

## EFFECT OF PELLET PRESSING ON THE INFRARED SPECTRUM OF KAOLINITE

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**Abstract**—Diffuse reflectance infrared (IR) spectra show that pressing kaolinite into pellets for transmission IR studies changes relative intensities of hydroxyl peaks between 3700–3600  $\text{cm}^{-1}$ . The magnitude of change depends on the absolute pressure, the pressing time and whether a salt matrix is used. Pressing with KBr causes larger differences than pressing neat. Diffuse reflectance IR does not require sample pressing, eliminating this variable in kaolinite studies. This improves IR's ability to distinguish kaolinites according to their hydroxyl group differences and may lead to a better understanding of kaolinite hydroxyl structures.

**Key Words**—Kaolinite, Diffuse reflectance infrared, Kaolinite hydroxyls, Kaolinite pressing.

### INTRODUCTION

Hydroxyl groups are a major structural component of kaolinite,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . Infrared spectroscopy (IR) is ideal for studying these hydroxyls because it directly detects four major stretching peaks at 3695, 3670, 3655 and 3620  $\text{cm}^{-1}$ . Several research groups have used IR alone or in combination with other methods to improve our understanding of the hydroxyl structure's role in rheology, defect structures, iron substitution and particle size. Much of this work has been reviewed by Giese (1988). Cruz-Complido *et al.* (1982) and Barrios *et al.* (1977) used hydrazine intercalation, Aglietti *et al.* (1988) used acid attack, and Kodama *et al.* (1989) used mechanical grinding; all found hydroxyls are sensitive to these treatments. Lombardi *et al.* (1987) noted differences in hydroxyl intensities as a function of size fractions of a sedimentary kaolinite. Brindley *et al.* (1986) found a correlation between a series of kaolinites of increasing XRD Hinckley indices and IR hydroxyl peak frequencies and widths. They found no correlation between ESR-detected structural iron impurities and IR hydroxyl data. Earlier, however, Mestdagh *et al.* (1980a, 1980b) reported a correlation between ESR detected "E" and "I" structural iron impurities and the relative extinction coefficients of the 3695 and 3670  $\text{cm}^{-1}$  peaks. Petit and Decarreau (1990) recently published work showing a decrease in the 3695/3620  $\text{cm}^{-1}$  hydroxyl intensity ratio with increasing incorporation of iron into synthesized kaolinites. These studies indicate there is a wealth of information available from IR data and that kaolinite hydroxyls are very sensitive to physical and chemical changes. However, the lack of detail in the results obtained and the lack of agreement between different laboratories (Giese 1988) suggest an experimental variable has been inadvertently overlooked in hydroxyl studies. One variable not specified in all the above publications

is the effect of pressing kaolinite when making pellets for transmission IR studies.

Diffuse reflectance IR does not require pressed pellets. Using this method, we have found hydroxyl intensities correlate with several kaolinite physical properties, including surface areas and iron contents. Using transmission IR with the kaolinites pressed into KBr pellets we can only distinguish the extremes of these correlations. In this paper, we use diffuse reflectance IR to show how pressing a kaolinite into pellets distorts its hydroxyl intensities and results in a lack of precision. This makes it difficult to distinguish different kaolinites and obscures details important in correlations between hydroxyl structures and kaolinite properties.

### EXPERIMENTAL

#### *Pressed pellets versus diffuse reflectance*

Transmission IR of powders is commonly done by diluting the solid to approximately 5% in a halide salt, often KBr, and pressing at 1000 to 20,000 lbs ( $3 \times 10^7$  to  $7 \times 10^8$   $\text{N/m}^2$ ). A typical recommended pressure for powdered minerals is 18,000 lbs (Afrechow 1969). Diffuse reflectance IR as an alternative to pressing pellets involves no sample alterations. Commercial reflectance cell design has improved over the past decade (Leyden and Shreedhara, 1987) with a concurrent improvement in understanding of optimal sampling and data reduction methods (Fuller and Griffiths, 1987). Although solids can be run neat by diffuse reflectance, quantitation is complicated by specular reflectance superimposed on the diffuse reflectance spectrum (Brimmer and Griffiths, 1986). This is minimized by dilution with a salt matrix, use of particle sizes less than 75  $\mu\text{m}$ , and physically blocking the specular component of the reflected radiation (Messerschmidt, 1985). For samples which are not damaged by pellet pressing, carefully run

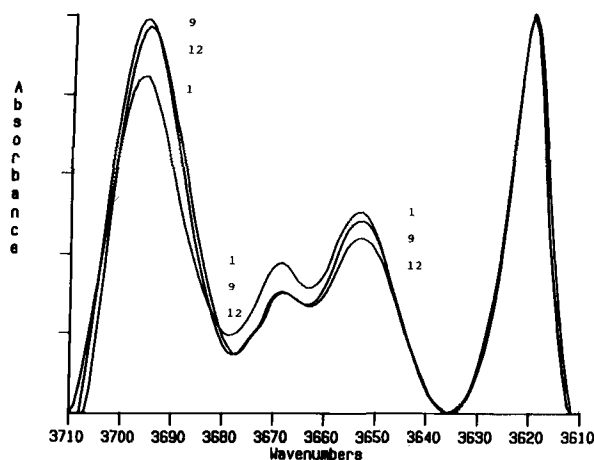


Figure 1. Hydroxyl region IR of Washington County kaolinite aliquots 1 (unpressed), 9 (pressed neat), and 12 (pressed in KBr). Spectra are expanded to overlay at 3636 and 3620  $\text{cm}^{-1}$ .

diffuse reflectance and pressed pellet/transmission methods give identical data.

#### *Kaolinite aliquots and infrared spectroscopy*

All data are for a Washington County kaolinite, particle size 0.5–25  $\mu\text{m}$ . We did not treat aliquots 1 to 7 in any way before diluting them to 5% in powdered KBr (Aldrich) for diffuse reflectance. The remaining aliquots were all pressed in a Janos 13 mm stainless steel die with a Carver press. We pressed aliquot 8 neat at 15,000 lbs for one hour. For aliquot 9, also neat, we quickly applied and removed pressure to 15,000 lbs four times. Aliquots 10, 11 and 12 were diluted to approximately 25% in KBr before pressing. Sample 10 received 1000 lbs for one minute, sample 11, 5000 lbs for one minute and sample 12, 15,000 lbs for five minutes. We ground each pellet to a powder, then diluted it to obtain 5% kaolinite in KBr for diffuse reflectance studies.

We collected spectra on a Bio-Rad FTS-60 near-IR spectrometer using 256 scans, 2  $\text{cm}^{-1}$  resolution and a Spectra-Tech "Collector" diffuse reflectance cell with a specular reflectance blocker. Determining a ratio of each kaolinite spectrum to pure KBr resulted in absorbance data.

#### *Data reduction*

Systematic changes in hydroxyl peaks as a function of pressing severity are qualitatively apparent in the raw data. However, distorted baselines in the more severely treated samples make it meaningless to measure absolute intensities in the conventional sense. We therefore used an arbitrary method to monitor peak changes. The four major hydroxyl peaks occur at approximately 3695, 3670, 3655 and 3620  $\text{cm}^{-1}$  (Figure

Table 1. Ratios for unpressed vs pressed kaolinite.

Aliquot	$I_{v4}/I_{v2}$	$I_{v1}/I_{v3}$
Unpressed		
1–7, average	1.65	2.66
Standard deviation	0.02	0.05
Pressed neat at 15,000 lbs		
8	1.74	2.66
8 (rerun)	1.71	2.64
9	1.89	2.51
9 (rerun)	1.89	2.47
Pressed in KBr		
10 (1000 lbs)	1.88	2.62
11 (5000 lbs)	2.06	3.29
12 (15,000 lbs)	2.25	3.01

1). The lowest point between these peaks is always at 3636  $\text{cm}^{-1}$  which we arbitrarily set to zero absorbance. We then measure the intensity of each hydroxyl peak above this point and compare intensity ratios,  $I_{v4}/I_{v2}$  and  $I_{v1}/I_{v3}$ , where v1 through v4 indicate the peaks in decreasing frequency. This method does not necessarily indicate the amounts of each type of hydroxyl present, merely the degree of distortion in the IR spectra. However, using different kaolinite samples, we have previously compared the results to total peak areas. Numerical values differ but both methods rank nine kaolinites in the same order for several physical properties. Our "arbitrary" method is slightly better at resolving similar kaolinites according to surface area or iron content. We attribute this to a relative insensitivity to baseline distortions. Nonetheless, for this sample set we cannot prove our method parallels absolute hydroxyl intensities and therefore emphasize it is simply a measure of spectral distortion.

## RESULTS

Pressing kaolinite distorts its IR hydroxyl peak intensities. Figure 1 shows the upper portion of the hydroxyl peaks of aliquots 1, 9 and 12 normalized to overlay at 3636 and 3620  $\text{cm}^{-1}$ . Table 1 lists intensity ratios  $I_{v4}/I_{v2}$  and  $I_{v1}/I_{v3}$  for all samples. The seven unpressed aliquots give  $I_{v4}/I_{v2}$  and  $I_{v1}/I_{v3}$  ratio averages of 1.65 and 2.66, with standard deviations of 0.02 and 0.52, respectively. Duplicate scans of four of the aliquots show deviations of less than 0.01 for both ratios due to instrumental effects.

$I_{v1}/I_{v3}$  for aliquot 8 (kaolinite pressed neat) is within the standard deviation of unpressed kaolinite data. However, the  $I_{v4}/I_{v2}$  ratio differs by more than three standard deviations. For aliquot 9, pressed several times to the same pressure as aliquot 8, both ratios differ by more than three standard deviations. This shows the importance of both absolute pressure and the pressing technique. For kaolinite mixed with KBr before pressing, only  $I_{v1}/I_{v3}$  for the lowest pressure aliquot 10 is within the standard deviation of the unpressed ali-

quots. For 11 and 12 the deviation in the ratios is much greater. Both pressure and the presence of a matrix alter the hydroxyl peaks.

### CONCLUSIONS

This simple experiment shows that IR hydroxyl peaks change irreversibly when kaolinite powder is pressed into pellets. This may be due to optical or chemical effects. Hydroxyl intensities of oriented kaolinites show pleochroic behavior, i.e., changes in the peak intensities according to platelet orientation in the IR beam. Rouxhet *et al.* (1977) oriented single crystals of kaolinite onto a KRS5 crystal and showed that with polarized IR excitation the  $3695\text{ cm}^{-1}$  peak more than doubles in intensity as a function of refraction angle. Pressing kaolinite may induce localized orientation which is not reversed when the pressure is released. Our diffuse reflectance spectra use powdered kaolinite in powdered KBr which should randomize any localized orientation. An alternative explanation is a change in the kaolinite structure itself such as changes in hydrogen bond lengths or orientations, or particle breakage which converts internal hydroxyls to surface hydroxyls. It is curious that the changes are affected by the simultaneous presence of KBr. It is possible that potassium has exchanged with some of the hydroxyl groups, further distorting their intensities. Alternatively, the plastic behavior of KBr may affect how pressure is distributed in the kaolinite platelets within the die thereby affecting how the kaolinite is changed by pressure.

Regardless of the cause of the hydroxyl intensity changes, valuable structural information is lost when kaolinite IR spectra are acquired using pressed KBr pellets. Looking at the spectra as plotted in Figure 1, the hydroxyl changes seem relatively minor. However, this magnitude of change is greater than the hydroxyl-region differences we find correlate with kaolinite physical properties. In light of this study, it is not surprising that IR/structural correlation studies have sometimes given ambiguous results. The diffuse reflectance method improves precision and may improve our chances of understanding the role of hydroxyls in kaolinite structure.

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