varies greatly relative to the intensity of the 3644 cm^{-1} band (2698 cm^{-1} in the OD).

The slow diffusion for water out of the channels during folding may explain why an ordered state is not observed for folded palygorskite with 50 percent of its coordinated water left, as has been observed for sepiolite (Serna *et al.*, 1975). Two factors can contribute to the slower diffusion rate out of the channels for the water in palygorskite: the smaller channel size, and the less stable structure due to its dioctahedral character. This less stable structure is evidenced by the low temperatures (80°C) at which the initial loss of coordinated water occurs and folding begins.

Dehydration of palygorskite

Continued heating of palygorskite in vacuum to temperatures of 400 and 500°C (Figs. 2, 3 and 4) results in loss of the remaining coordinated water and the structural hydroxyls. The temperature at which dehydroxylation was complete depended on the rate of heating. Both the last half of the coordinated water and the structural hydroxyls appear to be lost at the same rate.

Folding and dehydroxylation of ammoniated palygorskite

The surface area for palygorskite, as determined by N_2 and NH_3 adsorption, has been found to be 195 m²/g and 685 m²/g, respectively (Barrer and Mackenzie, 1954). Therefore, they concluded that the NH_3 entered the channels of the mineral and was adsorbed onto both the external and internal surfaces, whereas N_2 only adsorbed onto the external surface. We exposed a palygorskite film to NH_3 to observe this adsorption process by infrared spectroscopy (Fig. 6). Ammonia replaced all of the coordinated water and the absorption bands for the structural hydroxyls are clearly seen at 3625, 3595 and 3560 cm^{-1} (Fig. 6A). The presence of the ammonia is determined by the absorption bands at 3500 to 3100 cm^{-1}, 1800 to 1400 cm^{-1} and 1300 to 1100 cm^{-1}. Evacuation for one minute at 25°C removed the excess NH_3 vapor and left coordinated NH_3, as detected by the stretching
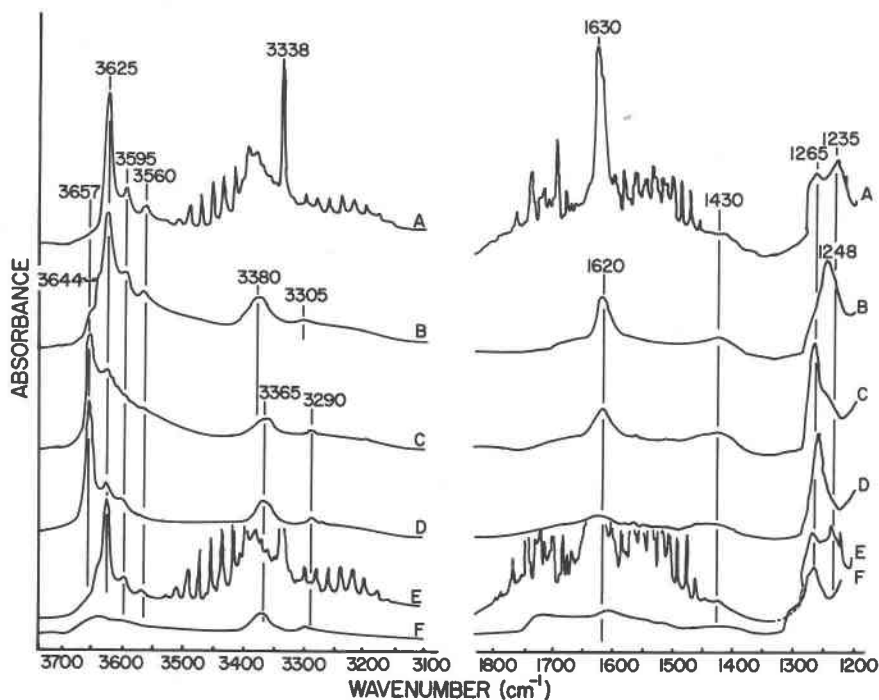
Fig. 6. Spectra of ammoniated palygorskite (A) not evacuated; (B) evacuated 1 min at 25°C; (C) evacuated 90 min at 25°C; (D) evacuated 20 min at 200°C; (E) re-exposed to NH₃ vapor; (F) evacuated for 30 min at 450°C.

bands at 3380 and 3305 cm⁻¹ and the bending vibrations at 1620 and 1248 cm⁻¹ (Fig. 6B).

Structural hydroxyls. In the stretching region for the structural hydroxyls, the 3625, 3595 and 3560 cm⁻¹ bands still remain after one minute of evacuation; however, the characteristic bands for folded palygorskite at 3657 and 3644 cm⁻¹ each appear as shoulders on the 3625 cm⁻¹ absorption band. Further evacuation (90 min at 25°C) resulted in most of the structural hydroxyl bands shifting to higher frequency (Fig. 6). These high-frequency peaks indicate that the crystals have folded. Heating to 200°C sharpened the peaks at 3657, 3625 and 3595 cm⁻¹, indicating a more ordered environment for each of the structural hydroxyls.

Due to the mild conditions under which ammoniated palygorskite folded, we were unable to obtain an experimental environment under which X-ray analysis of the folded state could be made. The slightest impurities of H₂O within the X-ray chamber unfolded the crystal. Therefore, the folded state of the ammoniated palygorskite is only inferred by the perturbation to high frequency of the OH stretching absorption bands.

Folding the crystal in the presence of coordinated ammonia shifted each structural hydroxyl vibration to higher frequency by 30 to 35 cm⁻¹, compared to 19 cm⁻¹ when the crystal folded on coordinated water. Considering the model for folded palygorskite in Figure 5, this greater shift in frequency would be expected for a molecule like ammonia compared to water. Since the 3644 cm⁻¹ band also appears as a shoulder in the NH₃ system, it would seem that both the 3657 and 3644 cm⁻¹ bands are characteristic of the folded state. The position and intensity of perturbed absorption bands observed depends on the molecule coordinated to the Mg, the degree and uniformity of folding that has occurred in the crystal, and the rate of diffusion for the molecule out of the channel.

When the folded palygorskite was re-exposed to NH₃ vapor, the absorption bands for the structural hydroxyls immediately returned to the 3625, 3595 and 3560 cm⁻¹ positions characteristic of the unfolded palygorskite (Fig. 6). The 3657 and 3644 cm⁻¹ absorption bands appear only as small shoulders on the 3625 cm⁻¹ vibration. Rapid rehydration of palygorskite from the folded state was also observed when water was coordinated to the octahedral Mg in the channel. This demonstrates the easy reversibility of the folding process.

Heating to 450°C removed most of the structural hydroxyls, as had been observed for palygorskite with coordinated water.

Coordinated NH₃. The stretching vibrations for coordinated ammonia in palygorskite (Fig. 6) appear at 3380 and 3305 cm⁻¹. As the crystal folds, these vibrations shift to lower frequency (3365 and 3290, respectively), indicating that the three protons have moved from their freer environment in the channel to a more restricted environment near the hexagonal hole of the adjacent amphibole chain. The absorption bands at 1620 and 1248 cm⁻¹ (Fig. 6) are caused by the respective anti-symmetrical and symmetrical deformation modes of coordinated ammonia (Russell, 1965). During the folding, the band at 1620 cm⁻¹ decreases in intensity, due to the loss of coordinated NH₃. At the same time, the 1248 cm⁻¹ band shifts to higher frequency (1265 cm⁻¹), perhaps as a result of hydrogen-bonding by the NH₃ to the surface oxygens of the hexagonal hole towards which these protons are forced. This shift could also result from a change in coordination number of the Mg cation upon loss of one of the coordinated ammonia molecules (Russell, 1965).

Flushing the film with NH₃ causes the 1265 and 1235 cm⁻¹ bands to reappear (Fig. 6). Since neither of these absorption bands are characteristic of NH₃ vapor alone, we speculate that the 1265 cm⁻¹ band is due to NH₃ coordinated to the octahedral Mg and hydrogen bonded to NH₃ vapor in the channel, and that the 1235 cm⁻¹ band is due to NH₃ vapor in the channel. Loss of the 1235 cm⁻¹ band following evacuation plus a shift of the 1265 cm⁻¹ to lower frequency would support this hypothesis.

As the sample is dehydroxylated at 450°C, the deformation bands decrease intensity, but do not completely disappear, indicating that some NH₃ is still coordinated to the clay (Fig. 6).

Formation of ammonium. Ammonia may be adsorbed on clay minerals by a reaction with H⁺ from water coordinated to exchangeable cations to form NH₄⁺ (Mortland *et al.*, 1963). The amount of NH₄⁺ produced is a function of the mineral and the type and concentration of exchangeable cations present (Russell, 1965; Ahlrichs *et al.*, 1972). Infrared spectroscopy permits easy identification of adsorbed ammonia as either being coordinated NH₃ or NH₄⁺.

In the spectra in Figure 6, the absorption bands for coordinated NH₃ have already been identified, and it was shown that ammonia replaced the coordinated H₂O and in turn became coordinated to the edge magnesiums of the channels. However, the existence of some adsorbed NH₄⁺ is confirmed in the spectra by the presence of the small band at 1430 cm⁻¹, which is due to the ammonium deformation mode. The small relative intensity of this band indicates very little ammonium formation, as would be expected in a sample with low cation exchange capacity. The small cation exchange capacity present may be due to a slight contamination by montmorillonite (Serna *et al.*, 1977).

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