

# DEHYDRATION AND REHYDRATION STUDIES OF CLAY MINERALS BY INFRARED ABSORPTION SPECTRA

*by*

J. M. SERRATOSA

Instituto de Edafología, C.S.I.C.,  
Madrid, Spain<sup>1</sup>

## ABSTRACT

The processes of dehydration and rehydration of montmorillonite and nontronite samples have been studied through infrared absorption spectra.

The changes observed in the intensity of the bands during dehydration show the analogy between absorption at  $915\text{ cm}^{-1}$  (montmorillonite) and at  $820\text{ cm}^{-1}$  (nontronite), their origin being a deformation vibration of OH groups.

During rehydration of the montmorillonite sample, the recovered OH groups occur in two different forms, in accordance with the results of differential thermal analysis.

Infrared spectroscopy has been shown to be an efficient method for structural study of OH groups in laminar silicates (Serratosa and Bradley, 1958).

The frequency of the absorption band corresponding to the fundamental valence vibration of the O—H bond depends upon the degree of association of these groups. For free groups, the absorption frequency is around  $3700\text{ cm}^{-1}$ ; this frequency is lower under the influence of associations, the decrease being a measure of the strength of the hydrogen bond. As a general rule, in layer silicates, structural OH groups that are comparatively slightly associated show absorption at high frequencies ( $3600\text{--}3700\text{ cm}^{-1}$ ) whereas adsorbed water shows absorption at lower frequencies ( $3400\text{ cm}^{-1}$ ). Another band appears in this latter case too, around  $1640\text{ cm}^{-1}$ , corresponding to the deformation vibration ( $\nu_2$ ) of water.

Any changes in the OH-group content can be followed through measurement of absorption band intensity. Buswell and Dudenbostel (1941) have applied this method to the study of the hydration of montmorillonite saturated with various cations, Romo (1954) to the exchange of OH-groups for fluoride ions in kaolinite, and recently Stubican (1959) to the dehydration of minerals of the kaolin group.

<sup>1</sup> Experimental work conducted while on leave at the Illinois State Geological Survey, Urbana, Illinois.

Dehydroxylation and rehydroxylation processes in minerals of the montmorillonite group are studied in this paper through infrared absorption spectra.

Samples studied consist of a montmorillonite from Tidinit (Morocco), which contains Al as main occupant of the octahedral positions, and a nontronite from Utah.<sup>1</sup> Both samples previously had been characterized by X-rays.

These samples were dispersed in water, and the fraction  $< 1 \mu$  was separated. Films of adequate concentration were prepared from the suspension by permitting it to evaporate on a plastic support plate. These films were withdrawn from the support plate and heated, and then their infrared absorption spectra between 2 and  $15 \mu$  were obtained with a Perkin-Elmer 21 spectrometer equipped with a NaCl prism.

Figs. 1 and 2 show the infrared absorption spectra of both samples, dried at room temperature and at  $200^\circ\text{C}$ . In this latter case, Nujol<sup>2</sup> was used in order to prevent rehydration, and the spectra were obtained at two different angles of incidence, in order to ascertain whether the absorption bands showed some polarization. Adsorbed water gives rise to a broad band around  $3400 \text{ cm}^{-1}$ , modified by a weak shoulder at  $3240 \text{ cm}^{-1}$ , and a simpler band around  $1640 \text{ cm}^{-1}$ . These three bands disappear when the samples are heated at  $200^\circ\text{C}$ .

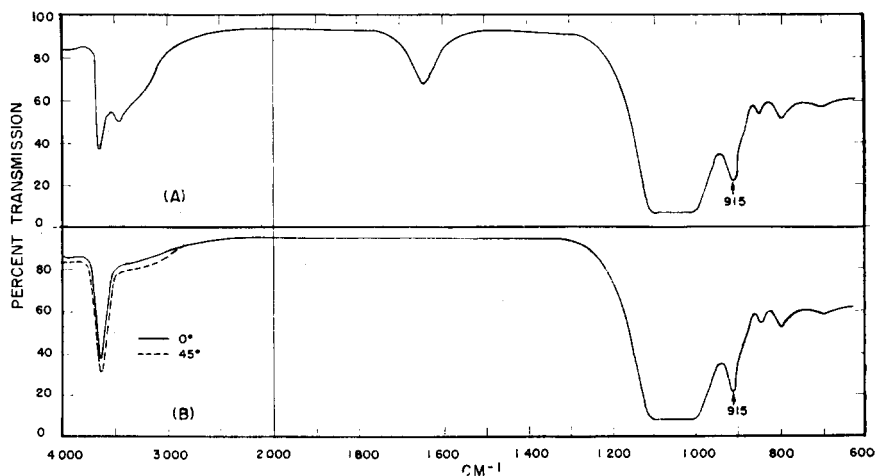


FIGURE 1.—Infrared absorption spectra of Tidinit montmorillonite: (A) Air dried. (B) Dried at  $200^\circ\text{C}$  and for two incidence angles.

<sup>1</sup> Sample was supplied through the courtesy of Prof. R. E. Grim, University of Illinois, Urbana.

<sup>2</sup> Nujol bands have been omitted for clearness.

Both minerals show, for normal incidence, a strong absorption between 3600 and 3700  $\text{cm}^{-1}$ , which corresponds to the fundamental valence vibration of structural OH groups. No sensible change is noted in this region of the spectrum upon variation of the angle of incidence. All this confirms the dioctahedral character of these silicates (Serratoso and Bradley, 1958).

Between 5 and 15  $\mu$ , the most significant difference is in the absorption at 915  $\text{cm}^{-1}$  for Tidinit montmorillonite and at 820  $\text{cm}^{-1}$  for nontronite.

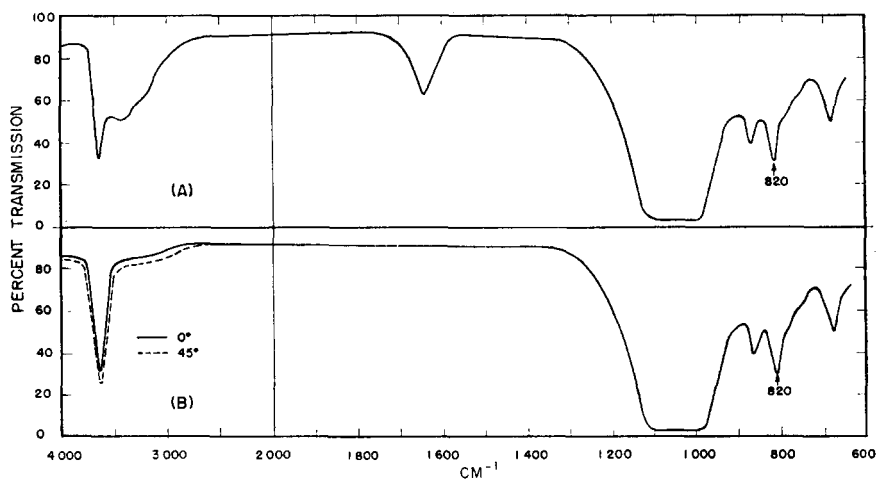


FIGURE 2.—Infrared absorption spectra of nontronite: (A) air dried. (B) Dried at 200°C and for two incidence angles.

Figs. 3 and 4 show the infrared absorption spectra of both samples in the temperature range in which the structural OH groups are released. A progressive decrease of the 3600–3700  $\text{cm}^{-1}$  band, concurrently with the decrease of the 915  $\text{cm}^{-1}$  (montmorillonite) and 820  $\text{cm}^{-1}$  (nontronite) bands, can be observed. These two absorptions therefore can be assigned the same origin, *i.e.* a vibration of protons associated with the octahedra layer. Each octahedral hydroxyl has two cation neighbors and the frequency difference relates to the nature of the cations occupying the octahedra ( $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ ). This assumption is also confirmed by the fact that the band at 915  $\text{cm}^{-1}$  is shown only by laminar silicates with Al in the octahedral positions (muscovite, pyrophyllite, kaolinite, etc.).

The regular decrease of these bands with the loss of OH and their positions indicate that these absorptions correspond to a deformation vibration of the O–H bond. This has been confirmed by Stubican and Roy (1960) on the basis of comparison of spectra of kaolinite and nontronite with those of their deuterated synthetic analogs.

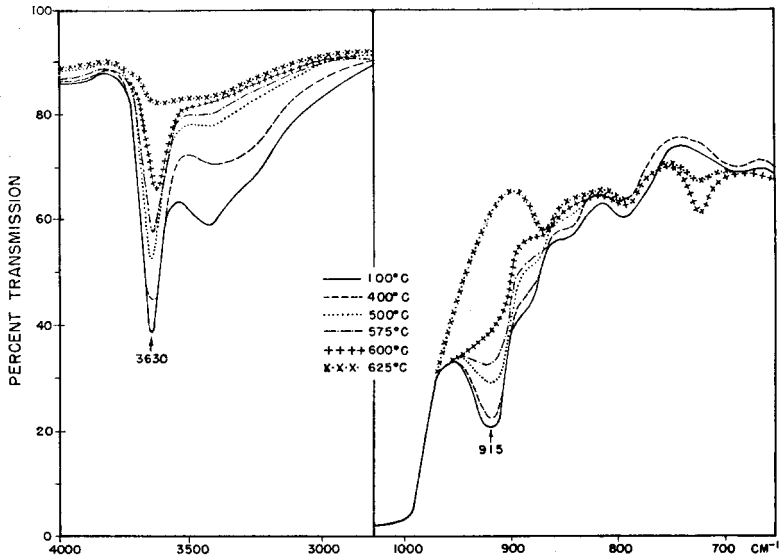


FIGURE 3.—Infrared absorption spectra of Tidinite montmorillonite heated at increasing temperatures.

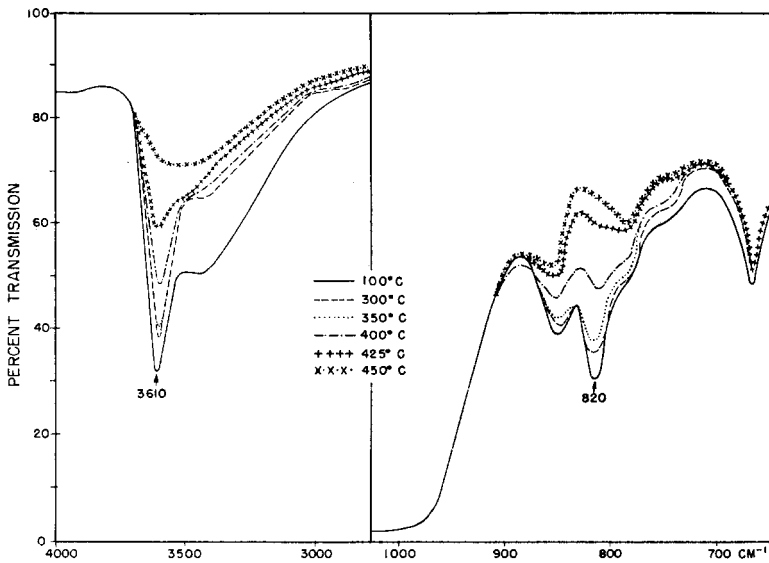


FIGURE 4.—Infrared absorption spectra of nontronite heated at increasing temperatures.

The observation that nontronite releases OH groups at lower temperature (300°–500 °C) than montmorillonite (400°–700 °C), agrees with the dehydration and DTA curves of these minerals.

Other changes take place in the spectra during heating; their relation with the release of OH groups does not seem to be so direct. However, in these dioctahedral compositions the two octahedral ion neighbors of the OH structural group may be different. This can account for other smaller absorptions that also decrease in intensity during heating. For example, in nontronite, the absorption at about 860  $\text{cm}^{-1}$ , which loses intensity less rapidly than the 820  $\text{cm}^{-1}$  band, may represent hydroxyls that have one Fe and one Al or Mg neighbor.

After all the OH groups had been released, the montmorillonite sample was placed in a saturated water atmosphere, and the infrared absorption spectra were obtained after various time intervals. Prior to the determination of the spectra, the sample was heated at 300 °C, always being protected with fluorolube in order to eliminate adsorbed water. In Fig. 5, curve *A* corresponds to the original sample, curve *B* to the sample heated to 700 °C; all the OH groups have been released, and therefore there is no absorption in the OH groups valence vibration range. Curve *C* was plotted at 30 days of standing in a saturated water atmosphere; part of the OH groups had been recuperated. The rehydroxylation process continued after 150 days

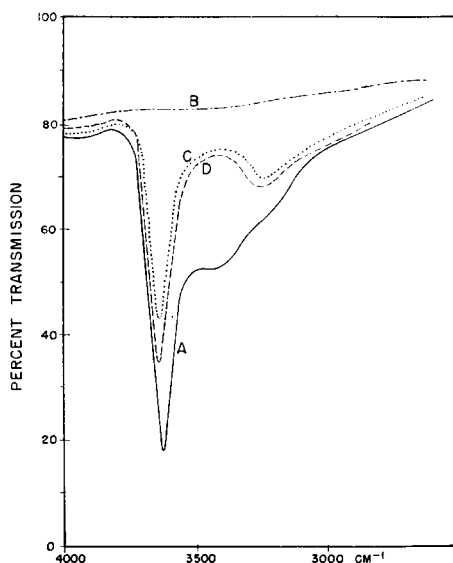


FIGURE 5.—Infrared absorption spectra of Tidinit montmorillonite: (A) Natural sample. (B) Heated at 700 °C. (C) and (D) After 30 and 150 days in a saturated water atmosphere.

(curve *D*). The spectrum shows two well defined bands—the former located at  $3640\text{ cm}^{-1}$ , as in the original montmorillonite sample; the latter, broad and of lesser intensity, around  $3260\text{ cm}^{-1}$ . This frequency corresponds to OH groups partaking in comparatively strong hydrogen bonds. It is not likely that this absorption be due to water molecules, for we have already mentioned that the samples were previously heated to  $300\text{ }^{\circ}\text{C}$  and, on the other hand, no water absorption at  $1640\text{ cm}^{-1}$  (deformation frequency) is observed.

These facts suggest that recovered OH groups occur in two forms. In order to ascertain this point, the rehydrated sample was heated to different temperatures, so as to determine the ranges at which the different OH-groups classes are released. Fig. 6 shows that OH groups corresponding to the  $3260\text{ cm}^{-1}$  absorption band are released at a temperature under  $520\text{ }^{\circ}\text{C}$ . The rest of the OH groups are released at higher temperatures, as in the original sample. These results agree with those obtained by Grim and Bradley (1948) by differential thermal analysis in a Wyoming montmorillonite sample.

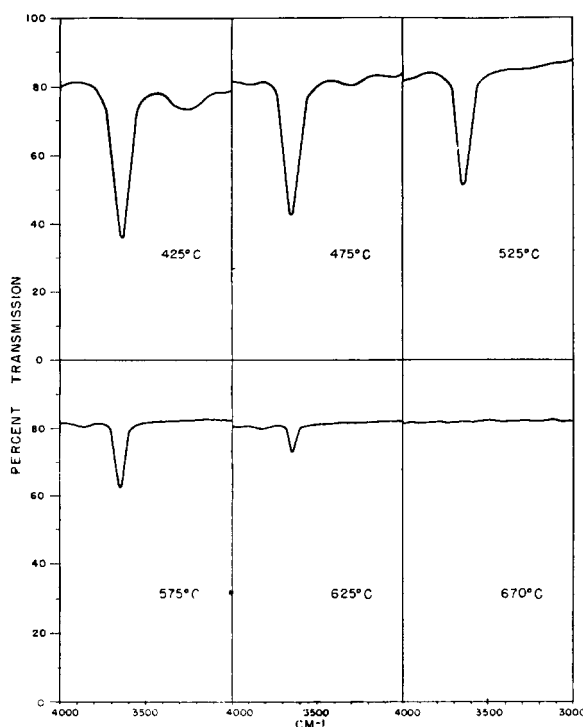


FIGURE 6.—Infrared spectra of the rehydrated sample of Tidinit montmorillonite heated at increasing temperatures.

## ACKNOWLEDGMENTS

The author thanks Prof. R. E. Grim and Dr. W. F. Bradley for their advice and encouragement in the realization of this work and also for critical review of the manuscript.

## REFERENCES

- Buswell, H. M. and Dudenhostel, B. F. (1941) Spectroscopic studies of base exchange materials: *J. Amer. Chem. Soc.*, v. 63, pp. 2554–2558.
- Grim, R. E. and Bradley, W. F. (1948) Rehydration and dehydration of the clay minerals: *Amer. Min.*, v. 33, pp. 50–59.
- Romo, L. (1954) Role of lattice hydroxyls of kaolinite in phosphate fixation and their replacement by fluoride. *J. Colloid Sci.*, v. 9, pp. 385–392.
- Serratos, J. M. and Bradley, W. F. (1958) Determination of the orientation of OH bond axes in layer silicates by infrared absorption: *J. Phys. Chem.*, v. 62, pp. 1164–1167
- Stubican, V. (1959) Residual groups in the metakaolin range: *Min. Mag.*, v. 32, pp. 38–52.
- Stubican, V. and Roy, R. (1960) Influence of controlled ionic substitution on the infrared absorption spectra of synthetic clay minerals: Abstracts of Cleveland Meeting of the American Chemical Society, April, 1960.