THE ABSORPTION OF INFRARED
RADIATION BY CLAY MINERALS

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ABSTRACT. Infrared absorption spectrograms by pulverized minerals of the kaolin, montmorillonite, and illite groups in the 2 to 15 micron wave length bands are shown. The kaolin minerals have a distinctive absorption but those from the other groups are less clearly defined. Spectrograms of gibbsite, brucite, quartz, opal, and muscovite are shown because of their structural relationships to the clay minerals.

INTRODUCTION

VARIOUS techniques, such as optical, chemical, thermal, and structural methods, have been used to determine and differentiate clay minerals. Another tool, infrared absorption by the pulverized clay minerals has been proposed (Keller, 1948). Although this technique is still in the exploratory stages enough information has been accumulated from numerous empirical measurements on clay minerals to present some typical patterns characteristic of them. The preliminary report will also supply information about which inquiries have been received. It should be realized that only a beginning in the work has been made, and only qualitative results have been obtained. Instrumentation needs to be improved, and after more measurements are made on various different mineral groups probably some definite assignment of absorption peaks to specific atomic groups will be possible. Quantitative methods are still before us.

The absorption of infrared radiation has been utilized as a powerful determinative and analytical tool by chemists, especially in work on organic compounds. So characteristic are the absorption bands within the 2-15 micron wave length spectrum of certain chemicals that they may be "finger printed" by their absorption spectrograms. The possible application of the technique to mineral determination has not been tested, particularly not for pulverized minerals like clays, and therefore the measurements reported herein constitute in part a trial of the applicability of the method to pulverized minerals as well

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as a report on the properties of clay mineral specimens. Some preliminary work on the absorption of infrared by pulverized silica minerals has been reported (Keller and Pickett, 1949).

The principle involved in the selective absorption of infrared radiation depends upon the fact that the atoms of molecules are continuously in vibration at frequencies which fall within those of the infrared range (10^{13} to 10^{14} cycles per second) and that incident infrared radiation may be absorbed wholly or in part through interaction with the vibrating atoms. Moreover, in the infrared range there are absorptions correlating with the slower rotations of the molecules or the massive lattice vibrations of crystals. Although discrete "molecules" seldom exist in the crystal structure of most minerals, insofar as characteristic absorptions may be found, even empirically, for minerals, the basis for the results is sound.

The absorption frequency of simple or highly symmetrical molecules may be calculated approximately by the equation:

$$\nu = \frac{1}{2 \pi c} \sqrt{\frac{k}{u}}$$

Where ν is the frequency in cm.$^{-1}$, c is the velocity of light, u is the reduced mass of the vibrating atoms, and k is the force constant which exists between the atoms. The formula has been simplified by reduction of constants, etc., in the concise and lucid introductory treatment of the subject by Barnes, Gore, Liddel and Williams, in their "Infrared Spectroscopy", but nevertheless, many chemical compounds, and certainly most minerals do not represent simple molecules, and it therefore lies beyond our present ability to calculate *a priori* their absorption characteristics. To this point, Barnes *et al.*, write:

"Although the mathematical approach has been of great value when applied to simple or highly symmetrical molecules, most of the information derived from infrared spectra is obtained by the application of the empirical method. This method consists of comparing the spectra of the largest obtainable number of different molecules having a common atomic group. By a process of elimination, it is often possible to find an absorption band whose frequency remains constant throughout the series. The presence, in an unknown, of an absorption at this frequency may reasonably form the basis for a guess

that the particular atomic group is present. Confidence in this method can be obtained only by successful applications in a large number of cases."

The apparatus used in these measurements is a Beckman Model IR-2 infrared spectrophotometer. Briefly, infrared radiation from a rich source is dispersed by a rock salt prism into a spectrum from which relatively narrow wave length bands are selected and transmitted along a path to a sensitive thermocouple. The intensity of the radiation transmitted is measured with the sample, and without it, in the absorption chamber, and the per cent transmission obtained thereby. High sensitivity of the instrument is achieved by suitable electronic amplification. The current infrared spectrometers embody highly advanced improvements over the apparatus which was available only a few years ago. Many of the older measurements of infrared absorption have been revised.

In this study, from 5 to 10 milligrams of the finely pulverized mineral was stirred and dispersed in 2 drops of Nujol (medicinal mineral oil) which filled the absorption chamber. The latter consists of rock salt plates which are separated by shims of variable and selected thicknesses, and held together by a metal frame. Nujol has been used as a suspending medium because it has a satisfactory viscosity, because its index of refraction lessens the scattering reflectance from the mineral particles, and because its own absorption spectrum is relatively simple. It should be recognized that the indices of refraction of both Nujol and a dispersed mineral may be radically different in the infrared range than they are in the visible spectrum. Regarding the absorption spectrogram of the suspending medium, it has been suggested that a single pure substance which could be purified chemically and reproduced closely might be preferred as a suspending medium to one like Nujol which is a complex mixture. Theoretically this is correct, but practically no pure liquid is known which has a simple absorption spectrum and also possesses the other properties which are desired for the infrared work. Because Nujol is a mixture, many tiny absorption peaks of individual constituents are averaged out, and the curve is flat enough that absorptions occurring within the susupended mineral show up.

About four hours are required to make a run and plot it.

After this manuscript had been prepared for publication it was shown by the laboratory of the Carter Oil Company* that improved spectrograms in the higher wave lengths can be obtained by grinding the particles to sizes less than the wave lengths of the radiation used. The writers obtain better resolution in the OH absorption band using Nujol, but confirm from a few runs that the resolution at higher wave lengths is superior as run by Carter Laboratory. Absorption peaks may also be made to appear sharper if the horizontal axis is shortened in relation to the vertical, but maximum detail is maintained with ample length of horizontal axis.

EXPERIMENTAL RESULTS

An absorption graph of Nujol alone in the specimen chamber is shown in figure 1. Along the base of the abscissa is plotted the wave length of the radiation in microns and along the top is the corresponding frequency in wave numbers or reciprocal centimeter. Transmission of radiation in per cent is plotted on the ordinate. Nujol is relatively transparent to most infrared radiation, transmitting from 80 to 90 per cent over most of the spectrum. Slight absorption occurs at approximately 2.3 and 2.4 microns, and almost complete absorption (opacity) for a band at about 3.43 microns in wave length. Lesser absorption occurs from 3.6 to 3.72 microns and pronounced absorption at 6.86 and 7.28 microns. Numerous slight absorptions extend over wave lengths to about 11.0 microns and another prominent peak occurs at 13.86 microns. This "background" of absorption is unavoidably present in every measurement where a mineral was immersed in Nujol. It may be "subtracted" from the mineral graph to obtain the absorption characteristics of the mineral. The telltale characteristics of a positive nature of an irradiated compound are its absorption "peaks" or depressions. High transmission bands may be characteristic of certain compounds, but they constitute evidence of a negative type.

It may be recalled here that chemists have found OH groups absorb at different wave lengths between 2.7 and 3.1 microns depending upon the degree of hydrogen bonding of these groups with each other or with other O atoms in the lattice.

* Personal communication from Parke Dickey, 1949.

Where OH groups are held independently, *i.e.*, monomeric, within a crystal lattice the absorption is at about 2.75 microns. Where two or more OH groups are sufficiently close together, the hydrogen of the OH groups may assume an oscillating position between two oxygen atoms with the formation of a resonating bond between both oxygen atoms simultaneously, the so-called hydrogen bond. The dimeric groups absorb at about 2.85 microns and polymeric groups at about 2.95 microns. Evidence from minerals indicates that the absorptions for the polymeric bonding may extend to perhaps 3.1 microns. Free water, H_2O, absorbs in the 6.0 to 6.1 micron range, in addition to the 2.7 to 2.9 micron band. Many other absorption bands have been correlated with chemical bonds (Barnes *et al.*, 1944; Randall *et al.*, 1949) but most of these are not applicable to minerals. If mineralogy from infrared data is developed it may require a considerable backlog of factual data before generalizations can be accurately made (as was the case with organic chemistry).

INFRARED SPECTROGRAMS OF CLAY MINERALS

The kaolin group. Infrared absorption spectrograms typical of kaolinite, dickite, halloysite and endellite are shown in figure 2. Nos. 14, 70, 71, and 72 are of kaolinite clays from Georgia, South Carolina, Nevada, and California respectively. The infrared absorption of kaolinite is characterized by "free" hydroxyl absorption at about 2.75 microns (commonly 2.72 microns) and a comparatively lesser amount of ill-defined hydrogen bonded hydroxyl up to 3.1 microns The band between 3.1 and 7.55 microns is relatively featureless, except that free water, H_2O, may or may not be shown at about 6.1 microns. Absorption begins at about 8.1 microns and increases regularly in intensity to about 8.95 microns. Another peak of slightly greater absorption occurs at about 9.15 microns. Still higher absorption peaks occur at about 9.54 and 9.95 microns, whereupon transmission increases up to 10.46 microns. Two more pronounced absorptions occur at about 10.75 and 11.0 microns. Transmission (transparency to the band) increases as the radiation lengthens to about 12.2 microns. At higher wave lengths, notable absorptions occur at about 12.7, 13.4, and 14.5 microns.

Spectrograms of numerous other kaolinite samples show high similarity to these illustrated. The absorptions are so consistent that confidence in recognition of a kaolin group from its infrared spectrogram is soon established. Pronounced free OH absorption correlates well with the kaolinite crystal structure as interpreted from X-ray diffraction data.

Miloschite, No. 71, for example, appears from infrared data to fall within the kaolin group, confirming prior evidence (Grim and Rowland, 1942; Kerr and Hamilton, 1949). The commercial Edwin #2 clay, spectrogram No. 72 from California likewise shows kaolinite infrared absorption.

Dickite shows the same general type of infrared absorption as does kaolinite, and cannot be differentiated from it with certainty at the present stage of our measurements. No. 65 shows very pronounced monomeric OH absorption at 2.72 microns which was lost upon calcination at 780°C. for 14 hours (see 65A). The characteristic absorption of the raw clay from 7.5 to 15 microns has also been obliterated or subdued after the 780° calcination, which likewise breaks down the crystal structure. Obviously the bonds between silica, alumina, and hydroxyl groups are responsible for the several absorptions shown by the raw clay but their specific assignment is not now known.

Dickite No. 69 shows less intense OH bonding than did No. 65. Various intermediate intensities of absorption in the 2.75 band have been observed on other dickites.

Endellite, No. 3, is characterized by pronounced absorption at 2.8 microns, due to free OH groups, and at 3.0 and 3.2 microns, due to hydrogen-bonded hydroxyl. At higher wave lengths the absorption of endellite parallels that of kaolinite but it is more subdued. The endellite sample was prepared by grinding under water endellite clay still wet with quarry moisture, drying sufficiently at room temperature and irradiating immediately. Another sample of powder which was "dried" in an atmosphere of 80 per cent relative humidity for two weeks gave the same absorption curve as the one shown. Molecules of interlayer water sheets in endellite, as postulated by Hendricks, are linked by polymeric bonds, and are linked to O of silica tetrahedra by hydrogen bonds of a slightly different type. Infrared absorption is in accord.

Halloysite, No. 73, shows strong OH absorption at 2.74

microns but notably less in the higher hydroxyl bands. This is in keeping with its lower water content than endellite.

As has been stated previously, we lack information on the correlation between the absorption peaks and the chemical bonds responsible for them. However, it may be suggested that the peaks occurring at 12.7 and 14.5 microns in kaolinite may arise from silica tetrahedra, or a variety of silica structure, because pulverized quartz shows infrared absorption peaks at 12.6 and 14.5 microns (Keller and Pickett, 1949). Other assignments may be speculated but do not justify printing.

The montmorillonite group. Infrared spectrograms of montmorillonite group minerals are shown in figure 3. A Ca montmorillonite, No. 43, exhibits free OH at 2.72 microns, and well-defined hydrogen bond peaks at 2.91 and 3.1 microns. Strong absorption occurs between 8.0 and 10.3 microns, above which more radiation is transmitted. Smaller absorption peaks occur at 11.0, 11.8, and 13 microns.

Na montmorillonite, No. 45, shows less well-defined hydrogen-bonded OH than does its Ca analogue. Other specimens of Na and Ca montmorillonite similarly indicate that the absorptions of the latter are more sharply defined than those of Na montmorillonite. A possible reason for this may be that the interlayer water in the Na, swelling type, of montmorillonite has greater mobility of movement than in the more tightly bonded Ca montmorillonite. At wave lengths above 7.5 microns the absorptions of the two clays are usually similar.

Beidellite, No. 9, from Creede, Colorado, and No. 12, a H beidellite from Missouri Putnam soil colloid, show spectrograms like Ca montmorillonite plus a small, but recognizable absorption peak at 10.3 microns. Insufficient samples of beidellite have been run to know if the 10.3 micron absorption is diagnostic from other montmorillonites.

Nontronite, No. 8, shows a typical montmorillonite spectrogram. We have insufficient infrared data to differentiate between the members of the montmorillonite group.

The illite group. Figure 4. Illite from Illinois gave spectrogram No. 7. The OH and hydrogen-bonded hydroxyl are prominent in the 2.75-3.2 band, similar to that in montmor-

illonite. Probably the similarity between the two mineral groups in the hydrogen-bonded OH is due to interlayer water rather than their similar 2:1 layer structure. Illite differs from montmorillonite by absorbing relatively more intensely at 12.0, 12.6, about 12.8, and 14.5 microns. Kaolinite showed peaks at 12.7 and 14.5 microns, and quartz absorbs at 12.6, 12.9, and 14.5 microns. These absorptions at similar wave lengths are probably significant but the full meaning of them is not presently clear.

Spectrogram No. 42 is of the "Sarospatak clay" from Sarospatak, Hungary, which may be a mixed layer, illite-montmorillonite clay. The OH absorption might be assigned to either of the groups. The remainder of the spectrogram is disappointingly featureless. Such an absorption is logical however, if the distribution between the two clays is such that the low intensities of absorption of each are "diluted" and subdued by the cushioning effect of the other clay. Higher resolution and higher intensity of absorption is needed; improvement or modification in apparatus is necessary.

Attapulgite. A spectrogram of the amphibole-like atta-pulgite, is shown in No. 16. The absorption of OH and water at 2.75-3.1 and 6.0 microns is intense. Further absorptions occur at 8.2, 8.7-8.9, 9.75, 10.2, 11.0, 11.7, 12.6, 12.95, and 14.5 microns. Some of the absorptions of attapulgite are common to montmorillonite and some to kaolinite. Only a few specimens of attapulgite have been measured and therefore insufficient empirical data are available to make a very positive statement about the constancy of the above absorptions.

Clay lattice components. Because modified sheets of silica tetrahedra, gibbsite, and brucite are present in the clay minerals, their infrared absorption spectrograms are shown in figure 5. Gibbsite, No. 22, shows both free and hydrogen bonded hydroxyl in considerable quantity. Strong absorption occurs above 8.0 microns in wave length. Brucite, No. 21, shows primarily free OH groups. This difference in structure confirms the evidence from crystal structure by X-rays as described by Bragg (1937):

"The difference" (in brucite-gibbsite structures) "lies in the way in which the layers are packed on each other. In

brucite, the OH sheets of neighboring layers fit into each other in a close-packed way, one OH touching three OH in the next layer. In Al (OH)$_3$ each OH of one layer is *opposite* (italics by Bragg) an OH of the next layer, as if there were a strong specific attraction of one OH for the other . . . . Brucite and hydrargillite illustrate a progressive change in the nature of the OH group which has been summarized as follows by Megaw. At one extreme when the polarizing influence of the cation is small we have (OH)$'$ groups which act much like F$'$ ions. They pack together as if neutral towards each other, and the distance between O centres is large (3.22 Å for Mg (OH)$_2$). At the other extreme when the polarizing influence of the cation is large, there appears to be a powerful attraction between (OH) groups which draws them close together" (2.79 Å for Al (OH)$_2$). Hence the infrared absorption accords with crystal structural evidence.

Brucite absorbs strongly and with little evident characteristic fine structure above 8.0 microns.

Quartz is shown in spectrogram No. 66. No OH absorption is present. Some of the absorptions above 9.0 microns may be represented in the clay mineral absorptions, especially in kaolinite and illite. As more empirical data are assembled tentative computations of vibrational frequencies appear more logical and less conjectural. Evidence must be obtained, however, from different silica, alumina, and water linkages in various minerals. This is time-consuming and progress has not gone far.

Hyalite opal, No. 40, shows the water (2.7-3.0 microns) associated with silica. However, the clearly evident quartz absorptions, above 9.0 microns, presumably due to organized tetrahedral linkage, are not present in amorphous opal. A sheet of muscovite shows strong monomeric, free OH, in No. 30 N. Its absorptions above 8.0 microns are correlateable in part with those of the 3-layer clays, and are encouraging despite present inadequacies.

We are optimistic that infrared absorption measurements contain considerably more structural information about minerals than we are able to interpret now. The technique appears to merit more investigation.

REFERENCES

Barnes, R., Gore, R. C., Liddel, Urner, and Williams, Van Zandt, 1944. Infrared spectroscopy, New York, Reinhold Publishing Company.

Bragg, W. L., 1937. Atomic structure of minerals, Ithaca, N. Y., Cornell University Press.

Grim, R. E., and Rowland, R. A., 1942. Differential thermal analyses of clay minerals and other hydrous materials, part 2: Am. Mineralogist, vol. 27, pp. 801-818.

Keller, W. D., 1948. Absorption of infrared radiation by clay minerals: Geol. Soc. America Bull., (abstract). vol. 59, p. 1332.

———, and Pickett, E. E., 1949. Absorption of infrared radiation by powdered silica minerals: Am Mineralogist, vol. 34, pp. 855-864.

Kerr, Paul F., and Hamilton, P. K., 1949. Preliminary report No. 1, API Project 49, Clay Mineral Standards, Am. Petroleum Inst., Dallas, Texas.

Randall, H. M., Fowler, R. G., Fuson, Nelson, and Dangyl, J. R., 1949. Infrared determination of organic structures, New York, D. Van Nostrand Co., Inc.

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Fig. 3. Infrared spectrograms of the montmorillonite group of clay minerals.
No. 43. Ca montmorillonite, Arizona. From R. E. Grim.
No. 45. Na montmorillonite, Wyoming. From R. E. Grim.
No. 9. Beidellite, Creede, Colorado. From U. S. National Museum.
No. 12. Beidellite, Putnam soil colloid, Soils Dept. Univ. of Missouri.
No. 8. Nontronite, near Troy, Idaho. Col. with V. E. Scheid.

Fig. 4. Infrared spectrograms of illite and attapulgite.
No. 7. Illite from Illinois.
No. 42. Clay from Sarospatak, Hungary. From R. E. Grim.
No. 16. Attapulgite, Attapulgus, Georgia. From Paul F. Kerr, Columbia University Collection.

Fig. 5. Infrared spectrograms of minerals related structurally to clays.
No. 22. Gibbsite, New Caledonia. Univ. of Missouri mineral collection.
No. 21. Brucite, Wakefield, Quebec. Univ. of Missouri mineral collection.
No. 66. Quartz, Graniteville, Missouri.
No. 40. Hyalite opal, Guanajato, Mexico. Univ. of Missouri mineral collection.
No. 30N. Muscovite, Jackson, No. Carolina. Univ. of Missouri mineral collection.