Infrared Spectroscopy of Clay Mineral Systems[1]

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Infrared spectroscopy in the past few years has reached a place of importance in clay mineral studies comparable to that of x-ray diffraction. The two techniques are complementary with the former having the advantage that the material studied need not be crystalline. This new tool for clay mineral studies should rapidly add to an understanding of the minerology of Indiana soils which is needed in soil research, and also for the correct placement of Indiana's soils in the new soil classification system.

General Theory

The infrared energy from 2.5μ to 20μ wavelength is the particularly useful range for clay studies. The frequencies corresponding to these wavelengths are 4000 to 500 waves per centimeter (4000 cm^{-1} to 500 cm^{-1}). The most frequently used source of infrared radiation is a semiconducting filament or rare earth oxides heated electrically until it glows brightly. The desired frequencies of infrared energy are separated out by a prism or a grating.

The atoms in molecules and crystals are in a constant state of motion and have particular modes of vibration with respect to each other. The frequencies of these vibrations occur in the same range as infrared frequencies. The frequency of any vibrational mode of two or more atoms is dependent mainly on the mass of the atoms involved and the strength of the bonds between them. Thus each group of atoms in a molecule has its own characteristic vibrational frequency modes. If the vibration involves a dipole moment change which is not parallel with the incident beam, then the vibrating atoms are capable of absorbing infrared energy of the same frequency.

Infrared energy of a specific frequency will be absorbed when passing through a thin sample that has atoms with a vibrational mode of the same frequency. Thus a slow scanning of a sample with the infrared energy from 4000 cm^{-1} to 500 cm^{-1} will show a measured reduction in transmission whenever the instrument is measuring a frequency which is identical to the frequency of vibration of an atom group in the sample. Comparison of the measured frequencies with known frequencies of specific atom groups then gives information on the structure and composition of the sample. Stretching and bending modes of vibration are the most prominent frequencies observed. Combination and overtone frequencies occur less prominently.

Figure 1 shows a typical spectrum of montmorillonite over the 4000 cm^{-1} to 500 cm^{-1} frequency range. The first sharp decrease in
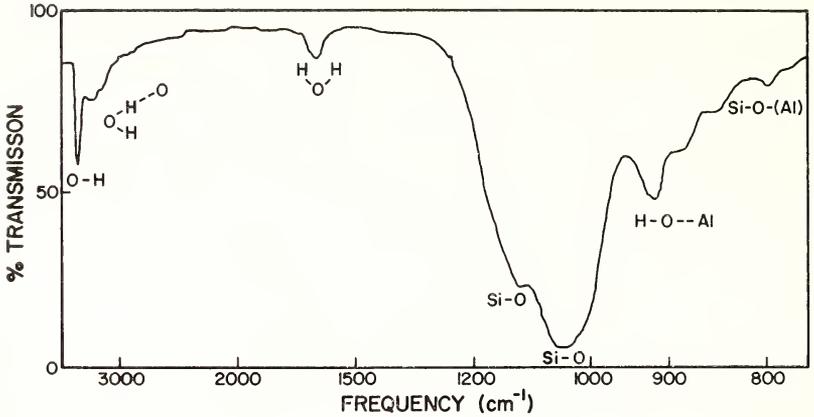
Figure 1. Infrared Spectrum of Montmorillonite Clay.

infrared transmission, i.e. the first absorption band, is at 3620 cm^{-1} This is the frequency at which hydroxyl groups in the clay crystal have a stretching vibration. The absorption band at about 3400 cm^{-1} is associated with hydroxyls in water. Their frequency of vibration is lower because they are involved in interaction, hydrogen bonds, with adjacent water molecules. This interaction results in weaker oxygen to hydrogen bonds and thus a lower frequency. The absorption band at 1630 cm^{-1} arises from an angle bending vibration of the two hydroxyl groups in water on the clay surface. The bands at lower frequencies are from various vibrations between silicon, oxygen, aluminum and hydroxyl groups of the crystal lattice as labeled.

Beers' law, which states that the log of the transmittance is proportional to concentration, holds well in infrared systems. Therefore, approximate concentrations of components in a sample can be made from the absorbance at characteristic frequencies of absorption for these components.

Shifts in the frequency of absorption of any atom group may occur if the environment of any of the atoms of the group changes. Association of one atom of a group with a force field such as that surrounding a highly polarizing cation like Al^{3+} will alter its electron distribution and thus the strength of its bond to the rest of the group. For example, the characteristic stretching frequencies will decrease if the bond is weakened and increase if the environmental change strengthens the bond. This is a useful tool in clay study.

Lastly, the stretching vibrational modes are particularly sensitive to orientation. If the change in dipole moment is parallel to the incident infrared beam, then no infrared energy of that frequency is absorbed. If the dipole moment change is perpendicular (normal) to the incident beam, maximal absorption will occur. This is also a useful tool in clay studies because clay crystals can be oriented in one plane by drying from suspension into flat surfaces, or may be randomly oriented by certain "pellet" techniques.

Discussion

In clay studies certain data are needed in order to identify and characterize the specimen: for example, is it triphormic (2:1) or diphormic (1:1); is it trioctahedral (3 out of 3 sites of the octahedral layer occupied by a structural cation) or dioctahedral (2 sites out of 3 occupied); what is the kind and amount of isomorphous substitution; what is the degree of hydration of the crystals; what is the nature of the crystal
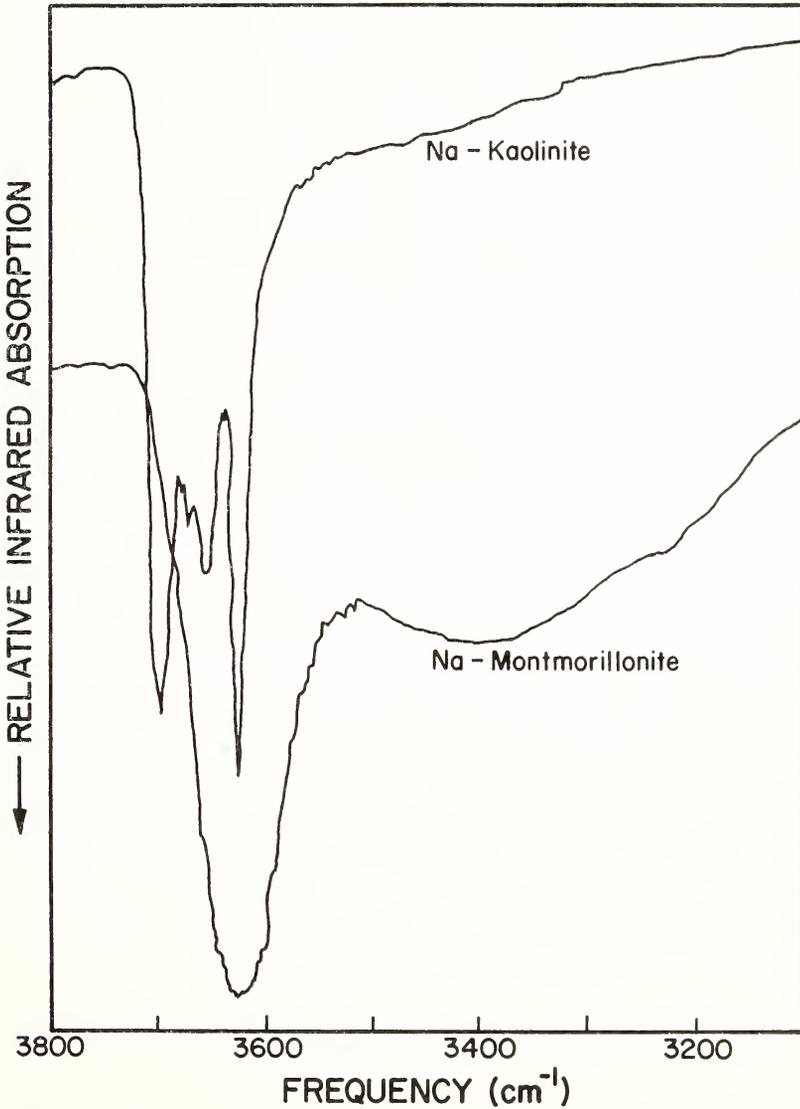

Figure 2. Infrared Spectra of the Hydroxyl Region of Triphormic Na-Montmorillonite and Diphormic Na-Kaolinite.

surfaces; what relative quantity of each component is present in clay mixtures; how prevalent are amorphous (non-crystalline) substances? Infrared spectra can give information on all of these.

Triphormic or Diphormic

Triphormic and diphormic minerals can be distinguished particularly by the hydroxyl stretching frequencies in the 3600 cm^{-1} region of a spectrum. Triphormic minerals, like micas and montmorillonite, have hydroxyls in one main environment associated with the octahedral cations located at the base of the hole in the tetrahedral surface of the clay. Since all are in nearly the same environment, all have nearly the same frequency and give one strong absorption band in the 3600 cm^{-1} region. The montmorillonite curve in figure 2 illustrates this. However, some of the hydroxyls in these triphormic minerals may have a slightly different frequency because of location near a site where some other cation has substituted for octahedral aluminum or tetrahedral silicon. Thus weak inflections on the main band are common.

Diphormic minerals of the kaolin group have a distinctive infrared absorption spectrum in the hydroxyl stretching region because they have a crystal surface composed of hydroxyl groups in addition to the hydroxyls common to the triphormic minerals. Thus kaolin shows four distinct hydroxyl absorption frequencies (figure 2). Variations of this pattern occur for other kaolin-group minerals.

Trioctahedral or Dioctahedral

Trioctahedral minerals can be readily distinguished from the dioctahedral forms. Dioctahedral minerals (pyrophyllite, montmorillonite, nontronite, kaolinite, etc.) give a different orientation affect than do the trioctahedral minerals (phlogopite, biotite, hectorite, etc.). Serratosa and Bradley (4) first illustrated this in a study of trioctahedral phlogopite. When the crystal was in the infrared beam with its 001 plane normal to the beam only a very weak absorption band was observed at 3710 cm^{-1}. The interpretation was that the O-H bond axis was parallel to the incident beam. The three octahedral sites are all occupied by Mg^{2+} which equally repel the hydrogen of the O-H group causing it to vibrate normal to the 001 plane. Decreasing the angle between the 001 surface and the incident infrared beam increases the hydroxyl absorption at 3710 cm^{-1}. The phlogopite pattern in figure 3 illustrates this strong increase in hydroxyl absorption with increasing angle. This orientation property is referred to as pleochroism.

The dioctahedral minerals have this same hydroxyl group but it is at a low angle to the 001 surface of the clay because only two of the three cations sites are occupied and thus repel the hydrogen toward the empty octahedral site. As the angle of an oriented sample of dioctahedral clay is decreased with respect to the incident infrared beam some hydroxyls are becoming more normal to the incident beam and increasing their absorption while others are becoming more parallel to the beam and decreasing their absorption. The net result is almost no change in absorption with such minerals as montmorillonite.
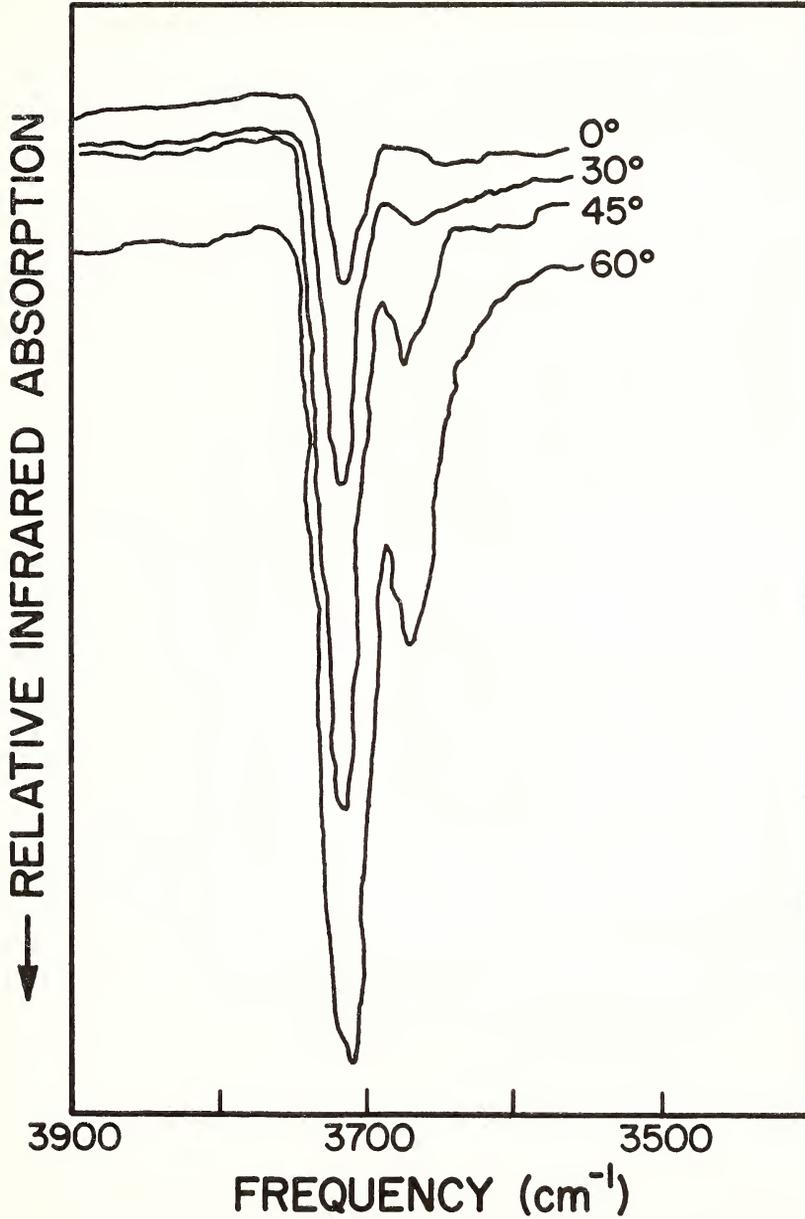
Figure 3. Pleochroic Effect of Phlogopite Hydroxyl Groups as the Angle of the Incident Infrared Beam to the 001 Axis Changes.

Isomorphous Substitution

Stubican and Roy (6) made controlled-composition, synthetic, clay minerals under high-temperature, high-pressure conditions to compare with natural materials. Talcs and pyrophyllites with substitutions of Ni^{2+} or Fe^{2+} for Mg, Ga^{3+} or Fe^{3+} for Al^{3+}, and Ge^{4+} for Si^{4+} enabled them to correlate absorption bands with particular atom groups in the structures. When the atom group was closely involved with the structural cation substituted it shifted its frequency as illustrated in
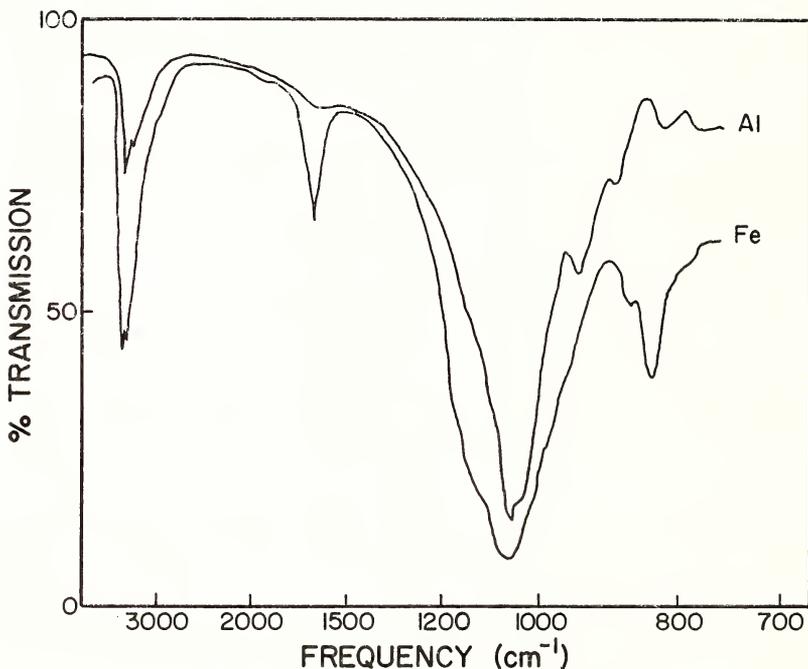

Figure 4. Spectra of Beidellite (Al) and Nontronite (Fe) from the Work of Stubican and Roy (6).

figure 4 from their work. Note that, absorption at several frequencies in the 450 cm^{-1} to 950 cm^{-1} range are shifted greatly as the octahedral cation becomes Fe rather than Al. The most prominent shifts is of the 935 cm^{-1}, H-O—Al band of beidelilte to an 827 cm^{-1} H-O—Fe band in nontronite.

The location of the sites of substitution in the octahedral or tetrahedral layer is important in the characterization of a clay mineral. Stubican (5) with synthetics, and Tuddenham and Lyon (7) with natural micas found that the Si-O band in the 600 cm^{-1} to 750 cm^{-1} region diminished in intensity as Al—for—Si substitution occurred in the tetrahedral layer.

Hydration

The degree of hydration of a clay is characteristic of both the particular micelle and its exchangeable cations. Water gives a broad absorption band in the 3400 cm^{-1} range from hydroxyl stretching vibrations. The absorption band is very broad because of the many degrees of hydrogen bonding between the water molecules at any one instant. The stronger the hydrogen bond the lower the stretching frequency. The hydroxyl of water mainly appears at lower frequencies than the hydroxyls of the clay crystals. Water also has a bending mode at approximately 1640 cm^{-1} which is less affected by hydrogen bond strengths.
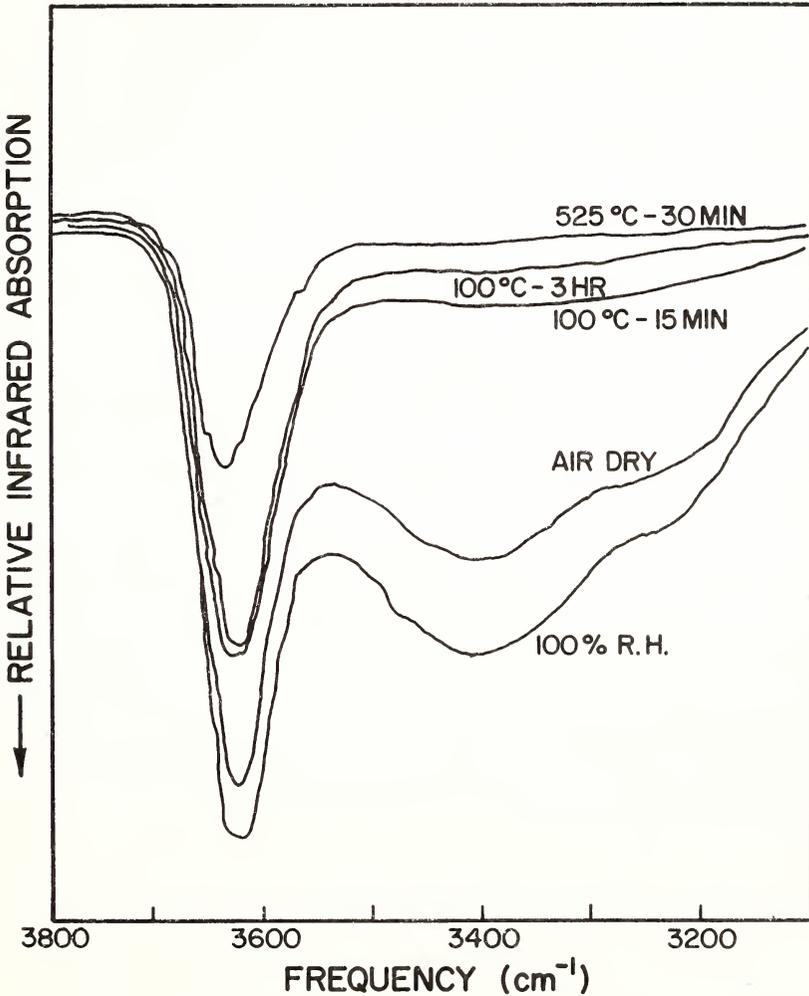

Figure 5. Dehydration and Dehydroxylation Effects on the Hydroxyl Region Spectrum of Montmorillonite.

The water band in the 3400 cm^{-1} region is characteristically strong in the highly hydrated montmorillonite type minerals and weak in the kaolin and micas which have very low hydration. Figure 5 shows how water removal from a montmorillonite decreases the 3400 cm^{-1} absorption. The absorption at 3620 cm^{-1} also has some contribution from water as evidenced by its decrease on drying. Drying at very high temperature (525° C) causes the crystal hydroxyls to be driven off as is seen by the sudden decrease in the 3620 cm^{-1} absorption. In more refined work Russell and Farmer (3) in recent studies have found that a relationship exists between the nature of the water bands from the first layers of water associating with a clay and the exchangeable cations around which they are oriented.

Surface Reactions

The character of the surfaces of the clay crystals is determinable from infrared spectral changes occurring when organic and inorganic compounds react with the surfaces. Ledoux and White (1) washed expanded kaolin with D_2O and found that a certain OH band changed to an OD band which occurs at a lower frequency because of the higher mass of the deuterium atom. This illustrated the ready exchangeability of surface hydroxyls in expanded kaolin as well as clarifying its infrared spectrum.

In other surface studies we have found that benzoic acid-sodium benzoate solutions dried with clay of the same suspension pH show an increase in the acid (COOH) band of the benzoic acid at 1700 cm^{-1} and a decrease in its 1550 cm^{-1} salt (COONa) band. The change in these two band intensities shows acidities of as much as 2 pH units more acid near the dry clay surface than exists in the clay-water suspensions.

Current infrared work with NH_3 and NH_4^+ and many organics is clarifying how clays interact with pesticides, fertilizers, soil conditioners and other soil additives.

Quantitative Analysis

Since the infrared spectral absorption appears to follow Beer's law the concentration of a compound should be proportional to the measured absorbance at a characteristic frequency for that compound. Current work in this laboratory shows this relationship to be true for kaolinite if the samples are randomly oriented to avoid pleochroic effects. Attempts are now being made to quantitatively determine kaolinite and other clays in mixtures.

Amorphous Clays

The importance of amorphous materials in soil has been recognized for many years. Methods for the investigation of these amorphous components, especially those of inorganic nature, are limited. However reliable results have been obtained by differential thermal analysis, surface area, electron microscopic, infrared absorption and x-ray diffraction techniques. The only application of the last technique to amorphous inorganic material lies in the recognition of ordering within the amor-

phous structure; completely amorphous systems show no x-ray diffraction.

Unlike diffraction techniques, infrared absorption methods of analysis do not require the sample under investigation to be ordered or crystalline; it is the masses of constituent atoms and ions, and the length and strength of bonds between them which control the absorption of infrared radiation. For this reason amorphous hydrated oxides of Al, Fe and Si have characteristic absorption infrared absorption spectra, and it is possible to observe well defined shifts in absorption bands resulting from substitution of Al for Si, for example in coprecipitated silica-alumina gels (3). Most important in this respect is the ability of infrared analysis to indicate the presence of an amorphous inorganic constituent in soil clay, the degree of polymerization of silica in the amorphous phase, and the possible major cation present.

Summary

Infrared spectra of clay mineral systems can separate trioctahedral from dioctahedral, triphormic from diphormic, and minerals with different degrees and types of isomorphous substitution. It can measure degree of hydration of a mineral, observe its surface character and interactions with organic and inorganic reactants, quantitize some clay systems, and indicate the prevalence and kind of amorphous substances present. It is an excellent new tool to complement the x-ray diffraction in clay mineral research.

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