INFRARED STUDY OF SEPIOLITE AND PALY-GORSKITE ON HEATING

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Abstract

In addition to X-ray and thermal analysis, infrared absorption spectra of sepiolite and palygorskite from the Kuzu District, Tochigi Prefecture, Central Japan, have been obtained in the hydroxyl stretching region. Absorption bands are assigned on the basis of behavior during dehydration and rehydration.

Introduction

It is well known that water in sepiolite and palygorskite consist of the following four groups: (1) hygroscopic water, (2) zeolitic water in the channel of structure, (3) water molecules bound on the edges of octahedral sheet—bound water—, and (4) hydroxyl groups associated with octahedral sheet. (Nagy and Bradley, 1955; Martin-Vivaldi and Cano-Ruiz, 1956a and b; Preisinger, 1959 and 1963; Bradley, 1940). However, regarding the thermal behaviour of these minerals in relation to the bonding character of water, various opinions have been expressed. In the course of an extensive study of Japanese sepiolite and palygorskite, the present writers have focussed their attention on the dehydration of these minerals. Infrared spectra were obtained of sepiolites and palygorskites which were unheated, and heated at characteristic temperatures. In this paper, the infrared study of sepiolite and palygorskite on heating is reported. Infrared spectra of these minerals unheated have already been published (Otsuka, Hayashi and Shimoda, 1968).

Materials and Experimental

The materials used in this study are sepiolite and palygorskite from the Kuzu District, Tochigi Prefecture, Central Japan. They are listed below.
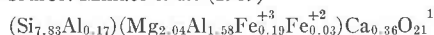
α-sepiolite

source: Imai *et al.* (1966)

$(Si_{11.79}Al_{0.21})(Mg_{7.89}Al_{0.06}Fe^{+3}_{0.01})Ca_{0.12}O_{32}$[1]
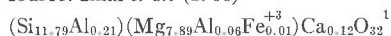
palygorskite

source: Minato *et al.* (1969)

$(Si_{7.83}Al_{0.17})(Mg_{2.04}Al_{1.58}Fe^{+3}_{0.19}Fe^{+2}_{0.03})Ca_{0.36}O_{21}$[1]

[1] Structural formulae have been calculated from the assumption according to Caillère and Hénin (1961a; 1961b) that the dehydrated half-unit cell contains 32 oxygens in sepiolite and 21 oxygens in palygorskite.

Of the above two materials, fractions less than 2 microns were collected by sedimentation and centrifuging in distilled water. The material for the X-ray and infrared analyses was prepared as follows:

(1) The material was heated at an average rate of 5°C/min. When heated to a required temperature, which was decided from the result of the thermal analysis, the material was rapidly cooled in a desiccator. In order to prevent rehydration, it was kept in nujol. The material for the infrared measurement was prepared by the nujol paste method. This material was designated as *h*. For example, sepiolite heated to 250°C was denoted by S-250°C-h.

(2) The material was heated at a required temperature for one hour. After heat treatment the material was divided into two halves. The one half was used for the X-ray and infrared analyses. This material was designated as H; for example, sepiolite heated at 250°C for one hour was denoted by S-250°C-H. The other half was wetted with distilled water. After drying in air, measurement was made. The material in this case was designated as H-R; for example, sepiolite heated at 250°C for one hour, with subsequent rehydration with distilled water, was denoted by S-250°C-H-R.

The DTA and TGA curves were recorded simultaneously at an average heating rate of 5°C/min. with a Simultaneous Thermobalance Analyzer (Saito *et al.*, 1964). The infrared absorption spectra were obtained with a Hitachi EPI-G Grating Infrared Spectrophotometer.

THERMAL ANALYSIS

The DTA and TGA curves are shown in Figure 1. The sepiolite had four endotherms with peak temperatures of 90–200°C, 325–400°C,

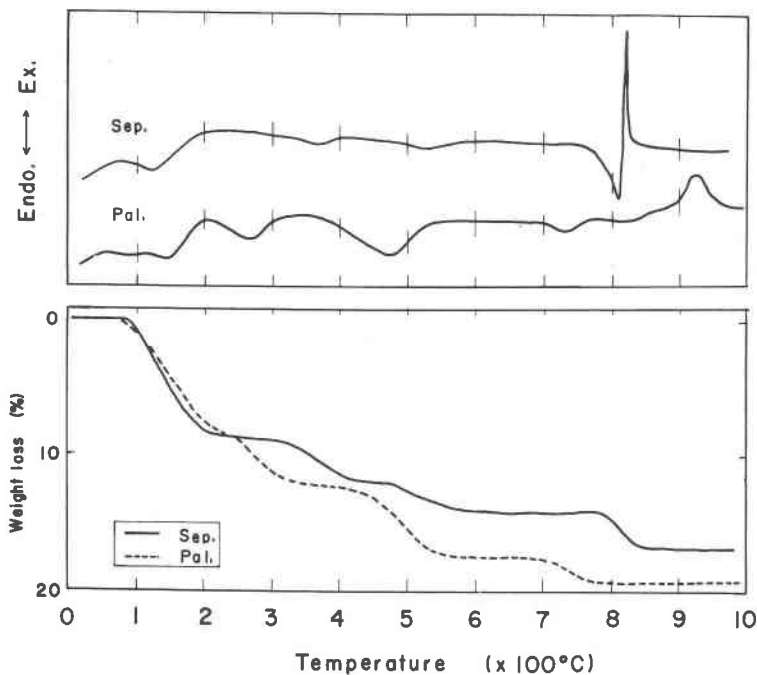FIG. 1. DTA and TGA curves of sepiolite and palygorskite.

TABLE 1. OBSERVED WATER LOSSES OF SEPIOLITE AND PALYGORSKITE

		Step of dehydration				Total loss
		1	2	3	4	
Sepiolite	Range of temperature (°C)	<250	250–450	450–610	610–860	—
	Weight loss (%)	8.3	3.5	2.4	3.0	17.2
Palygorskite	Range of temperature (°C)	<210	210–350	350–580	580–800	—
	Weight loss (%)	8.0	4.1	5.2	2.1	19.4

450–580°C and 750–810°C; an exotherm at about 820°C. The palygorskite had also four endotherms with peak temperatures of 80–210°C, 210–325°C, 350–540°C and 690–770°C; an exotherm at about 925°C. As can be seen in Figure 1, dehydration of these materials proceeded in four steps. Table 1 shows the water losses found experimentally at different temperatures with these materials.

X-RAY INVESTIGATION

Sepiolite. X-ray diffraction patterns of the materials after heat treatment for one hour: The X-ray diffraction patterns of the heated materials are shown in Figure 2-A. In the natural state, the reflections of the sepiolite were generally sharp and strong, and the resolution of each reflection was well-established. Especially, the reflections at 12.2, 4.5, 4.3, 4.0, 3.8, 3.4, and 3.2 Å were very sharp and well resolved. In the X-ray patterns of S-250°C-H, the reflections at 12.2, 4.5, 3.8, and 3.4 Å decreased their intensity and the 7.6 and 6.7 Å reflections were hardly discernible, while new reflections at 10.4 and 8.2 Å appeared. In the diffraction patterns of S-450°C-H, the reflections at 10.4, 8.2, and 4.3 Å increased their intensity. This fact indicates that a new crystalline phase designated as sepiolite II (Migeon, 1936; Longchambon, 1937) or sepiolite "anhydride" (Preisinger, 1959) appeared. Sepiolite "anhydride" persisted up to 730°C. The reflections due to enstatite appeared after heating at 860°C.

X-ray diffraction patterns of the rehydrated materials after heat treatment for one hour: The X-ray diffraction patterns of the rehydrated
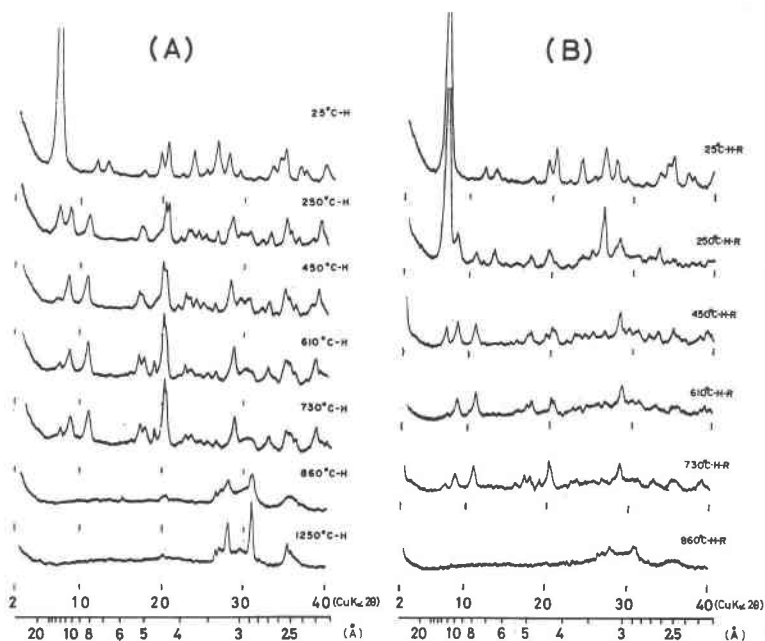
Fig. 2. X-ray diffraction patterns of sepiolite; (A) unheated and heated at various temperatures; and (B) rehydrated after heated at various temperatures.

materials after heating are shown in Figure 2-B. The 12.2 Å reflection of S-250°C-H-R was markedly stronger in intensity than that of S-250° C-H. This reflection was also clearly recognized in the patterns of S-450° C-H-R. This fact shows that some rehydration took place at least up to 450°C. After heating at 610°C, 730°C and 860°C, respectively, rehydration did not result in any change in the diffraction patterns.

Palygorskite. X-ray diffraction patterns of the materials after heat treatment for one hour: As shown in Figure 3-A, the material showed sharp, strong reflections at 10.5, 6.4, 5.4, 4.5, 3.68, and 3.23 Å. When the material was heated at 210°C for one hour, the intensity of the reflections at 10.5, 4.5, and 3.23 Å decreased, and the 3.68 Å reflection increased slightly in intensity. New reflections at 9.2 and 4.7 Å appeared. After heat treatment at 350°C, the 10.5 Å reflection was markedly weakened and diffused, the 3.23 Å reflection decreased, while the 9.2 and 4.7 Å reflections increased their intensity. These diffraction patterns were considered to be due to the presence of palygorskite "anhydride" (Long-chambon, 1936; Preisinger, 1963). The 10.5 Å reflection disappeared and the 9.2 Å reflection decreased in intensity at 600°C, while the reflections
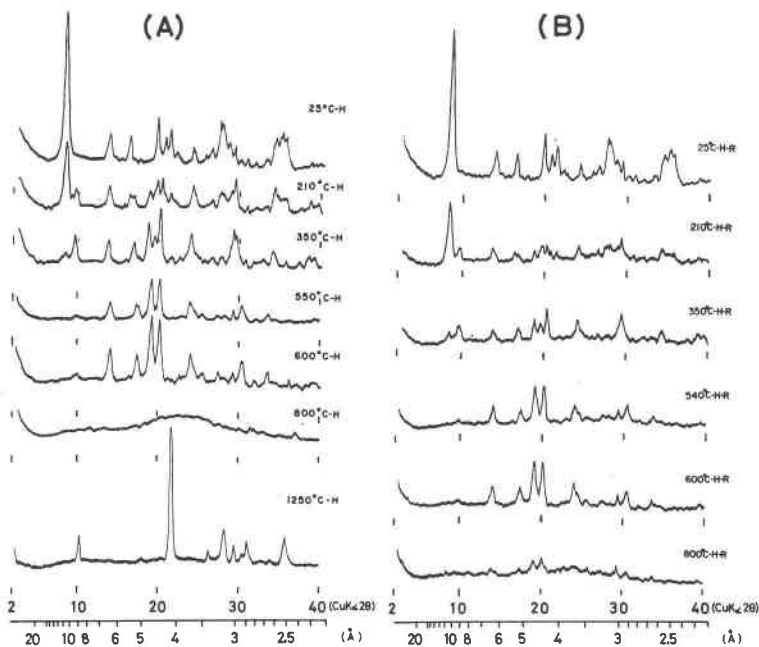
FIG. 3. X-ray diffraction patterns of palygorskite: (A) unheated and heated at various temperatures; and (B) treated with rehydration after heated at various temperatures.

at 6.4, 5.4, and 4.5 Å increased their intensity. The X-ray diffraction patterns of P-800°C-H were similar to those of an amorphous substance. The reflections due to enstatite appeared at 1000°C, and a mixture of enstatite and cristobalite was recognized at 1250°C.

X-ray diffraction patterns of the rehydrated materials after heat treatment for one hour: The X-ray diffraction patterns of the rehydrated materials after heating are shown in Fig. 3-B. The diffraction patterns of P-210°C-H-R were similar to those of P-210°C-H. The intensity of the 10.5 Å reflection of P-210°C-H-R, however, was stronger than that of the same reflection of P-210°C-H. The effect of rehydration was observed even after heating at 350°C. It was unrecognized above 540°C.

INFRARED ABSORPTION SPECTRA

Sepiolite The untreated material gave the absorption bands at 3685, 3617 (with a shoulder at 3645), 3571, 3350, 3200 and 1660 (with a shoulder at 1625) cm⁻¹. The absorption bands of S-25°C-R were identical with those of the unheated material except that the former had clearly a shoulder at 1620 cm⁻¹. The change of the OH stretching and bending vibrations of the sepiolite with heat and rehydration treatments are shown in Figure 4.
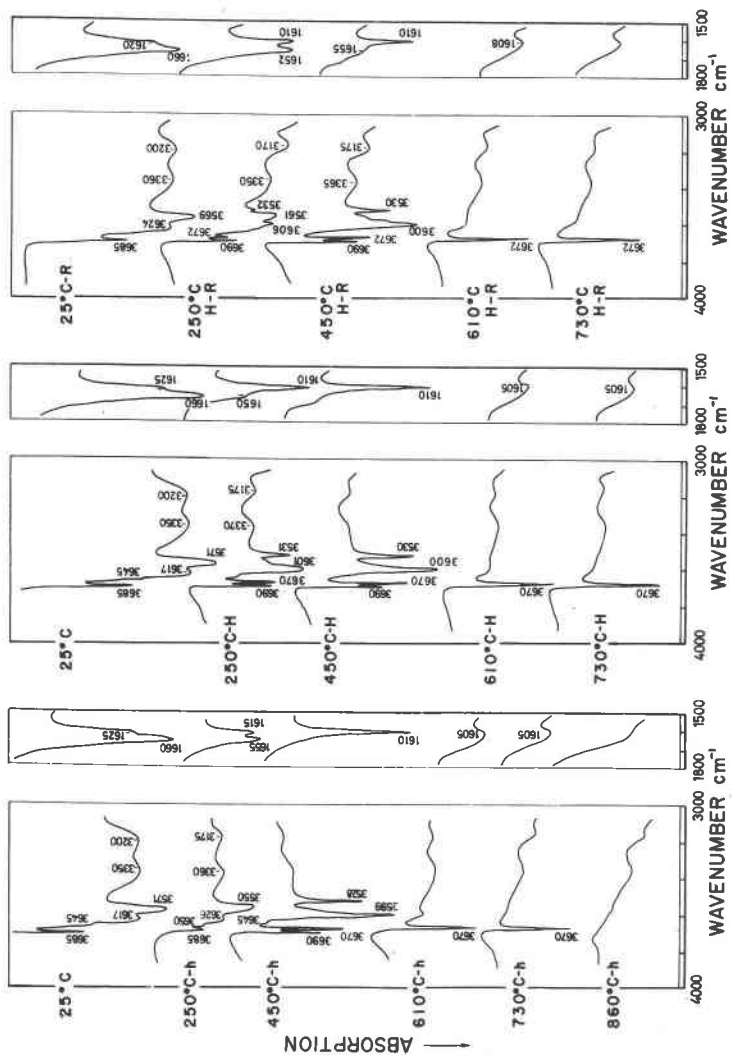
Fig. 4. Infrared absorption spectra of sepiolite with heating and rehydration treatments.

Palygorskite. The untreated material gave rise to three sharp bands and three broad bands; the first sharp one at 3609 (with shoulder at 3685) and 3645 cm^{-1}, the second at 3533 (with a shoulder at 3573) cm^{-1}, and the third at 1650 (with a shoulder at 1665) cm^{-1}. The broad ones appeared near 3350, 3260, and 3200 cm^{-1}. The spectrum of P-25°C-R was the same as that of P-25°C. The change of the OH stretching and bending vibrations of the palygorskite with heat and rehydration treatments are shown in Figure 5.

DISCUSSION

Clay minerals contain various kinds of water together with the hydroxyl water (OH). Therefore, their infrared absorption bands are always found in the OH region. Numerous reports have discussed these absorption bands from various viewpoints, such as the variation of absorption bands through hydrogen-deuterium exchange, the orientation of the OH group, the change in OH absorption bands on heating, and so on. Trioctahedral layer silicate where all octahedral positions are filled with Mg, will have an absorption band near 3700 cm^{-1}. (The OH groups have their axes normal to the mineral cleavage.) The substitution of Fe^{2+} for Mg^{2+} in trioctahedral layer silicates causes a shift to lower frequency in the OH vibration (Vedder, 1964; Jørgensen, 1966; Farmer and Russel, 1967). Splitting of the OH stretching fundamental by Fe^{2+}-Mg^{2+} substition has been observed in talc by Vedder (1964), and in amphiboles by Burns and Strens (1966). Wilkins and Ito (1967) have observed the same effect in synthetic talcs. They emphasized that an empirical approach is the most useful through the study of the absorption spectra of a simple synthetic compound which has been suitably substituted. In order to clarify the process of dehydration or rehydration of clay minerals, infrared studies have been carried out on heated materials by many researchers. In general, the changes in clay minerals in thermal treatment coincide well with the result of X-ray, thermal and infrared analyses. Based on variations of infrared absorption spectra in heating various clay minerals, particularly chlorite and vermiculite, Hayashi and Oinuma (1963) and Oinuma and Hayashi (1966) were able to find directly the behaviour of the OH groups in heating. They concluded that the bands at 3586 and 3420 cm^{-1} are assigned to the OH stretching vibration in brucite layer, and the band at 3685 cm^{-1} may be attributed to the OH stretching vibration in talc-like layer.

Sepiolite. As shown in Figure 1, the sepiolite showed the 8.3 percent weight loss below 250°C. The loss was due to the elimination of zeolitic water as well as hygroscopic water, therefore, there was no noticeable
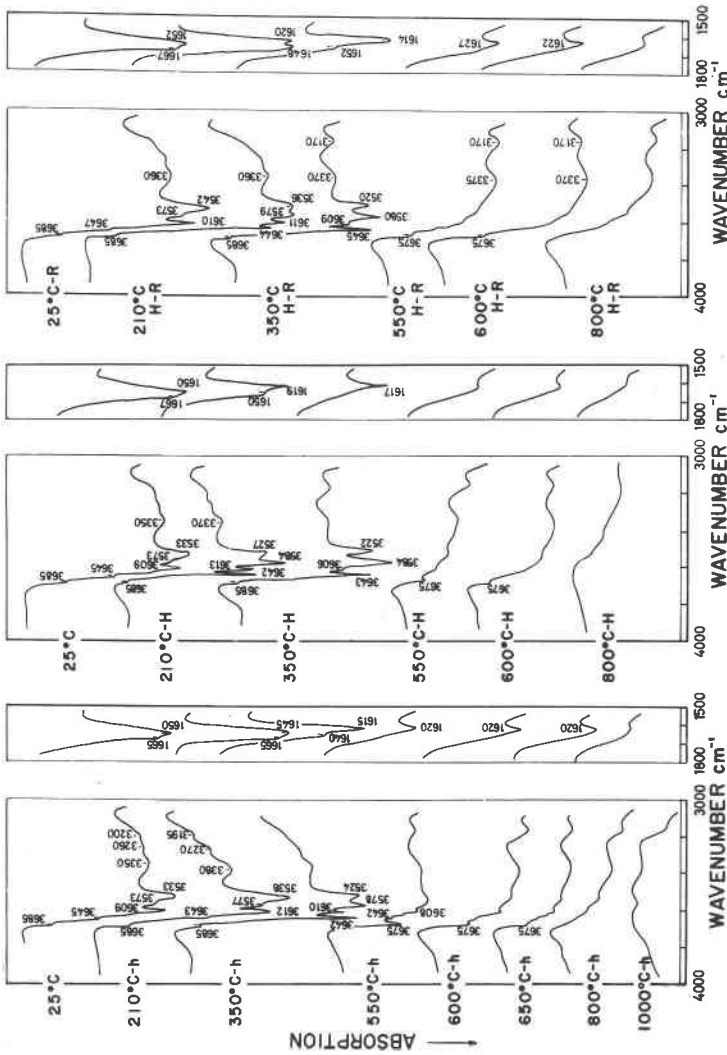
Fig. 5. Infrared absorption spectra of palygorskite with heating and rehydration treatments.

changes in its structure. These waters were easily regained, whereas the water lost at higher temperature than 250°C was not taken up again. The loss of bound water began above 250°C and the structure of sepiolite gradually changed into sepiolite "anhydride". The transformation of sepiolite into sepiolite "anhydride" was accomplished at about 450°C. The sepiolite "anhydride" remained stable up to 730°C. The endothermic reaction near 820°C as seen on the DTA curve was due to the loss of hydroxyl groups associated with octahedral sheet, and with the rise of temperature recrystallization occurred immediately.

a. Hydroxyls. The sharp band at 3685 cm^{-1} of the sepiolite shifted to near 3670 cm^{-1} by heat treatment at 610°C and 730°C, but this band disappeared at 860°C. Similar phenomena were observed in the infrared spectra of talc, chlorite and stevensite, which were heated below and above the temperatures of the exothermic peak (Oinuma and Hayashi, 1963). From the resemblance between the OH absorption bands of talc, chlorite and stevensite and those of the sepiolite, in both wave number and behaviour on heating, the band at 3685 cm^{-1} as observed in the sepiolite was assigned to the OH stretching vibration in octahedral layer of sepiolite structure. In other words, this band was attributed to hydroxyl groups associated with octahedral sheet. Another sharp band at 3690 cm^{-1} occurred together with the band at 3670 cm^{-1} in the spectra of S-250°C-H, S-250°C-H-R, S-450°C-h, S-450°C-H and S-450°C-H-R. Sepiolite and sepiolite "anhydride" coexisted under these experimental conditions. Generally speaking, in a structurally related mineral group, lowering of the OH stretching frequency has usually been correlated with shortening of the OH—O distance in the structure and resulted in increased strength of hydrogen bonding. This splitting on heating indicated the presence of difference in the distance of OH—O in talc-like ribbons during the transformation of sepiolite into sepiolite "anhydride". When this transformation was completed, there was no difference in the OH—O distance in talc-like ribbons since splitting of absorption band was not recognized.

b. Bound water. The spectra of S-450°C-h and S-450°C-H gave fine sharp bands at 3645, 3600, 3530, and 1610 cm^{-1} in addition to the bands at 3690 and 3670 cm^{-1} which were due to hydroxyl groups associated with octahedral sheet. The band at 3600 cm^{-1} became broad due to rehydration. When the sepiolite was heated to 610 and 730°C respectively, the sharp 3670 cm^{-1} and the broad 1605 cm^{-1} bands which were ascribed to hydroxyls in octahedral layer of sepiolite, still remained and other bands disappeared. Judging from the thermal and X-ray data of the materials

under these experimental conditions, the absorption bands at 3645, 3600, 3530, and 1610 cm^{-1} may be attributed to bound water contained in the treated materials.

c. Zeolitic water. The bands at 3617, 3571, and 1660 cm^{-1} of the unheated material shifted to 3620, 3550, and 1655 cm^{-1}, respectively, in S-250°C-h. When sepiolite was heated at 250°C for one hour, these bands were not recognized, but the bands due to bound water and hydroxyls in talc-like ribbons were recognized. However, the bands at 3561 and 1652 cm^{-1} were observed in the spectrum of S-250°C-H-R. The rehydration effect was observed in the spectrum of S-450°C-H-R, showing that the band at 3600 cm^{-1} became broad and very diffuse bands appeared at 3365, 3175 and 1655 cm^{-1}. The behaviour of the bands at 3620, 3550 and 1655 cm^{-1} which are affected by dehydration and rehydration showed that they may be caused by zeolitic water. Also the bands at 3350 and 3200 cm^{-1} may be attributed to zeolitic water. These facts are not inconsistent with the infrared analytical data of zeolite (Oinuma and Hayashi, 1967).

Palygorskite. The loss of water up to 210°C was not accompanied by any structural changes. About 8.0 percent of the total weight was lost. The water driven off below 210°C was easily regained. Therefore, this water seemed to be both hygroscopic and zeolitic water. Above this temperature, the structure gradually changed into palygorskite "anhydride" owing to the elimination of bound water. Palygorskite "anhydride" remained stable up to 780°C, but near 800°C the structure was broken into amorphous phase, and transformation into enstatite and cristobalite occurred between 900°C and 1000°C.

a. Hydroxyls. With increasing temperature, the band at 3685 cm^{-1} became clear and at 550°C and 600°C it was recognized as a sharp band at 3675 cm^{-1}. However, this disappeared at 800°C. From the resemblance of OH absorption bands in wave number and behaviour on heating among trioctahedral clay minerals, sepiolite and palygorskite, the band at 3685 cm^{-1} of palygorskite was attributed to hydroxyls in octahedral layer of palygorskite structure.

b. Bound water. On heating to 210°C, the bands of the untreated palygorskite slightly changed in their wave number (P-210°C-h). The band at 3642 (with a shoulder at 3685) cm^{-1}, and the bands at 3613, 3584, 3527, 3370, and 1619 (with a shoulder at 1650) cm^{-1} were observed in the spectrum of P-210°C-H. Treatment with distilled water of the material heated at 210°C caused the bands at 3644, 3611, and 3579 cm^{-1} to de-

creased their intensity (P-210°C-H-R). Furthermore, the band at 3527 cm^{-1} of P-210°C-H shifted to 3536 cm^{-1} and became broad, the 1619 cm^{-1} band decreased and the 1650 cm^{-1} band increased their intensity. After heated to 350°C, the intensity of the bands at 3685 (hydroxyls), 3642, 3610 and 3578 cm^{-1} increased, and new bands at 3524 and 1615 cm^{-1} appeared (P-350°C-h). A new band at 1640 cm^{-1} seemed to be a shoulder of the sharp band at 1615 cm^{-1} in this spectrum. The following sharp bands were recognized in the spectrum of P-350°C-H; the 3643 band (with a shoulder at 3685), the 3584 band (with a shoulder at 3606) the 3522 band, and the 1617 cm^{-1} band. Treatment with distilled water gave no noticeable changes in the spectrum of P-350°C-H-R. Only the 3675 cm^{-1} band persisted and other bands disappeared in the spectra of P-550°C-H- and P-600°C-H. Judging from the thermal and X-ray data of the treated materials and the behaviour of the bands at about 3642 3610, 3580, 3525, and 1615 cm^{-1}, these bands may be attributed to bound water. Some of these bands were recognized on the spectra of P-210°C-h, P-210°C-H and P-210°C-H-R.

c. Zeolitic water. The behaviour of the bands at 3533 and 1665 cm^{-1} were particularly noticed. The band at 3533 cm^{-1} shifted to 3538 cm^{-1} in the spectrum of P-210°C-h. On heating 210°C for one hour, this band decreased in intensity and was recognized at 3527 cm^{-1} which might be attributed to complex of bound water and zeolitic water. Furthermore, the band at 3527 cm^{-1} of P-210°C-H shifted to 3536 cm^{-1} by treatment with distilled water. The band at 1665 cm^{-1} decreased in intensity and its wave number value on heating at 210°C for one hour. Treatment with distilled water of the material heated at 210°C caused the 1650 cm^{-1} band increased and the 1619 cm^{-1} band decreased in their intensity. The bands between 3527 and 3542 cm^{-1}, 3350, 3200, and 1650 cm^{-1} in the material could be attributed to zeolitic water, because the bands were influenced by dehydration or rehydration.

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