ON THE POSSIBILITY OF REMOVAL OF NON-STRUCTURAL IRON FROM KAOLINITE-GROUP MINERALS

K. BAHRANOWSKI, E. M. SERWICKA*, L. STOCH† AND P. STRYCHARSKI‡


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ABSTRACT: The efficiency of removal of the free iron from kaolinite-group minerals by means of acid leaching was followed by chemical, AES, XRD and ESR analyses. Structural Fe responsible for the $g \approx 4$ ESR signal represented only a small fraction of Fe impurity in the natural samples. The remaining non-structural Fe was found to exist both as forms easily extractable with acid, as well as deposits that were moderately resistant to the acid treatment. At least part of the latter could be associated with the broad $g \approx 2$ ESR signal typical of clustered Fe$^{3+}$ ions, which in most samples persisted even after prolonged acid leaching. The data demonstrate that procedures commonly used to clean kaolinite of free iron are by no means 100% efficient. In particular, frequently encountered quantitative association of the Fe remaining in the deferrated solids with purely structural Fe, homogeneously distributed in the kaolinite matrix, is probably significantly overestimated and should be treated with great caution.

Extensive research into the nature of iron impurities in kaolinites (e.g. Jefferson et al., 1975; Meads & Malden, 1975; Herbillon et al., 1976; Angel & Vincent, 1978; Mestdagh et al., 1980; Fysh et al., 1983; Brindley et al., 1986; Stone et al., 1988) has led to the conclusion that Fe may be present in kaolinite as a part of its structure or as separate Fe-rich phases. Usually both types of contamination, referred to herein as “structural” and “non-structural”, or “free” iron, coexist. In the former case, Fe may either substitute for Al in the octahedral sheet or Si in the tetrahedral Si-O skeleton. In the latter it belongs to separate, Fe-rich phases such as Fe-bearing micas or iron oxides/oxhydroxides.

As the presence of free iron phases is detrimental to the application of kaolinites in ceramic and paper industries, considerable research has been focused on designing procedures leading to their selective removal. The methods most frequently used are: magnetic separation (e.g. Iancielli, 1976); chemical bleaching with mineral acids (Fysh & Clark, 1983) or dithionite (Mehra & Jackson, 1960), and the photolytic method of De Endredy (1963).

It has been generally accepted that Fe remaining in the sample after deferrating treatment is present in the structure, and its quantity is usually assessed by chemical analysis of the deferrated solid. However, there are some indications that the selective dissolution techniques may be not quite as efficient as commonly believed. Angel & Vincent (1978) found that some forms of microcrystalline hematite- or goethite-like phases associated with the surface of kaolins could resist the De Endredy procedure. Komusinski et al. (1981), on
the basis of their electron spin resonance (ESR) and Mössbauer study also noted that treatment with sodium dithionite seemed to be only partly effective in removal of non-structural iron. A Mössbauer study by Fysh et al. (1983) pointed to the presence of free iron remnants at the surface of kaolinites subjected to treatment with dithionite and/or oxalic acid, although the latter was found to be more efficient in free iron removal.

The aim of the present work was to investigate in more detail the efficiency of non-structural iron removal from kaolinites. Treatment with mineral acid, regarded as the most efficient, albeit the most aggressive procedure, affecting the kaolinite structure (Stoch, 1974; Badyoczek et al., 1982), has been chosen as the means for selective removal of free iron. Following the earlier approach of Brindley & Youell (1951), Osthaus (1956), Gastuche & Fripiat (1962), Horvath (1976), Herbillon et al. (1976), and Brindley et al. (1986), the comparative kinetic analysis of Al and Fe release served to differentiate between the various forms of Fe impurities. A quantitative estimate of the Fe impurity distribution was achieved by comparing the results of the chemical, spectrographic (AES) and ESR analyses obtained after each stage of dissolution, the first two methods providing information about the total Fe content released and/or retained by the sample, and the last distinguishing between the truly substitutional and heterogeneous components of the Fe remaining in the solid residues.

EXPERIMENTAL

Materials

The eight clay minerals examined in the present study differed in degree of crystallinity and in the amount of the XRD-detectable impurities. Details of their mineralogical characteristics are given in Table 1. Samples 2–7 contained kaolinites differing in their degree of structural order; samples 4 and 7 contained, beside kaolinite, significant amounts of Fe-rich phases; samples 1 and 8 represented monomineral phases of a very high and a very low degree of crystal order, respectively, and as such could be regarded as crystallinity standards in the dissolution experiments.

The chemical composition of the raw materials is presented in Table 2. The samples were digested by HF and the solutions analysed with a Philips PU9100 Atomic Absorption Data Station.

X-ray diffraction

The purity of the samples and the degree of structural order were determined with XRD, using a DRON-1.5 diffractometer and Ni-filtered Cu-Kα radiation. The Hinckley index $k_H$ (1963) and/or Stoch factor $f_S$ (1974) were taken as a measure of structural order. In the presence of quartz impurity, the Hinckley index is of limited use, while the Stoch factor, corresponding to the intensity ratio of the 020 and 110 XRD peaks, is affected to a lesser extent. Both indices arrange the samples in the same order (Table 1). External standards were used to determine the mineralogical composition of the samples. Georgia kaolinite CMS-K Ga-2, well crystallized ($k_H = 0.81$, $f_S = 0.88$) served as a standard for the quantitative estimation of the kaolinite content in the Maria and Kalno samples; other samples had this content measured using the Georgia CMS-K Ga-2 poorly crystallized standard ($k_H = 0.39$, $f_S = 1.20$). Brazilian quartz and hematite from Rudki (Poland) were
Iron in kaolinite-group minerals

Table 1. XRD characteristics and origin of the investigated kaolinite-group minerals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Origin</th>
<th>XRD-detectable impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dickite</td>
<td>kaolinite polymorph of high degree of crystalline order</td>
<td>folerite, Nowa Ruda, Lower Silesia, Poland</td>
<td>–</td>
</tr>
<tr>
<td>2. Kaolinite Maria</td>
<td>&lt;2 μm fraction, high degree of crystalline order $k_H = 1.31, f_S = 0.63$</td>
<td>kaolinite-containing sandstones, Maria III mine, Oldřichów, Lower Silesia, Poland</td>
<td>4% quartz, &lt;5% dioctahedral micas</td>
</tr>
<tr>
<td>3. Kaolinite Kalno</td>
<td>&lt;2 μm fraction, medium degree of crystalline order $k_H = 0.63, f_S = 0.90$</td>
<td>residual kaolin, Antoni deposit, Kalno, Lower Silesia, Poland</td>
<td>&lt;5% dioctahedral micas</td>
</tr>
<tr>
<td>4. Kaolinite Tur I</td>
<td>medium degree of crystalline order $k_H = 0.35, f_S = 1.23$</td>
<td>mica-rich rocks enclosing brown coal deposits, Turoszów, Lower Silesia, Poland</td>
<td>30% iron cont. trioctahedral mica, 20% quartz</td>
</tr>
<tr>
<td>5. Kaolinite Tur II</td>
<td>&lt;2 μm fraction, low degree of crystalline order $k_H = 0.24, f_S = 1.42$</td>
<td>mica-poor rocks enclosing brown coal deposits, Turoszów, Lower Silesia, Poland</td>
<td>&lt;5% dioctahedral micas, 14% quartz</td>
</tr>
<tr>
<td>6. Kaolinite Jar</td>
<td>&lt;2 μm fraction, low degree of crystalline order $k_H = 0.22, f_S = 1.55$</td>
<td>kaolinite clay, Jaroszów, Lower Silesia, Poland</td>
<td>10% dioctahedral micas</td>
</tr>
<tr>
<td>7. Kaolinite Bar</td>
<td>&lt;2 μm fraction, low degree of crystalline order $k_H = 0.18, f_S = 1.62$</td>
<td>sedimentary deposits, Baranów, Lower Silesia, Poland</td>
<td>12% hematite, 10% quartz</td>
</tr>
<tr>
<td>8. Halloysite</td>
<td>halloysite clay, strongly disordered</td>
<td>karst funnels in limestones, Lubno, Upper Silesia, Poland</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of the clay samples (wt%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{Al}_2\text{O}_3$</th>
<th>$\text{Fe}_2\text{O}_3$</th>
<th>$\text{TiO}_2$</th>
<th>$\text{MgO}$</th>
<th>$\text{K}_2\text{O}$</th>
<th>$\text{CaO}$</th>
<th>$\text{MnO}$</th>
<th>$\text{Cr}_2\text{O}_3$</th>
<th>$\text{V}_2\text{O}_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dickite</td>
<td>37.01</td>
<td>0.12</td>
<td>0.01</td>
<td>0.11</td>
<td>0.08</td>
<td>0.001</td>
<td>0.002</td>
<td>0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>Maria</td>
<td>34.05</td>
<td>0.62</td>
<td>0.49</td>
<td>0.16</td>
<td>0.48</td>
<td>0.002</td>
<td>0.007</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>Kalno</td>
<td>34.23</td>
<td>1.07</td>
<td>0.52</td>
<td>0.17</td>
<td>0.53</td>
<td>0.004</td>
<td>0.006</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Tur I</td>
<td>22.45</td>
<td>7.88</td>
<td>2.67</td>
<td>1.80</td>
<td>2.73</td>
<td>0.008</td>
<td>0.016</td>
<td>0.001</td>
<td>0.008</td>
</tr>
<tr>
<td>Tur II</td>
<td>30.01</td>
<td>1.24</td>
<td>0.49</td>
<td>0.21</td>
<td>0.49</td>
<td>0.006</td>
<td>0.011</td>
<td>0.005</td>
<td>0.007</td>
</tr>
<tr>
<td>Jar</td>
<td>33.48</td>
<td>1.29</td>
<td>0.60</td>
<td>0.28</td>
<td>0.80</td>
<td>0.003</td>
<td>0.007</td>
<td>0.008</td>
<td>0.007</td>
</tr>
<tr>
<td>Bar</td>
<td>28.20</td>
<td>11.45</td>
<td>0.80</td>
<td>0.38</td>
<td>0.98</td>
<td>0.003</td>
<td>0.014</td>
<td>0.010</td>
<td>0.009</td>
</tr>
<tr>
<td>Halloysite</td>
<td>32.21</td>
<td>0.33</td>
<td>0.04</td>
<td>0.17</td>
<td>0.05</td>
<td>0.003</td>
<td>0.012</td>
<td>0.002</td>
<td>0.001</td>
</tr>
</tbody>
</table>

used to determine the quantity of quartz and hematite impurities, respectively. The amount of XRD-detectable mica impurity was assumed to correspond to the difference in the total mineralogical balance.
Electron spin resonance

The ESR spectra were recorded at room temperature and at 77 K with an X-band SE/X (Technical University Wroclaw) spectrometer. DPPH and an NMR marker were used for the determination of g factors. Spin concentrations were calculated by double integration of the ESR signals and referred to a VOSO₄ standard.

Acid dissolution

All samples, prior to acid dissolution, were kept in a hygrostat at 55% humidity. Weighed portions of 2 g were put into conical flasks equipped with reflux condensers and mixed with 200 ml of hot, 15% H₂SO₄. The experiment was conducted under constant stirring, at 95°C, for various periods of time ranging from 0-5-14 h. After the desired time, the acid-clay suspension was diluted with cold distilled water, centrifuged immediately, and washed until the filtrate had a neutral pH. The acid extract and the residue were subsequently subjected to chemical and spectroscopic analyses.

Iron determination

Iron in the acid extracts was determined by complexometric titration at pH 2 with 0.01 N EDTA solution, in the presence of salicylic acid as an indicator. The Fe content in the residues was determined with atomic emission spectroscopy (AES), using a PGS-2 Karl Zeiss Jena spectrograph. Each standard and analytical sample (ca. 20 mg) was distributed over three electrode craters in order to obtain spectra from three independent excitations. The spectra of analytical samples and corresponding standards were always recorded together on the same photographic plate. Optical density measurements, performed with a microphotometer MD-100 Carl Zeiss Jena, were repeated three times for each spectral line and background, and converted to concentration values by means of a calibration equation (Rokosz & Strycharski, 1988). The calibration curve was provided by 10 samples of the Bar kaolinite treated with H₂SO₄ for various periods, for which the Fe content had been determined with atomic absorption spectroscopy and ranged from 0.5%-11.5% Fe₂O₃.

Aluminium determination

Following determination of Fe in the acid extract, the Al content was determined using the method of Flaschka & Abdine (1956). The method consists of complexometric titration with EDTA, at pH 3, of the boiling acid extract in the presence of copper complexonate and PAN as an indicator.

RESULTS AND DISCUSSION

Acid leaching

The overall results of acid treatment are presented in Fig. 1, in the form of diagrams showing the Fe% release (αFe₂O₃) with respect to the corresponding value for Al (αAl₂O₃). The principal finding is that, except for the dickite, Bar and halloysite samples (Fig. 1a,g,h) for which the ratio αFe₂O₃/αAl₂O₃ remains constant irrespective of the time of treatment, the relative efficiencies of Fe vs. Al extraction for all other minerals
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Fig. 1. Fraction of iron ($\alpha_{Fe_2O_3}$) vs. fraction of aluminium ($\alpha_{Al_2O_3}$) released in the dissolution experiments: (a) dickite, (b) Maria, (c) Kalno, (d) Tur I, (e) Tur II, (f) Jar, (g) Bar, (h) halloysite.

(Fig. 1b,c,d,e,f) change with time, exhibiting upward shifts at the beginning of the graphs. It points to the presence of easily soluble Fe contamination of non-structural character in these samples.

Further information is provided by the analysis of kinetics diagrams of Fe and Al dissolution. In accordance with earlier findings of Osthaus (1956) and Gastuche et al. (1960), an attempt was made to fit the data to pseudo first-order equations. The results for Al (open circles) and Fe (full circles) are presented jointly in Fig. 2. It may be seen that in all but one sample, the kinetics of Al dissolution follow the assumed model well and the reaction rate constant remains unchanged over the entire period of the acid treatment. The only exception is kaolinite Tur I (Fig. 2d), containing 30% trioctahedral mica. The latter is more soluble in acid than kaolinite, thus causing a swifter release of Al in the initial stage of dissolution. It is only after 3 h of treatment, when the mica contamination, as evidenced by XRD, disappears, that the kinetics of Al dissolution settle down to that which is characteristic of the kaolinite component. On the other hand, the attempts to describe the kinetics of Fe dissolution with a single pseudo first-order equation failed in most cases.

It seems sensible to assume that the rather straightforward picture of Al release is due to the uniqueness of its source, i.e. in all cases most Al originates from the octahedral sheet of the kaolinite structure, while the complexity of Fe dissolution kinetics reflects contributions from more than one form of iron.

Of the minerals investigated, samples Bar and Tur I contained XRD-detectable, non-structural Fe, present as hematite and mica, respectively. In both cases, as shown in Fig. 1 (d and g), the acid treatment proved very efficient in their selective removal. Dissolution of these impurities contributed most of the Fe released and obscured the behaviour of other possible forms of iron. For the Tur I sample the slope of the graph illustrating Fe release changes after removal of ~80% of the total Fe content (Fig. 1d). This happens after ~3 h of acid treatment, and corresponds to the virtual disappearance of XRD patterns of the mica.
impurity. Obviously, at this stage, Fe released from other sources, possibly from the kaolinite structure, becomes significant enough to control the overall kinetics.

Similar changes in the slopes of graphs presented in Fig. 2, pointing to a quicker release of Fe at the beginning of the acid treatment, occur also for other kaolinites (Figs. 2b,c,e,f), for which no definite Fe-rich contamination could be identified. It seems reasonable to assume that in these cases also, the deviations are due to the presence of easily soluble non-structural Fe, in amounts too small to allow detection by XRD. It is noteworthy that, in an additional experiment, Maria and Kalno kaolinites cleaned with sodium dithionite released Fe at rates close to those observed in the later period of dissolution of natural samples. This indicates that the dithionite deferration procedure chiefly removes this part of Fe contamination which is easily soluble in acid.

In the later stage of dissolution of Kalno, Tur II and Jar kaolinites and throughout the entire time for dissolution of the halloysite sample, the dissolution of Fe, as judged from the diagrams presented in Fig. 2c,e,h, proceeds more slowly than that of aluminium. A similar behaviour was observed by Herbillon et al. (1976) and was tentatively assigned either to the presence of Fe substitution in the tetrahedral sheet, or to the presence of Fe-containing impurities, more resistant to acid attack than the kaolinite structure.

On the other hand, samples such as Maria and dickite release Fe more quickly than Al over the whole dissolution time, although for the former, there is a change in the slope pointing to a slowing down of the process in the later stage. The reason for such behaviour might be preferential extraction of Fe from the octahedral sheet, but the possible contribution from non-structural contamination is also a plausible explanation. Both samples represent minerals most resistant to acid attack and with the lowest total Fe content; thus even small amounts of Fe-rich, soluble, foreign phases could affect the results.

![Fig. 2. Kinetics of aluminium (lg(A12O3)-o) and iron (lg(Fe2O3)-●) dissolution ((A12O3)—difference between the initial concentration of A12O3 in the sample and the amount of A12O3 dissolved in time t, in wt% (Fe2O3)—difference between the initial concentration of Fe2O3 in the sample and the amount Fe2O3 dissolved in time t, in wt%): (a) dickite, (b) Maria, (c) Kalno, (d) Tur I, (e) Tur II, (f) Jar, (g) Bar, (h) halloysite.](image-url)
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For the Tur I sample, similar slopes for Al and Fe in the later stage of dissolution indicate that, after removal of mica contamination, both elements are released at similar rates, which might point to the structural origin of Fe, but the presence of non-structural impurities, dissolving at the same rate as the octahedral sheet, cannot be excluded.

The above discussion shows that while the acid leaching experiments represent a sensitive probe able to differentiate between various forms of Fe impurities, to decide unequivocally about their origin and location on the basis of the kinetic data alone is by no means straightforward.

Electron spin resonance study

ESR spectroscopy is one of the few techniques capable of detecting and identifying purely structural Fe, i.e. substitutional Fe$^{3+}$ ions within the kaolinite structure. Numerous studies (Angel & Hall, 1972; Angel et al., 1974; Jones et al., 1974; Meads & Malden, 1975; Herbillon et al., 1976; Mestdagh et al., 1980; Hall, 1980; Cuttler, 1980; Brindley et al., 1986; Chaikum & Carr, 1987; Coyne et al., 1989) have shown that in a typical ESR pattern of a kaolinite sample, essentially three groups of resonances may appear: (a) signals near $g \approx 4$, usually split into three components and associated with a peak at $g \approx 9$, all originating from an overlap of resonances due to magnetically dilute Fe$^{3+}$ ions built into the kaolinite structure by substitution; (b) sharp signals at $g \approx 2$ assigned to lattice defects within the kaolinite structure, and (c) very broad, structureless signals at $g \approx 2$ usually interpreted as being due to clusters of Fe$^{3+}$ ions present either as non-structural Fe-rich phases of the oxide-oxyhydroxide type attached to the kaolinite surface or small heterogeneous inclusions within its framework. It is known that kaolinites may contain other paramagnetic transition metal impurities (Cu, Mn, Cr, V) which, in some of their oxidation states, are capable of producing ESR signals centred around $g \approx 2$. When clustered, they might be expected to generate a similar broad absorption. However, in the present study, such a possibility may be ruled out since these elements appear only in trace amounts (Table 1); thus, any possible contribution to the broad resonance from a magnetic phase containing any of these ions, if present, would be negligible. From the above classification it follows that it is the possible variation of the resonances belonging to the first group that would be indicative of the behaviour of the truly structural Fe upon acid treatment. Unfortunately, as far as the non-structural Fe is concerned, the broad resonance at $g \approx 2$ is far less informative. The magnetic properties and the ESR signal of clustered Fe species depend strongly on the nature of mutual interactions within clusters, sometimes making them virtually ESR silent, as in goethite or hematite, sometimes enhancing their ESR intensity, as in magnetite, or maghemite (Tsay et al., 1971). Also, it has to be borne in mind that the naturally occurring oxide/hydroxide contaminations may be partly aluminous, thus showing magnetic properties different from the pure forms (Goodman et al., 1988). In view of this, it must be remembered that the $g \approx 2$ signal, although pointing to the presence of clustered Fe$^{3+}$, does not unequivocally reflect the nature of the contamination or its concentration.

Figure 3 shows the spectra of all samples before treatment with the sulphuric acid and after maximum exposure time (solid and dashed lines, respectively). The spectra exhibit all the characteristic features discussed earlier. Additionally, in the natural dickite and halloysite samples, extra sets of absorptions appear around $g \approx 2$. In the former case they are attributable to traces of V$^{4+}$ (eight-line hyperfine structure due to the $^{51}$V nucleus), in the latter to Mn$^{2+}$ (six-line hyperfine structure due to the $^{55}$Mn nucleus).
From the spectra, it may be seen that all samples, even those regarded as monomineralic from the point of view of XRD (dickite, halloysite), contain non-structural forms of Fe, producing the more or less pronounced broad signal at $g \approx 2$. Recording at 77 K reveals that in most samples the intensity of the $g \approx 2$ signal decreases while its width increases, indicating that at least part of the clustered Fe species is ferrimagnetically or ferromagnetically ordered (Tsay et al., 1971).

The intensity and the shape of the $g = 4$ signal vary. In agreement with earlier findings (Mestdagh et al., 1980; Brindley et al., 1986) there is a correlation between the line-shape of the $g = 4$ signal and the crystalline order of the samples. Generally, samples of better crystallinity show better resolution of signal components and a less pronounced central part of the ESR absorption. Quantitative estimation of this signal in the natural samples shows that it accounts only for a part of the total Fe content (Table 2). Its contribution in the untreated samples varies from ~30% in dickite to ~2% in the Bar sample but is generally much less than the total Fe content determined chemically. Thus, the ESR results indicate that in the minerals examined, only a minor part of the total Fe is truly structural, while most of the Fe contamination is of a heterogeneous, non-structural nature. This conclusion agrees well with the outcome of the dissolution experiments where the kinetics of Fe dissolution point to its mainly non-structural origin.
Treatment with sulphuric acid produces changes in the ESR spectra which can be described in the following way:

(a) The $g \approx 4$ signal intensity either increases, as for the Bar sample (Fig. 3g), decreases as for the Jar kaolinite (Fig. 3f) disappears completely, as for halloysite (Fig. 3h), or does not change substantially. This obviously depends on the relative solubility of the structural Fe-bearing component vs. other phases present in the solid. As the acid attack progresses, the solid residue becomes depleted of the easily soluble components and enriched in the more resistant ones. In the samples containing significant amounts of heavy Fe impurities readily dissolved in acid, such as the Tur I and Bar samples (Fig. 3d,g), the $g \approx 4$ signal becomes relatively more pronounced upon the acid treatment. In the samples containing easily soluble clay minerals, such as the Jar sample and halloysite (Fig. 3f,h), the acid treatment causes a decrease in the intensity of the $g \approx 4$ signal or even its disappearance, because the relative weight contribution of the clay phase becomes less and less important. The quantitative estimation of the $g \approx 4$ signal intensity in the residues remaining after acid extraction shows that, although in most cases the relative contribution of the structural Fe increases, it still does not account for the total Fe content (Table 3). The most spectacular effect is observed for the most soluble halloysite sample. The AES analysis of the residue shows that the solid still contains ~30% of the initial Fe content, while the $g \approx 4$ signal corresponding to the structural Fe all but disappears, as expected in view of the almost total destruction of the octahedral sheet (Fig. 1h). Since the presence of large quantities of ferrous ions within the mineral structure is not probable, the remaining Fe must belong to a non-structural Fe-rich phase, responsible for the weak broad absorption around $g \approx 2$.

(b) Broad signals at $g \approx 2$ also show variable behaviour. In the Maria, Kalno and Tur I samples, there is a large loss in the signal intensity (Fig. 3b,c,d). Most of this change occurs within the first hours of acid treatment and corresponds to the total removal of the more soluble Fe contamination, e.g. in the Tur I sample it parallels the disappearance of the Fe-bearing mica. Nevertheless, even in the acid-treated samples, the intensity of this signal is still appreciable, indicating that Fe clusters have not been removed completely. For the Tur II, and Jar samples, the signal decrease is much smaller and no specific change can be seen at the beginning of the dissolution process, indicating that in these samples the readily soluble

Table 3. Comparison of the total iron content in the investigated kaolinite-group minerals determined with atomic emission spectroscopy (AES) with the amount of ESR-detectable structural iron.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Fe$_2$O$_3$ (wt%)</th>
<th>Structural Fe$_2$O$_3$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AES</td>
<td>$g \approx 4$ ESR intensity</td>
</tr>
<tr>
<td></td>
<td>Before acid treatment</td>
<td>14 h acid treatment</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Before acid treatment</td>
</tr>
<tr>
<td>1. Dickite</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>2. Maria</td>
<td>0.62</td>
<td>0.34</td>
</tr>
<tr>
<td>3. Kalno</td>
<td>1.07</td>
<td>0.75</td>
</tr>
<tr>
<td>4. Tur I</td>
<td>7.88</td>
<td>0.74</td>
</tr>
<tr>
<td>5. Tur II</td>
<td>1.24</td>
<td>0.91</td>
</tr>
<tr>
<td>6. Jar</td>
<td>1.29</td>
<td>0.99</td>
</tr>
<tr>
<td>7. Bar</td>
<td>11.45</td>
<td>0.53</td>
</tr>
<tr>
<td>8. Halloysite</td>
<td>0.33</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Fe phase is ESR-silent. In the case of the Bar sample, a slight increase of the $g \approx 2$ signal can be observed, showing that the signal cannot be associated with the soluble hematite contamination present in this mineral. This result confirms that Fe$^{3+}$ in well crystallized hematite, representing the major soluble impurity in this kaolinite, is ESR-silent. Therefore, the signal observed must be due to some other Fe-containing phase, fairly unyielding to the acid attack and accumulating in the acid treated residue.

It is noteworthy that in all kaolinite samples, at least part of the broad signal persists after the maximum time of acid treatment. It seems reasonable to assume that the responsible Fe species would also resist any other deferration treatment. Indeed, the attempt to remove the free iron in the Maria and Kalno samples with dithionite resulted in ESR spectra resembling those after acid treatment. In particular, the broad $g \approx 2$ signal did not disappear, and the total Fe content exceeded that corresponding to the $g \approx 4$ signal. This observation is in agreement with previous findings (Angel & Vincent, 1978; Komusinski et al., 1980; Fysh et al., 1983; Stone et al. 1988) which pointed out that the standard deferration procedures may fail in the total removal of free iron.

In view of the earlier remarks on the variable ESR activity of different iron oxides/hydroxides, depending on the nature of magnetic interactions within their structures, it can only be concluded that the $g \approx 2$ signal observed in the natural samples is due to clustered Fe$^{3+}$ ions present in phases of different solubility and of different magnetic properties. To speculate on the mineralogical nature of the free iron deposits, resistant to acid dissolution, is a difficult task, especially since topotactic interaction with the kaolinite surface may change both the solubility and the magnetic properties of the solids. For instance, according to the observations of Angel & Vincent (1978), some forms of microcrystalline hematite or goethite, possibly aluminous (Goodman et al., 1988), can resist the De Endredy (1963) deferration procedure. A recent NMR study by Stone et al. (1988) suggesting that in kaolinites containing more than 0.5% Fe$_2$O$_3$, the homogeneous distribution of structural Fe is disturbed, presents another possible explanation. Locally concentrated Fe$^{3+}$ ions could be at least partly responsible for the $g \approx 2$ signal resistant to acid treatment. Such an “island” of Fe$^{3+}$, accumulated locally within the octahedral sheet would constitute a transient form between the magnetically dilute structural Fe and non-structural foreign Fe-rich contamination.

It can be concluded, therefore, that the broad $g \approx 2$ signal persisting after deferration is due to clusters of Fe$^{3+}$ present either as non-structural, hardly soluble phases or as local structural inclusions. A brief review of previous ESR studies shows that no deferring procedure could fully remove this absorption (Herbillon et al., 1976; Mestdagh et al., 1980, 1982), but, somewhat surprisingly, this signal has never been taken into account in quantitative estimates and the chemically determined total Fe content was exclusively associated with the $g \approx 4$ signal.

Results presented in this study show that the quantitative discrepancies between the structural Fe responsible for the $g \approx 4$ signal and the chemically determined total Fe content in samples subjected to deferrating treatment stem from the neglect of clustered Fe species resistant to selective removal.

To check whether the phases containing clustered ferric ions are located at the kaolinite surface or occluded within the bulk of the minerals, fractions differing significantly in external surface area have been obtained by extracting particles <0.2 µm from the <2 µm powders, and the respective ESR spectra compared. Figure 4 shows the results for the Kalno (a,b) and Jar (c,d) kaolinites, the first sample containing a $g \approx 2$ signal easily
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Fig. 4. ESR spectra of (a) Kalno kaolinite, particle size between 0.2 μm and 2 μm, (b) Kalno kaolinite, particle size <0.2 μm, (c) Jar kaolinite, particle size between 0.2 μm and 2 μm, (d) Jar kaolinite, particle size <0.2 μm. Recorded at room temperature.

removable by the acid treatment, the other a resistant one. In both cases there is a marked increase of the \( g \approx 2 \) signal in the higher surface area fractions, pointing to a mainly surface origin of the responsible species. The signal intensification, however, is accompanied by a change in the signal line-shape, indicating that contaminations revealed in the <0.2 μm fraction differ slightly in character from those dominating in the more crystalline material.

CONCLUSIONS

(1) Both types of Fe structural and non-structural, are present in the minerals examined. A substantial part of the Fe contamination is of a heterogeneous nature with respect to the kaolinite structure. This holds also for samples in which no XRD detectable Fe-rich phase could be identified.

(2) The amount of the ESR detectable structural Fe corresponding to the \( g \approx 4 \) signal is always lower than the total Fe content. The \( g \approx 2 \) signal associated with clustered Fe\(^{3+}\) persists, even after prolonged acid treatment. Both observations point to the presence of acid-resistant Fe-rich phases. Although it is difficult to speculate on the exact nature of these phases, it is suggested that they constitute either poorly soluble, partly aluminous, oxides/oxyhydroxides, e.g. of the goethite type, or, possibly, part of the structural Fe\(^{3+}\) concentrated into clusters within the kaolinite matrix.

(3) Results presented indicate that to clean the natural kaolinite of all but structural Fe is virtually impossible, even with aid of acid bleaching. In particular, treatment with sodium dithionite is capable of affecting only that part of the non-structural Fe contamination that is easily soluble in acid. In view of this, all quantitative assessments of structural iron based on the standard techniques of free iron removal have to be treated with great caution. In
particular, there is no justification for the assumption that all of the Fe remaining in the sample after a deferration procedure is associated with the $g \approx 4$ ESR signal.

REFERENCES


