

Infrared Spectra of Hydronium Ion in Micaceous Minerals

Abstract. *X-ray diffraction measurements of the $d_{(001)}$ spacing and the infrared absorption spectra of hydrogen-saturated micas show that an ion of approximately the same size and properties as hydronium is present and gives a unique absorption band at about 3470 cm^{-1} .*

The classical work of Denison, Fry, and Gile (1) on the weathering of the coarse fraction of soil micas established that the loss of K_2O and gain of H_2O was 1:1 in relative weight. Consideration of the chemical analyses of several hydromuscovites and illites by Brown and Norrish (2) led them to conclude that the excess water and deficiency of potassium in hydrous micas compared with normal micas can be explained by H_3O^+ in interlayer positions. However, Nelson (3) concluded from x-ray diffraction studies and a one-dimensional Fourier analysis of the data that little or no water had replaced the potassium presumed to have been weathered from micaceous minerals in Ohio shales.

The possibility of detecting hydronium ions in clays by means of infrared spectroscopy is suggested by work with H_3O^+ in other systems.

Bethell and Sheppard (4) and Ferriso and Hornig (5) independently studied the infrared spectra of H_3O^+ in crystalline acid hydrates. Basing their calculations on a symmetrical pyramidal H_3O^+ structure, of the four fundamental frequencies (ν) expected, they were able to assign definitely the bands occurring at about 1100 cm^{-1} and 1700 cm^{-1} as being ν_2 and ν_4 , respectively; ν_1 and ν_3 were less definite and were associated with bands occurring in the 3200 to 2600 cm^{-1} region. Falk and Giguere (6) noted three broad bands which were common in the infrared spectra of aqueous solutions of mineral acids. These bands were attributed to H_3O^+ : 1205 cm^{-1} (ν_2), 1750 cm^{-1} (ν_4), and 2900 cm^{-1} (ν_3).

The fraction less than $2\text{ }\mu$ in diameter of a two-layer monoclinic muscovite (Silversheen mica), which had been treated with molten lithium nitrate at 300°C to reduce the potassium content from 7.38- to 1.4-percent potassium, was hydrogen-saturated by shaking the lithium-saturated mineral twice with an excess of a hydrogen-saturated cation exchange resin (Dowex 50W-X8).

A film specimen of the hydrogen-saturated mineral was prepared by evaporating sufficient suspension to give a concentration of 0.5 mg/cm^2 on an IRtran window. The infrared spectra were recorded on a Perkin-

Elmer model 421 double-beam spectrophotometer. The spectra were recorded for the specimen which had been air-dried, and after heating it to the following temperatures: 105°C , 150°C , 160°C , 200°C , and 300°C . Each spectrum was recorded while the specimen surface was being flushed with dry nitrogen gas. After recording the infrared spectra, the sample was heated for 30 minutes at the same temperature and an x-ray diffraction pattern was made with a GE XRD-5 diffractometer while the sample was flushed with a stream of dry nitrogen. Thus, it was possible to study the change in the O-H absorption bands in the 2.5 - to $6.0\text{-}\mu$ (4000 to 1500 cm^{-1}) region and in the $d_{(001)}$ spacing of the mineral as a function of heat treatment.

The lithium-saturated mica showed a $d_{(001)}$ of $9.24\text{ }\text{\AA}$ when heated to 300°C with no O-H absorption bands other than those at 3620 to 3700 cm^{-1} and 1600 cm^{-1} . When this treated material was saturated with potassium and heated to 300°C the $d_{(001)}$ was $10.00\text{ }\text{\AA}$ and again the only O-H absorption bands were those in the 3620 to 3700 cm^{-1} and 1600 cm^{-1} regions. The original spacing of the untreated muscovite was $9.96\text{ }\text{\AA}$. In addition, a specimen which had been ammonium-saturated and heated at 300°C showed no evidence of a band at 3470 cm^{-1} .

Since the lithium nitrate treatment neutralized approximately one-half of the negative charges on the muscovite, water molecules might conceivably occupy the uncharged interlayer sites in the lithium-, potassium-, ammonium-, and hydrogen-saturated micas. The fact that no band was observed in the 3450 to 3470 cm^{-1} region for any system except the hydrogen-saturated mica indicates that the water molecule is associated with a charge in the hydrogen system and it is therefore concluded that the species occupying the interlayer exchange sites is hydronium.

As shown in Fig. 1, the intensity of the absorption bands for the O-H frequencies decreases with increase in temperature. A band becomes noticeable at 3450 cm^{-1} at 150°C ; this shifts to 3455 cm^{-1} at 160°C , then to 3465 cm^{-1} at 200°C , and finally to 3472 cm^{-1} at 300°C . The appearance of the band at a temperature of 160°C coincides with the decrease of the $d_{(001)}$ from a value of $11.0\text{ }\text{\AA}$ at 150°C to $9.96\text{ }\text{\AA}$. This decreases slightly on further heat-

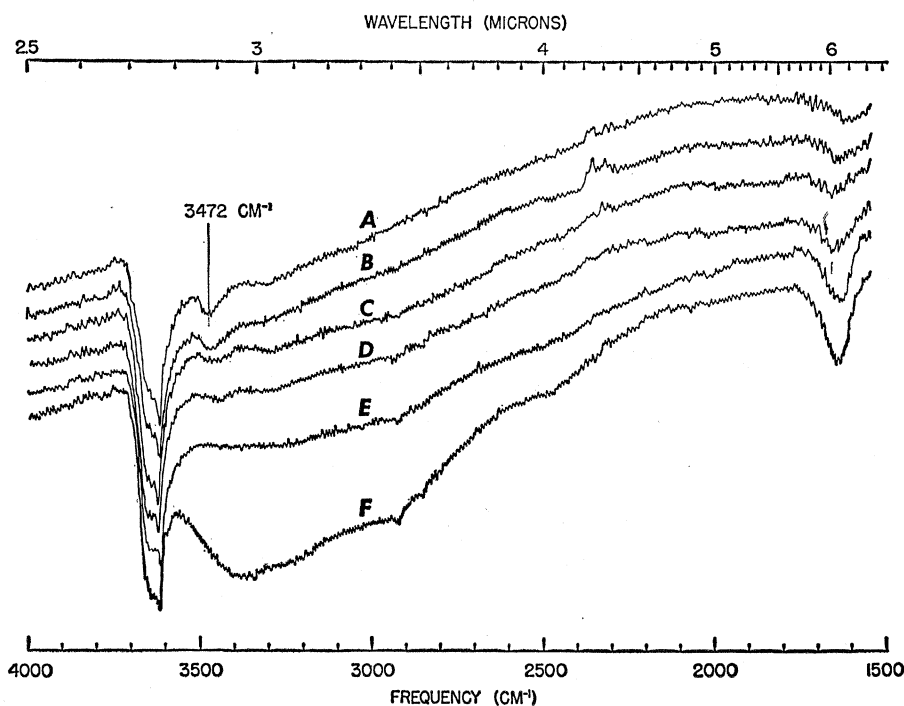


Fig. 1. Infrared spectra of lithium nitrate treated muscovite after hydrogen-saturation and heat treatment: A, 300°C (11 hr); B, 200°C (30 min); C, 160°C (10 hr); D, 150°C (30 min); E, 105°C (8 hr); and F, air-dried. $5\times$ scale expansion.

ing to a minimum of 9.92 Å at 300°C. Since hydrogen was the only cation introduced into the system in addition to the lithium saturating the clay initially, the failure of the mineral to collapse to a spacing of 9.24 Å indicates that an ion much larger than lithium and similar in size to potassium is preventing the silicate layers from making the closest possible approach. The keying effect and maintenance of the mica spacing of 9.92 Å is interpreted as an indication that hydronium ions are occupying the interlayer cation positions normally occupied by potassium ions. Thus, the absorption bands at 3472 cm⁻¹ are probably due to the hydronium ions, which have been isolated in the environment by the heat treatment producing collapse of the expanded mineral to a minimum spacing of 9.92 Å. Furthermore, the fact that the 3470 cm⁻¹ band persists even above 600°C for the hydrogen-saturated mica strongly suggests that the species involved is the hydronium ion and not an uncharged water molecule.

On the basis of the apparent relationship between the wavelength of the O-H stretching frequency of a H-bonded solid and the O-O bond distance suggested by Nakamoto, Margoshes, and Rundle (7), the O-O distance for the hydronium ion and the oxygens of the silicate surface is 2.88 Å. This corresponds to the nearest-neighbor distance of 2.88 Å (8) for water at room temperature. The K-O distance for the six inner oxygens surrounding the potassium ion in muscovite is 2.81 Å (9).

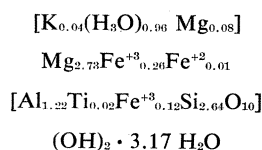
Since the hydronium ions are virtually all associated with exchange sites on the mica mineral, their environment differs from that in a system such as acid hydrates and aqueous mineral acids.

In samples that had been exposed to a high relative humidity or had not been completely air-dried, a band at 1723 cm⁻¹ was observed. This disappeared when the sample was thoroughly air-dried or heated. This band probably corresponds to the bands at 1700 to 1750 cm⁻¹ observed in aqueous solutions of mineral acids. When the water content of the clay is reduced by drying, the nature of the water remaining is such that hydrogen bonding between the hydronium ion and the surrounding water molecules is not possible to the same extent as in the initial system.

Thus, it should be possible to detect

hydronium ions in hydromicas and illites by infrared spectroscopy. Examination of Fithian illite under similar experimental conditions did not reveal any significant band at 3470 cm⁻¹.

Addendum. After this report had been accepted for publication we found a reference (10) to a paper in which the authors claim to have proved the presence of H₃O⁺ ions in vermiculite. We believe that the claim is invalid because there is an insignificant amount, if any, of H₃O⁺ in vermiculite (11); the authors generate a fictitious H₃O⁺ in the chemical formula from a basic error in calculation of the formula. Although the chemical analysis shows that the vermiculite contains 24 percent MgO, they give the following formula:



Their formula is calculated on the basis that only seven cations are coordinated with each 12 oxygen atoms as is the case for talc—but the actual count would be about seven and one-half. The one-half divalent ion which they omitted affords the one H₃O⁺ which they generated. On the basis of the formula which they calculated, they then state that the ratio H₂O:H₃O⁺ is about 3:1. The scheme which they show would generate 2 milliequivalents of H⁺ when 1 g of vermiculite is in NaCl solution; the actual operation does not even cause methyl red to change color, but it does yield Mg⁺⁺ in the salt solution.

A second reason to believe that their claim is invalid is that of the five infrared assignments they attempt to make for the H₃O⁺ ion in vermiculite, two are completely by inference since they coincide with the stretching vibrations of water and the Si-O bands of the vermiculite so that detection of the H₃O⁺ vibrations is virtually impossible. The other three assignments are made on the basis of the infrared assignments of Ferriso and Hornig (5) for oxonium in halogen acids; these specific assignments have been questioned by Falk and Giguere (6; 12).

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Size Distributions of Sedimentary Populations

Abstract. Separate sedimentary populations are not all characterized by lognormal size distributions. Populations of different sizes of material are produced by different mechanisms of abrasion: pebbles and gravel by single-stage crushing; sand by repeated abrasion; and silt and clay by chipping from larger grains. Each mechanism imposes a different size distribution on the product.

The polymodal nature of many sediments has been emphasized in a number of recent publications (1, 2). In particular, Spencer (2) has proposed that sediments can be considered to consist of mixtures of one or more of three separate populations, which he terms "gravel," "sand," and "clay." Such separate populations of sedimentary materials may be regarded as having originated from different methods of production of source material (2) or from different effects of transportational processes (1, 3).

Though it is commonly assumed that the size distributions of each of these separate populations are lognormal, the object of this report is to show that the populations are characterized by different distributions. Specifically, it is proposed that three distinct populations