ELECTRON-MICROSCOPIC AND MÖSSBAUER SPECTROSCOPIC STUDIES OF IRON-STAINED KAOLINITE MINERALS

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Abstract—An electron-microscopic and Mössbauer spectroscopic study of a range of kaolinites has revealed three distinct types of iron contamination within these minerals: a) Ferric ion may substitute for aluminium and be evenly distributed throughout the lattice. b) Ferric ion may be present as a crystalline coating of goethite, as indicated by lattice-imaging studies, or c) as an amorphous coating. The distribution of the iron in the groups b and c is non-uniform and is highest at the flake surfaces. Ferrous ion, when detected, is thought to be evenly distributed throughout the lattice. The size of the contaminating goethite crystallites and the observed Mössbauer spectra of these samples suggest that such particles are super-paramagnetic. All kaolinites can be cleaned by acid treatment except those having iron substituting for Al$^{3+}$.

INTRODUCTION

The minerals of the kaolinite group are of considerable industrial importance and many processes require that the clay mineral is relatively pure and stain-free. The kaolinites have been widely studied (see for example the survey of Bates, 1971) by electron-optical methods, in both the scanning and transmission modes, chiefly in order to obtain morphological information. However most studies have concentrated on relatively pure kaolinites and little is known about the detailed nature and origin of the iron staining often associated with kaolinite deposits. As part of a general study of the ultra-microstructure and chemical properties of the kaolinite/illite/montmorillonite minerals, stained kaolinites from a variety of locations listed in Table 1 have been examined in considerable electron-microscopic detail. As it is generally thought that the stains may contain iron oxides or oxy-hydroxides $^{57}$Fe Mössbauer spectroscopy has been used to further characterise the staining. Results of stain-removal experiments relevant to possible industrial methods are also reported.

EXPERIMENTAL

Each of the kaolinite samples was purified by sedimentation, the <2 micron fraction being selected for study. Portions of each sample were acid-extracted to investigate the rate of contaminant removal, the severity of the contamination requiring strong (30% wt) hydrochloric acid, although a weaker acid would have involved less risk of chemical attack on the kaolinite itself. All samples were left in contact with the acid for twenty-one days, apparent percentages of extractable iron being determined gravimetrically by conversion to Fe$_2$O$_3$.

Portions of untreated and acid-extracted samples were subsequently examined on a Phillips X-ray diffractometer and Guinier camera, using pressed, rather than sedimented specimens. For transmission electron microscopy, specimens were lightly ground in acetone suspension and deposited onto holey carbon film/copper grid mounts, and examined at intermediate and high magnifications in a Phillips EM-300 electron microscope, and in the scanning transmission mode in a J.E.O.L. JEM-100B analytical electron microscope. Lattice fringes, where recorded, were measured on an optical diffractometer by comparison with those from carbon black at the same magnification.

$^{57}$Fe Mössbauer spectra were also recorded for all samples prior to and following acid extraction, at 290 K. For reasons outlined later the sample CCBH7 was further studied at intermediate temperatures. A Harwell spectrometer of the constant acceleration type and a 10mC source of $^{57}$Co Rh was used, the spectrometer being periodically calibrated with an iron foil standard.

RESULTS

Acid extraction and X-ray diffractometry

Results from the acid-extraction tests are summarised in Table 1, the rate and extent of extraction varying from complete and rapid in the case of GP2 to incomplete and very slow in the case of the two South Carolina samples. X-ray diffractometer examination showed little difference between any of the samples, the only observable impurity being an illite-like material, occurring in all but the two South Carolina kaolinites. The latter were also the only samples to show clearly the b-axis disorder (Brindley, 1961) characteristic of certain kaolinites, shown by broad
Table 1. Extraction data for kaolinite samples. The two unstained samples (GP1 and TB146) used for comparison in the electron-microscopic study are omitted.

<table>
<thead>
<tr>
<th>Samples and origin</th>
<th>Extraction</th>
<th>Wt. % Fe extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB153 Cornwall</td>
<td>slow</td>
<td>not determined</td>
</tr>
<tr>
<td>TB169 Cornwall</td>
<td>slow</td>
<td>0.462</td>
</tr>
<tr>
<td>Cornwall CCBH7</td>
<td>rapid</td>
<td>2.459</td>
</tr>
<tr>
<td>Spain LBH22</td>
<td>rapid</td>
<td>0.956</td>
</tr>
<tr>
<td>Portugal LBH23</td>
<td>rapid</td>
<td>1.360</td>
</tr>
<tr>
<td>Portugal TPC1</td>
<td>rapid</td>
<td>0.923</td>
</tr>
<tr>
<td>Cornwall GP2</td>
<td>rapid</td>
<td>0.725</td>
</tr>
<tr>
<td>Cornwall BSC1</td>
<td>rapid</td>
<td>0.973</td>
</tr>
<tr>
<td>S. Carolina DRP1</td>
<td>rapid</td>
<td>0.725</td>
</tr>
<tr>
<td>S. Carolina</td>
<td>rapid</td>
<td>0.725</td>
</tr>
</tbody>
</table>

(hkl) diffraction bands. No peaks due to oxides or oxyhydroxides of iron were observed in the traces, or in a subsequent examination using a Guinier camera. In addition, no significant differences were noted in traces taken from untreated and acid-extracted portions of any one sample, except for a slight variation in the background level from the more iron-rich specimens (CCBH7 and TB153).

Electron microscopy

Transmission electron microscopy at intermediate magnifications revealed a considerable variation of flake shapes and sizes in all samples, with all but a small proportion of flakes examined having characteristically sharp and well-defined edges. Examination of flakes with irregular outlines in the analytical electron microscope suggested that they contained potassium, and were probably the illite-like impurity observed by X-ray powder diffraction. When micrographs of samples before and after extraction were compared, no differences were noted in the samples DRP1, BSC1, TPC1 and LBH23 which appeared to be identical to the unstained samples TB146 and GP1. One such micrograph is illustrated in Fig. 1(a).

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Electron micrographs, taken at intermediate magnification, of the GP2 sample did show noticeable differences before and after acid extraction. In approximately 10% of all flakes studied before acid treatment, a peculiar form of mottled contrast on the flake basal surfaces was observed, as shown in Fig. 1(b). The observed high contrast suggests the presence of relatively heavy atoms, rather than an organic contaminant, and the close similarity between these micrographs and published ones of unaged ferric oxide gel (Mackenzie, Meldau and Gard, 1962) implied the presence of such a gel on the flake surfaces in this sample. A test examination of an originally unstained kaolinite with freshly precipitated ferric oxide gel on the flake surfaces was undertaken, giving remarkably similar micrographs to those of GP2. After acid extraction this form of contamination was found to be completely absent.

The remainder of the samples (TB153, TB169, LBH22 and CCBH7) showed fine, spindle-shaped surface particles on the untreated specimens. These were evidently associated with the staining, as they were not present in the acid extracted portions. These particles, which have no orientation relationship to the kaolinite lattice, were very similar to particles of natural goethite described by Mackenzie, Follet and Meldau (1971), although their outline was more irregular than that of the crystallites of synthetic goethite reported by the same authors. The presence of iron in the surface particles was confirmed by examination in the analytical electron microscope. In the two most heavily stained samples (TB153 and CCBH7) particles were observed on virtually every kaolinite flake (Fig. 1c), whereas less than 50% of all flakes were so contaminated in TB169 and LBH22. The latter often showed clumps of particles at flake edges (Fig. 1d: reminiscent of the tactoid structures observed in natural akaganéite by Mackay (1962). The small size of the contaminating particles prohibited the conventional recording of selected area diffraction patterns, although certain maxima additional to the normal kaolinite pattern were observed, and micro-beam diffraction (in the scanning transmission mode) caused the particles to decompose before a pattern could be recorded.

High resolution examination

As a result of the inability to record selected-area diffraction patterns from the contamination when observed, an attempt was made to characterise the contamination by recording and measuring lattice spacings in the high resolution mode of operation. Examination of the GP2 sample in this way revealed no definable crystal lattice (Fig. 2a), implying an amorphous type of contamination quite compatible with a gel structure. However, the samples with the fine particle type of contamination gave reasonable lattice images, indicative of a fair degree of crystallinity. The images were recorded at approximately 90Å under focus, giving a phase contrast transfer function (Erickson and Klug, 1971) which favoured resolution of spacings in the range 3.5 to 10Å for the particular spherical aberration coefficient (Cs = 1.6 mm) of the instrument used.

The accuracy of the measured spacings was limited by the small size of the particles and hence the small number of fringes involved. Spacings of 4.91 ± 0.11Å (Fig. 2b) and 4.34 ± 0.13Å (Fig. 2c) were frequently recorded which reasonably correspond to goethite (020) and (110) lattice spacings, published values being 4.98Å and 4.18Å (Rooksby, 1961). In addition, spacings of 3.6 ± 0.10Å and 2.7 ± 0.18Å were recorded which either correspond to the (102) and (104) lattice spacings of hematite or the (120) and (130) spacings.
Fig. 1. (a) An unstained kaolinite (GP1) at intermediate magnification. (b) The stained GP2 sample at similar magnification, showing the mottled contrast effect. (c) The heavily stained CCBH7 sample, showing surface contaminating particles. (d) A clump of similar particles seen in the LBH22 sample.
Fig. 2. (a) High-resolution image of the amorphous coating of the GP2 sample. (b) Lattice image of a contaminating crystalline particle in sample CCB17. The spacing corresponds to the (020) spacing of goethite. (c) Lattice image of a contaminating crystalline particle in sample TB13. The spacing corresponds to the (110) lattice spacing of goethite. (d) Lattice resolution at the edge of a (surprisingly) kaolinite flake. The spacing in fact is approximately 10 Å.
of goethite. Previously published values of these spacings are 3.67 Å and 2.69 Å for hematite and 3.38 Å and 2.69 Å for goethite. As a result of this high resolution examination there is little doubt that the bulk of the contaminating material contributing to the staining was in fact goethite.

Lattice images were also obtained from the parent flakes in these samples. These show three systems of 4.6 Å fringes mutually inclined at 60° and are very similar to those observed in phyllophyllite by Dowell (1961). Observation of simultaneous lattice images of this type, and lattice images in the contaminating particles, confirmed that the particles were disposed with no definite orientation to the kaolinite lattice. Lattice images (00l) of the main flakes also were obtained. These are similar to those observed in organo-montmorillonites by Suito, Arakawa and Yoshida (1969), and show no trace of any contaminating particles within the body of the flakes themselves. Further images of this type were obtained from thin sections cut perpendicular to the basal cleavage using the method of Brown and Jackson (1973). One of these is shown in Figure 2(d). However, the interpretation of these images was open to some question as their spacing invariably corresponded to the 10 Å spacing of mica, suggesting in fact that these images were due to the illite impurity. Spot analyses in the analytical electron microscope seemed to confirm this, and a full discussion of images of this type will be made in a later report.

Mössbauer spectroscopy

The room temperature Mössbauer parameters of all samples are listed in Table 2. The spectra of DRP1 and LBH23 consisted of doublets having parameters compatible with the predominant presence of high-spin ferric ion in a six co-ordinated site (Bancroft, 1973), a typical spectrum being shown in Figure 3a. No significant changes occurred in the spectra at 80°K or following acid extraction. The spectrum of BSC1 was similar, except for the presence of ferrous ion (approximately 10 per cent) indicated by a small absorption at high velocities. Attempts to fit either single quadrupole doublets or two distinct doublets were not wholly satisfactory, and therefore it is probable that at least two sorts of ferric ion with very similar Mössbauer parameters were present, values quoted being averaged.

Spectra of samples GP2 and TPC1 at 290°K (Figure 3b) were characterised by a wide doublet corresponding to the ferrous ion together with an absorption at the center indicating ferric iron. In the 290°K spectrum of GP2 a shoulder was just resolved on the ferrous resonance at high energies and the spectrum was computer-fitted to two ferrous and one ferric quadrupole doublets. Following acid extraction both samples showed a marked diminution of the ferric signal relative to the ferrous signal, the ratio decreasing from 0.56 to 0.46 and 0.54 to 0.38 for GP2 and TPC1 respectively (Figure 3c). Isomer shifts and quadrupole splittings were compatible with the presence of the ferrous ion in a six co-ordinated site.

The remaining materials (CCBH7, LBH22, TB153 and TB169) all showed more complex behaviour indicative of magnetically ordered regions within the samples at 80°K. The room temperature spectra of

<table>
<thead>
<tr>
<th>Clay</th>
<th>$\delta$ mm s$^{-1}$ (rel. $-\text{Fe}$)</th>
<th>$\Delta$ mm s$^{-1}$ (Fe$^{3+}$ + Fe$^{2+}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSC1</td>
<td>Fe$^{3+}$ 0.36 0.52 &gt; 0.9</td>
<td></td>
</tr>
<tr>
<td>DRP1</td>
<td>Fe$^{3+}$ 0.35 0.55 1</td>
<td></td>
</tr>
<tr>
<td>LBH23</td>
<td>Fe$^{3+}$ 0.37 0.52 1</td>
<td></td>
</tr>
<tr>
<td>GP2</td>
<td>Fe$^{3+}$ 0.35 0.67 0.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$ 1.12 2.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe$^{3+}$ 0.31 0.69</td>
<td></td>
</tr>
<tr>
<td>TPC1</td>
<td>Fe$^{3+}$ 1.01 2.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe$^{2+}$ 1.14 3.14</td>
<td></td>
</tr>
<tr>
<td>CCBH7</td>
<td>Fe$^{3+}$ 0.37 0.61 1</td>
<td></td>
</tr>
<tr>
<td>LBH22</td>
<td>Fe$^{3+}$ 0.36 0.56 &gt; 0.9</td>
<td></td>
</tr>
<tr>
<td>TB153</td>
<td>Fe$^{3+}$ 0.39 0.48 1</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Room temperature isomer shifts and quadrupole splittings ($\pm 0.04$ mm s$^{-1}$) for the samples studied. In most cases the parameters represent the average of a number of sites. Where only traces of the ferrous ion are present the corresponding parameters are not reported because reliable location is difficult. The samples GP1, TB146 and TB169 (very weak spectra) are omitted.

Fig. 3. (a) Room temperature Mössbauer spectrum of untreated DRP1. (b) Room temperature spectrum of untreated GP2. (c) Room temperature spectrum of acid-treated GP2.
Fig. 4. Spectra of untreated CCBH7 as a function of temperature. Note the gradual appearance of a six-line pattern. Temperatures are accurate to ±1 K.

L BH22 and TB153 consisted of a doublet attributable to the ferric ion with a small trace of the ferrous ion in sample LBH22. Again the computer fits to a single doublet were not completely satisfactory. The spectrum of LBH22 at 80 K contained a weak six-line pattern ($H_{\text{int}} = 490$ K) together with a residual central doublet. The corresponding spectrum of TB153 was very similar with a stronger six-line pattern and only a very weak residual central feature. Following acid extraction the six-line pattern at 80 K was no longer obtained in all cases.

The room-temperature spectrum of CCBH7 (Figure 4a) consisted of a central quadrupole doublet due to the ferric ion superimposed on a broad background. The latter altered at liquid nitrogen temperature to an intense six-line pattern ($H_{\text{int}} = 492$ K, $\epsilon = 0.17$ mm s$^{-1}$) with a residual central singlet (in place of the doublet) with a pronounced shoulder at high energies. The sample was further studied in the temperature range 290 K to 80 K (Figures 4b to 4e). The resulting spectra showed how the broad background at room temperature gradually developed into a six-line pattern at the expense of the central doublet. This collapsing of the six-line pattern with increasing temperature is expected to arise when the relaxation frequency of the electronic spins (and hence the reversal frequency of the internal hyperfine magnetic field) is comparable with the Larmor precession frequency of the $^{57}$Fe nucleus (Wickman, Klein and Shirley, 1966).

DISCUSSION

Classification of samples

Each of the methods of study effectively subdivided the samples into three main groups, with some overlap when comparing different methods. On the basis of chemical attack, the two South Carolina samples (BSC1 and DRP1) formed one group, being incompletely cleaned by acid. These samples were among the first group established by electron microscopy in that they possessed no form of observed surface contaminant. They also formed the first group established by Mössbauer evidence showing only a single ferric doublet at all temperatures. Because no form of surface contaminant was visible the iron present must therefore be situated in the kaolinite lattice substituting for aluminium in octahedral co-ordination. Since the samples were only partially cleaned it must be assumed that much of the iron is inaccessible to chemical attack and therefore distributed uniformly throughout the lattice.

Chemical attack studies placed the GP2 sample in a unique group due to its extremely rapid acid extraction. Electron microscopy confirmed this grouping from the apparently amorphous coating exhibited only by flakes of this sample. Mössbauer data, however, would tend to group this sample with TPC1. For this reason they are considered together. For these samples the picture is complicated by the presence of two types of the iron atom, the ferric ion evidently is more accessible to acid attack than the ferrous, as revealed in the Mössbauer spectra before and after acid extraction. If this is due only to the position of the iron atoms in the kaolinite lattice, it seems probable that the ferric ion is located closer to the flake surfaces than the ferrous. The much faster acid extraction of GP2, as compared to TPC1, could be explained by the fact that the ferric ion in TPC1 is in the crystal lattice predominantly near the surface, while a great proportion of the ferric ion in GP2 is actually present on the surface in the form of an amorphous coating. These two samples could therefore represent subsequent stages in a gradual process of oxidation and staining in which the ferrous ion is oxidised to the ferric and then migrates towards the flake surfaces (TPC1) and eventually forms an amorphous gel structure on the surface (GP2).

The final group as determined by chemical extraction tests consisted of all samples completely but slowly cleaned by acid treatment. Although TPC1 fell
into this group it is best placed with the GP2 sample, 
as discussed above. The remainder of the samples 
TB153, TB169, LBH22, LBH23 and CCBH7) then form 
a reasonably consistent group. All can be 
completely cleaned. Therefore the iron present (vir-
tually all ferric) must be accessible to chemical attack.
For this reason LBH23 is included in this group re-
gardless of its lack of surface contamination and a 
six-line Mössbauer spectrum at 80°K. In a manner 
alogous to that of the previous group the samples 
can be regarded as representing different stages in an 
overall staining process but the lack of any notable 
trace of the ferrous ion prevents any conclusions 
being drawn regarding the ferrous/ferric oxidation 
process. The LBH23 sample represents the first stage 
in the staining process, having the ferric ion in 
the lattice but near the flake surfaces, while in the LBH22 
sample the first traces of a crystalline surface coating 
appeared as shown by the electron microscope evi-
dence and the very weak six-line Mössbauer spectrum 
obtained at 80°K. The growth of a crystalline coating 
at the expense of the lattice located ferric ion then 
proceeded much further in the three remaining sam-
ple. The final stage was reached in the TB153 sample 
in which Mössbauer spectra indicated an almost com-
plete absence of iron after acid extraction which sug-
gests that virtually all iron present was incorporated 
in the surface coating.

**Interpretation of Mössbauer spectra**

From the relatively low total iron content of the 
clays studied the iron within the lattice can be 
expected to be magnetically dilute and only a para-
magnetic doublet Mössbauer spectrum will be 
obtained. The appearance of a six-line pattern in the 
low-temperature spectra of certain samples therefore 
implies regions within these samples where high 
concentrations of iron exist locally and because these pat-
terns disappear following acid extraction such six-line 
spectra are associated with the surface contaminant. 
Lattice image studies prove that the contamination 
is crystalline and observed spacings are indicative of 
goethite even though at room temperature goethite 
is slightly smaller than that measured for bulk goeth-
ite. However, similar small reductions relative to 
the internal field for bulk samples have been observed 
for small particles of hematite (Gangas et al., 1972).

In addition, the quadrupole splitting deduced from 
the asymmetry of the six-line pattern at 80°K is com-
patible with the spins lying perpendicular to \( V_\perp \) 
which is positive, as is the case for bulk goethite, and 
the partially collapsed spectra are very similar to 
those of goethite close to its Néel point. The Mössbauer evidence is therefore fully compatible 
with the presence of small super-paramagnetic par-
ticles of goethite which constitute the surface staining 
of this particular kaolinite, and the samples grouped 
with it.

**Particle size determination**

Under certain circumstances, it is possible to obtain 
particle size distribution from a Mössbauer study of 
super-paramagnetic particles as a function of tempera-
ture. For instance by measuring the temperature vari-
ation of the ratio of super-paramagnetic doublet to six-
line pattern in the spectra of hematite it has been poss-
able to measure the size and distribution of hematite 
particles in soils (Gangas et al., 1972). In the case of 
 hematite either a six-line pattern, a completely col-
lapsed doublet or a superposition of both is observed. 
This is not the case with CCBH7 which exhibits only 
a partially collapsed spectra. This precludes a detailed 
examination of the particle size distribution but by 
comparing the spectra with calculated partially col-
lapsed spectra as a function of spin relaxation time 
and by reference to previous work on super-paramag-
etic particles of goethite by Shinjo (1966) some infor-
mation can be obtained. The critical volume of a 
goethite particle which leads to a collapse at 290°K 
of the six-line pattern is \( 3 \times 10^{-17} \) cm\(^3\) (equivalent 
to spherical particles of 300Å diameter). The broad 
background of the CCBH7 spectrum at 290°K shows 
that the six-line pattern has not completely collapsed 
and therefore places a lower limit of \( 3 \times 10^{-17} \) cm\(^3\) 
on at least a fraction of the surface contaminant 
particles. By comparison of the wings of the spectra with 
calculated spectra it is possible to estimate (Kundig 
et al., 1969) an upper limit of a kind of relaxation 
time for the spins of ca. \( 10^{-9} \) sec. From the relation-
ship \( \tau = (1/f_0)exp(KV/kT) \), with \( f_0 = 10^{10} \) c \( s^{-1} \) and 
\( K = 10^{4} \) erg cm\(^{-3} \) (Shinjo, 1966), an upper limit of 
equivalent spherical particle diameter of ca. \( 10^5 \)Å can 
then be deduced. This procedure applies to the par-
ticles contributing to the six-line pattern, but the resi-
dual central feature, although probably due to ferric 
ion within the kaolinite lattice, may arise from ex-
tremely small super-paramagnetic clusters of goethite 
still displaying a collapsed spectrum at 80°K.

**CONCLUSIONS**

1. Electron microscopy and Mössbauer spectroscopy 
   have revealed three distinct types of staining in 
   kaolinite minerals. All have some ferric ion substi-
tuted for aluminium uniformly throughout the lattice 
   and in type a) all the iron is present in this form. 
   In the other types the majority of the ferric ion is
present as b) a crystalline coating of goethite or c) as an amorphous coating. The last type also contains ferrous ion substituting for aluminium within the lattice.

2. Acid extraction studies showed the impossibility of cleaning kaolinites with the first type of staining, although those in categories (b) and (c) could be cleaned with varying amounts of stain removal. Samples in category (c) with amorphous surface coatings proved to be cleaned very easily.

3. The percentage of iron removed by acid extraction gradually increases throughout the three categories above with virtually all iron being removed from samples with crystalline surface coatings. In kaolinites included in category (c) the ferric form was removed preferentially.

4. The finely crystalline particles of category (c) are probably super-paramagnetic and particle size estimates from the Mössbauer spectra based upon this assumption agree reasonably well with those observed in the electron microscope.

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REFERENCES