to be quite compatible with the original analytical scheme. Incidentally, El-Attar and Jackson (1973) have observed considerable thermal decomposition at 550°C of Fe-rich layers and/or interlayers in montmorillonitic soils of Nile River alluvium.

Additional information that can be deduced from the above procedure is the CEC and K^+-fixation capacity of the amorphous constituents of the clays provided these values are determined for the original clays also. The present modification avoids the assignment of arbitrary, possibly erroneous, values of CEC and K^+-fixation capacity values to the amorphous inorganic constituents of soil clays.

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SOME EFFECTS OF GRINDING KAOLINITE WITH POTASSIUM BROMIDE

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In a significant note published recently in this journal, Miller and Oulton (1972) described effects of mixing–grinding of kaolinite with KBr on the ratio R of the absorbance values of the 3695 and 3620 cm^{-1} bands and the percentage changes P (percentage) in absorbance, for each of the two bands using the 1002 cm^{-1} band as a reference standard. They found an increase of R with increasing time of grinding principally due to a decrease in intensity of the 3620 cm^{-1} band and also, as they reported, due in part to an increase in the 3695 cm^{-1} band. Following Parker (1969) who was able to show a correlation between R values and the crystallinity and shape of the kaolinite, the authors concluded that their results are due in part to a delamination of the kaolinite particles (tactoids) by the KBr, possibly aided by intercalation of the kaolinite by the water sorbed during the grinding. Although this suggestion seems to be reasonable, it cannot be supported by their results. The observations reported here do provide strong evidence for the occurrence of that delamination.

According to Farmer and Russell (1966), delamination can be examined from the intensity and position of the vibration of the Si–O^- band which gives a dipole oscillation perpendicular to the plates. For delaminated kaolinite, an infrared absorption occurs when the radiation is perpendicular to the crystal plates. Due to a field which opposes the dipole vibration, the force constant increases causing a rise in the vibration frequency V_1. With laminated kaolinite (tactoid) absorbance and frequency of absorption depend on the angle between the optical axis and the normal to the lattice wave. Thus a broad shoulder having a range of values is obtained which corresponds to absorption by randomly oriented particles. The frequencies of these absorptions are always lower than that of the single layer kaolinite. The sharpness and position of this band can therefore give information on the delamination of kaolinite during grinding in the presence of KBr and is examined below.

A mixture of 5 mg kaolinite from Georgia (Oneal Pit, Macon, supplied by Ward's Natural Science Establishment, Inc.) and 500 mg of KBr (BDH suitable for i.r. spectroscopy) was ground in an automatic porcelain mortar for various time periods. To avoid grinding effects in the preparation of the discs, 15 mg of the mixture were gently mixed manually with 120 mg of KBr. I.R. spectra were recorded on a Perkin–Elmer spectrophotometer, model 237. To obtain the spectrum of an unground kaolinite, 0·4 mg of the clay was gently mixed manually with 135 mg of KBr. Some of the spectra are given in Fig. 1.

The following positions for the different bands of the unground samples are (in cm^{-1}): A, 3700; B, 3670 (shoulder); C, 3657 (weak); D, 3627; E, 1115; F, 1031; G, 1007; H, 937 (weak); I, 912. The assignment used here is that of Miller and Oulton (1970).

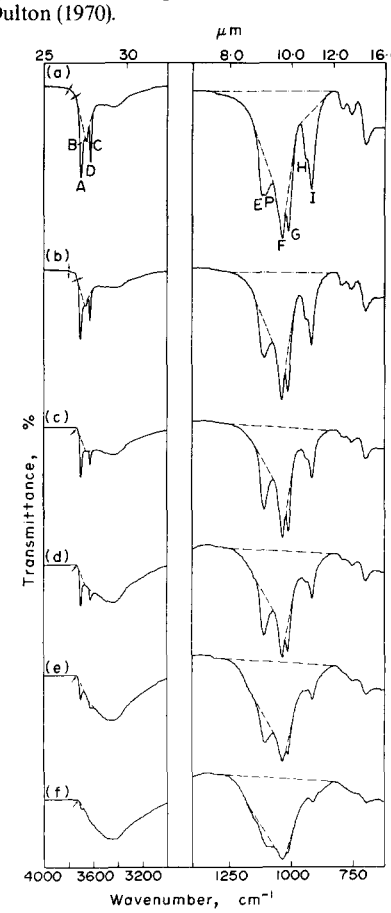


Fig. 1. The i.r. absorption spectra of kaolinite in KBr discs and the extrapolated base lines, (a) unground, (b) ground for 30 sec, (c) ground for 10 min, (d) ground for 20 min, (e) ground for 60 min and (f) ground for 120 min in the presence of KBr.

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Bands A, (B, C), D, H and I, which represent hydroxyl groups, although becoming weak on prolonged grinding, are not shifted to other frequencies. Bands F and G, Si–O in plane vibrations are slightly shifted on prolonged grinding to 1035 and 1010 cm^{-1} respectively. Band E, a Si–O in-plane vibration, which is clearly detected in the spectrum of the underground kaolinite almost disappears on grinding.

A $Si–O^-$ out-of-plane band which appears at 1098 cm^{-1} in the spectrum of the unground kaolinite (band P) moves to 1103 cm^{-1} on grinding and becomes sharp, indicating delamination of the tactoid. On prolonged grinding this band becomes broad and its maximum is shifted to lower frequencies. It also diminishes due to a destruction of the kaolinite structure.

In order to understand the broadening and shifting of this band, let us examine a previous publication of Miller and Oulton (1970) on prototropy in kaolinite during percussive grinding in the absence of KBr. By the use of i.r. absorption spectroscopy, they found that transfer of protons from one position in the kaolinite took place when this mineral was subjected to percussive grinding. In the earliest stage, the protons move away from the intralayer hydroxyls, those giving rise to band D. Later on, the basal hydroxyls giving rise to band A, also lose their protons. This leads to the diminishing of the OH stretching bands, band D being followed by band A. Other bands involving OH groups, namely bands H and I, diminish. Among the Si–O stretching bands, band P is the most sensitive to grinding, as has already been recognized by many investigators. This band involves a vibration of oxygens common to tetrahedral and octahedral layers, the nearest neighbors to the inner hydroxyls, and it is no wonder that prototropy will affect this band.

In order to show the individual effects of the grinding on bands A, D, G and P, the percentage changes in absorbance, P (percentage) values were calculated as described earlier by Miller and Oulton (1970), using equation 1, where A_{ig} is the absorbance of the i band in the given spectrum of the sample

$$P(\%) = \frac{100[(A_{ig} - A_{big})/(A_{Fg} - A_{bFg}) - (A_{io} - A_{bio})/(A_{Fo} - A_{bFo})]}{(A_{io} - A_{bio})/(A_{Fo} - A_{bFo})} \quad (1)$$

ground for g min; A_{big} is the absorbance of the extrapolated base-line at the wave length of band i in the spectrum; A_{Fg} is the absorbance of band F in the same spectrum; A_{bFg} is the absorbance of the extrapolated base-line at the wave length of band F in the same spectrum; A_{io}, A_{bio}, A_{Fo}, and A_{bFo} are the absorbance of band i, of the extrapolated base-line at the wave length of band i, of the band F and of the extrapolated base-line of band F, respectively in the spectrum of the unground sample.

Extrapolated base-lines are drawn for each peak as shown in Fig. 1. Thus, the sharpness of the bands may be measured and interferences of water bands or bands of amorphous material are practically avoided.

In this study, band F is used as a reference standard, and not band G, which was used by Miller and Oulton (1970, 1972). The preferability of this band is due to the fact that on prolonged grinding of kaolinite, band G disappears while band F persists even when X-ray and DTA show that the kaolinite is completely transformed into an amorphous material. Band F may therefore indicate the amount of total silica. Justification for this choice of reference standard can be seen also from the increase of absorbance of this band during prototropy when band G was used as a reference standard, as reported previously by Miller and Oulton (1970).

The decrease in absorbance of band D (Fig. 2) indicates that prototropy occurs as soon as the grinding process begins. Increase in absorbance of band P shows that more and more kaolinite is delaminated up to a grinding time of 12 min. With further grinding, both the destruction of the crystal and prototropy are sufficiently rapid to give a decrease in the absorbance of this band.

Fig. 2 shows that band A increases only up to two minutes grinding and then decreases. A similar observation is made if band G is used as the reference standard in equation (1).

Band A has a tail at 3720–3800 cm^{-1} which clearly appears in the spectrum of the unground sample (Fig. 1). The kaolinite was fractionated into several particle sizes after being dispersed ultrasonically. The presence of this tail does not depend on the particle size. Furthermore, this tail does not diminish if the kaolinite is ground without KBr. This tail diminishes on grinding kaolinite with KBr. Its diminution depends on the time of grinding. It seems that

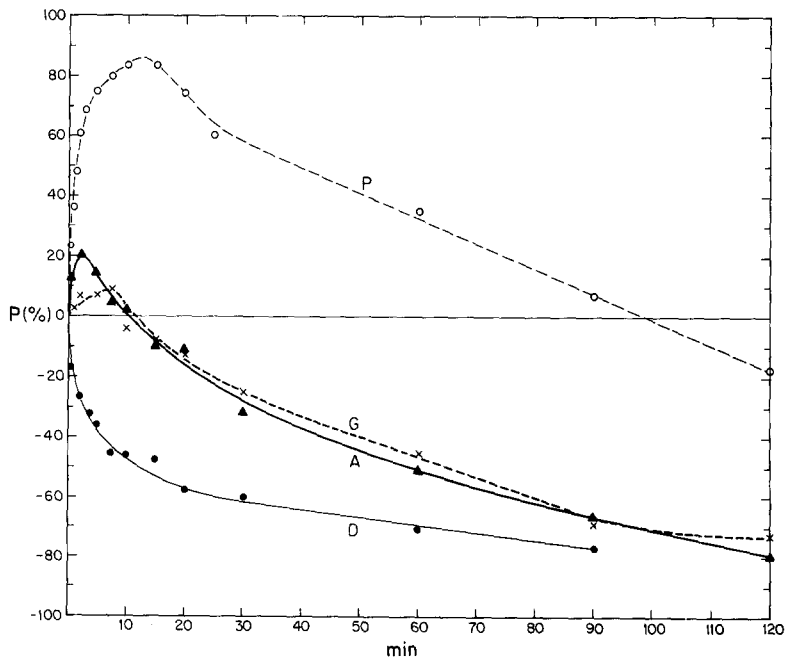


Fig. 2. Percentage change in absorbance P (%) as a function of grinding time for bands A (▲—▲—▲), D (●—●—●), G (×--×--×) and P (O--O--O).

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the dimunition of the tail is associated with the increase of band A. If we assume that the absolute absorbance of the band is proportional to the number of basal hydroxyls being inclined at a defined angle to the kaolinite sheet, then it is possible that some of the hydroxyls are inclined at a different angle due to some kind of tension (perhaps from flexure) existing in the layer when it is part of a tactoid. The dipole of such a group will contribute to the i.r. absorption of the tail rather than to that of the main band. On delamination of the tactoid, the tension of the layer may be released and the hydroxyls may turn to their ideal positions. At this stage, dipoles of these groups will also contribute to the i.r. absorption of the main 3700 cm^{-1} band.

In general, paired bands F and G are Si–O in plane vibrations, the oxygens being basal. The sharpness of these bands may give information as to whether the hexagonal sheet is more or less uniform. Due to the formation of amorphous material during grinding (which absorbs at 1035 cm^{-1}), no information may be gained from sharpness of band F. On the other hand, the method used here for baseline extrapolation enables one to obtain useful information from the sharpness of band G. In the tactoid, tension existing in the layers causes some basal oxygens to move from their ideal position. Increase in absorption of band G up to 8 min grinding (Fig. 2) shows that more and more oxygens move to their ideal positions due to the release of the tension in the layer as a result of delamination. The kaolinite layer thus obtained is more uniform. On further grinding, both the destruction of the crystal and the migration of protons from basal hydroxyls are sufficiently rapid to give a decrease in the absorption of this band.

Infra-red spectra of discs of kaolinite obtained by repeated gently pulverizing of discs of the unground mineral and repressing showed that even by gentle mixing, delamination of the tactoid may occur.

Similar observations were obtained with other kaolinites from various localities: (1) Makhtesh Ramon, Israel (S_5); (2) Um Bogma, Sinai; (3) Bath, South Carolina, USA; and with Flint Clay from Makhtesh Ramon, Israel.

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