ELECTRON SPIN RESONANCE STUDIES OF IRON OXIDES ASSOCIATED WITH THE SURFACE OF KAOLINS

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(Received 29 August 1977)

Abstract—The different types of iron oxide phases associated with the surfaces of two suites of kaolins from Georgia, U.S.A., and from the Southwest Peninsula of England, have been identified using electron spin resonance (ESR) spectroscopy combined with magnetic-filtration, thermal, and chemical treatments. It has been shown that the English kaolins are coated with a lepidocrocitelike phase, which is readily removed by de Endredy's method of deferrification, while the Georgia kaolins are coated with a hematite- or goethitelike phase, which is not removed by this treatment. Throughout the course of this study, the effects of the various physical and chemical treatments on the brightness values of the kaolins were examined.

Key Words—Goethite, Hematite, Iron, Kaolin, Lepidocrocite.

INTRODUCTION

Previous ESR studies of natural and selectively doped synthetic kaolinites in this laboratory (Angel et al., 1974; Jones et al., 1974) have been confined mainly to paramagnetic ions substituted in the structure. In particular, iron has been shown to be substituted in kaolinite in a number of different configurations.

Other workers (Weaver, 1968; Sayin and Jackson, 1975; Herbillon et al., 1976) have shown that iron is substituted in the structure of ancillary minerals such as anatase, rutile, quartz, and micas which are often found in association with kaolinite.

Iron impurities in kaolin deposits also can exist in the form of oxides and hydroxides either as discrete particles or as coatings which are bound to the surfaces of both the kaolinite and any ancillary minerals which may be present (Sumner, 1963; Anderson and Jenne, 1970). Iron impurities of this type are often termed "free iron oxides."

Considerable research effort has been made to study the effective removal of the free iron oxides from kaolin as they are detrimental to the application of kaolin in the paper coating industry. The various methods of removal have been reviewed by a number of authors (Mehra and Jackson, 1960; de Endredy, 1963).

The possible nature of the chemical bonding of iron oxides and hydroxides to kaolinite surfaces has formed the basis of a number of publications (Sumner, 1963; Greenland and Oades, 1968; Greenland, 1975). In general, electron microscopy, X-ray powder diffraction and chemical analysis have been applied to study samples of kaolinite on which hydroxides of iron have been precipitated.

On a more general basis, research into the fundamental properties of bulk samples of iron compounds has been aimed at identifying and characterizing the various precipitation products from iron (II) and iron (III) salts in solution (Towe and Bradley, 1967;

Schwertmann et al., 1968; Schwertmann and Taylor, 1972; Landa and Gast, 1973; Chukrov et al., 1973; Taylor and Schwertmann, 1974; Fischer and Schwertmann, 1975; Schwertmann and Thalmann, 1976). These studies have supplemented work which has been concerned with the nature of iron impurities in the soil (Gallez et al., 1975; Russell et al., 1975; Parfitt et al., 1976).

Previous ESR studies of iron oxides in synthetic zeolites (McNicol and Pott, 1972) and lunar samples (Tsay et al., 1973a; Weeks, 1973; Griscom et al., 1973) demonstrated the potential application of a similar approach to kaolinite.

DESCRIPTION OF SAMPLES

Sixteen kaolin samples were studied of which 10 (Avant, Chambers, Champion, Gray, Wrens, Mines 11, 15, 24, 50, and 51) came from various locations in Georgia, U.S.A., and were kindly supplied by the Georgia Kaolin Company. The remaining six kaolins originated in the Southwest Peninsula of England and were kindly supplied by English Clays, Lovering and Pochin and Company Limited. They were described as Blackpool, Cholwich Town, Dubbers, English, Lee Moor, and Supreme. Chemical analysis and particle size distributions were known for all of the samples.

PRELIMINARY ESR SURVEY

All of the samples exhibited resonances A and C (depicted in Figure 1) which are centered at $g = 2.0$ and $g = 4.0$, respectively. These resonances are known to be due to substituted defects and have been considered in detail elsewhere (Angel et al., 1975; Jones et al., 1974). At $g = 2.0$ an additional resonance approximately 0.1 tesla in width was present which is labeled F_1. In previous studies F_1 has been found to be relatively weak and has not been studied in detail.

For a number of the kaolins used in this work various size fractions were immediately available and, there-
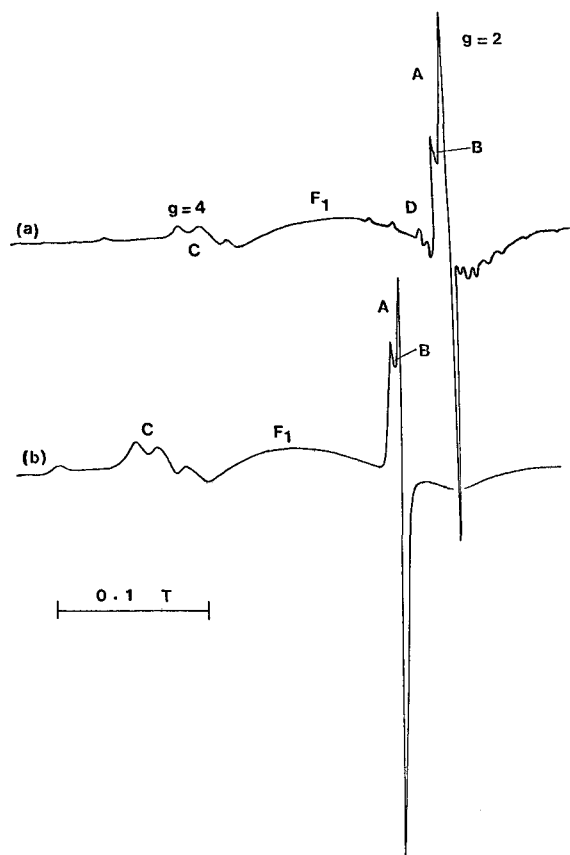
Fig. 1. ESR spectra (recorded at room temperature) of: a) a typical kaolin from Georgia, U.S.A.; b) a typical kaolin from the Southwest Peninsula of England.
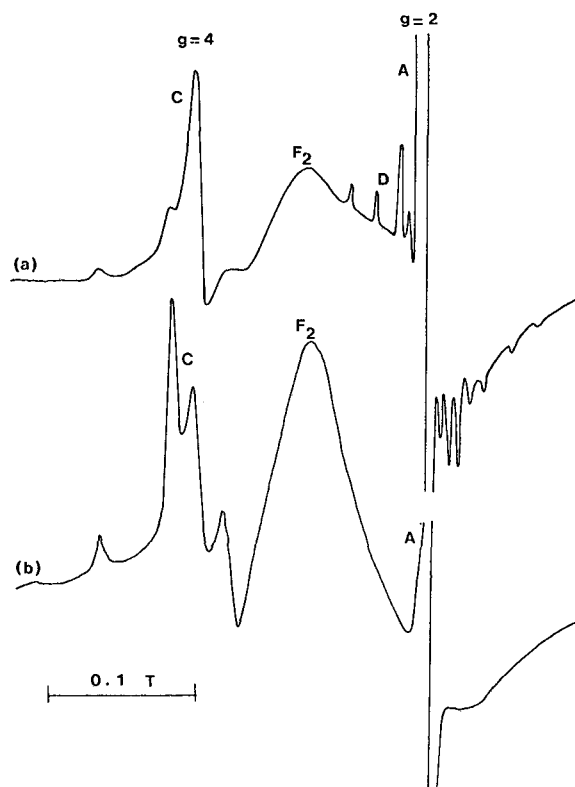

Fig. 2. ESR spectra (recorded at room temperature) of: a) Mine 24 kaolin heated at 400°C for 1 hr; b) Blackpool kaolin heated at 400°C for 1 hr.

fore, the possibility of any correlation between the intensity of resonance F_1 and particle size was investigated. The results showed that there were marked variations in the intensity of the signal F_1 both for different samples and different size fractions within a sample, but these variations could not be correlated with particle size.

The effect of heating only four samples at various temperatures between 200 and 1200°C for different periods from 1 to 24 hr produced interesting and contrasting results which provided the basis for a subsequent study of the effect of heat treatment on all similar kaolins.

In samples Mine 15 and Avant no change in resonance F_1 was observed when they were heated in air for periods of at least 1 hr at temperatures up to 700°C. Above this temperature the resonance began to decrease but did not collapse completely. In contrast, for samples Mine 24 and Blackpool, the effect of heating at 200°C for 1 hr in air was to produce an additional fairly intense broad resonance (F_2 in Figure 2) on the low field side of the resonance F_1. Using preheating times of 1 hr resonance F_2 was found to increase with

increasing temperatures up to a maximum of 400°C (Figure 2a, b). When the period of heating was increased to 24 hr at 700°C, the resonance gradually collapsed. In the Blackpool sample resonance F_1 remained after preheating at 1200°C, but in sample Mine 24 it decreased considerably above 900°C.

No changes in the XRD patterns were observed for these four samples when heated at 400°C for 1 hr. Prolonged heating above 500°C caused a decrease in intensity and above 650°C metakaolin was formed. At 1200°C mullite was detected.

Taking into account the chemical and mineralogical analysis, the crystallinity and the particle size distribution for the four samples examined, there was no obvious explanation for the contrasting ESR results following the heat treatment. A temperature of 400°C coupled with a period of heating of 1 hr was found to be the lowest temperature and corresponding time at which maximum development of resonance F_2 in the Blackpool and Mine 24 kaolins occurred. The remaining kaolins were, therefore, subjected to this type of heat treatment.

DETAILED ESR STUDIES

It was found that all of the English kaolins from the Southwest Peninsula when heated at 400°C for 1 hr pro-

duced resonance F_2, but, in contrast, only two of the kaolins from Georgia, namely Mine 24 and Champion, produced the effect and even then on a much weaker scale. Also, it was found that for each of the English kaolins the intensity of the resonance F_2 (in contrast to resonance F_1) increased with increasing particle size; but, for the two exceptional Georgia kaolins, there was no obvious relationship between F_2 and particle size. The XRD patterns of the English kaolins showed that resonance F_2 was not related to the crystallinity of the samples and most probably not related to the mica impurities. It was suspected, therefore, that the resonance F_2 was directly associated with the surface of the kaolins.

An observed decrease in the intensity of the resonance F_2 and an accompanying increase in line width with decreasing temperatures (Figure 3) are behavior patterns characteristic of ferromagnetic or ferrimagnetic materials (Tsay et al., 1973a).

MAGNETIC FILTRATION

As it was suspected that resonance F_2 in the English kaolins was probably associated with the kaolin surfaces and not the mica impurities, magnetic extraction was used to refine all the samples. The results obtained from the XRD and ESR analyses of the filtrates and the magnetic residues clearly indicated that in the English samples mica was not responsible for the resonance. However, for the two exceptional Georgia kaolins which originally produced the F_2 resonance, it was found that after magnetic separation only the magnetic residue, which contained mainly anatase, produces the resonance. It was clear, therefore, that resonance F_2 was associated with a surface iron contaminant which was common to the English kaolins and the anatase fraction in two of the Georgia kaolins.

In addition to differences between English and Georgia kaolins with respect to resonance F_2 it was found that after heating the samples at 400°C for 1 hr, the isotropic line of the ESR signal at $g = 4.0$ had increased in intensity in all the Georgia samples, but there was no similar change produced in the English kaolins. These contrasting changes associated with the substituted iron will be considered later.

THE EFFECT ON RESONANCES F_1 AND F_2 USING DE ENDREDY'S METHOD TO REMOVE FREE IRON OXIDES

It was anticipated that if either resonance F_1 or F_2 were associated with surface iron contaminants it probably would be affected by any chemical treatment of the kaolins which either modified or removed the iron species. Herbillon et al. (1976), in their ESR study of kaolinites from tropical soils, found that the method of de Endredy (1963) for removing iron oxides was more effective than that of Mehra and Jackson (1960). Ac-
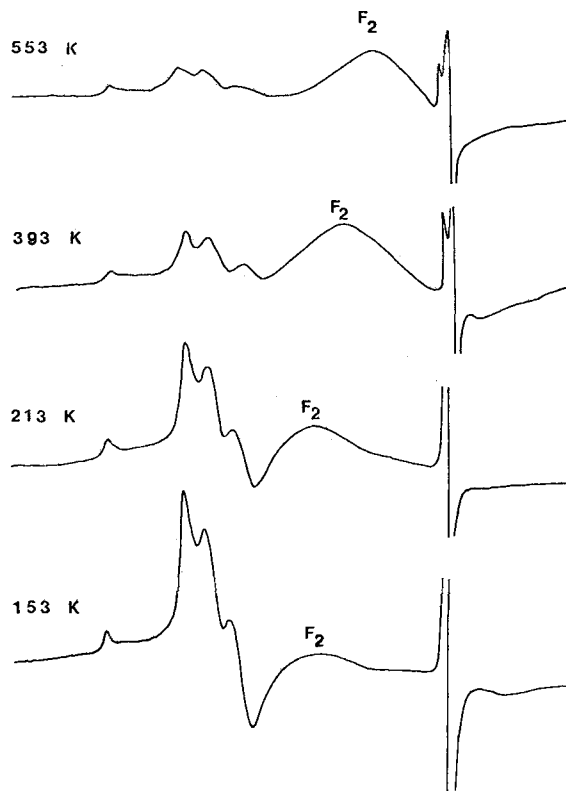

Fig. 3. ESR spectra of Blackpool kaolin heated at 400°C for 1 hr recorded at various temperatures.

cordingly, de Endredy's method was adopted in this work.

Suspensions of 2 g of sample in 100 ml of Tamm's solution (0.1 mol dm^{-3} with respect to oxalic acid and 0.175 mol dm^{-3} with respect to ammonium oxalate) were stirred magnetically and exposed to ultraviolet (UV) radiation from a medium pressure mercury lamp. Exposure times were limited to 2 hr to prevent the precipitation of iron (II) oxalate (Herbillon et al., 1976). The suspensions were then centrifuged and the supernatant tested for iron using the ammonium thioglycollate test (Vogel, 1969). The residues were washed with deionized water and the procedure was repeated until no iron was detectable in the supernatant. At this stage, the residues were washed free of oxalate and dried at 110°C. It was found that, in general, the Georgia kaolins required considerably more extraction cycles compared with the English samples to produce a negative test for iron contaminant in the supernatant. This result gave the first indication that the iron contaminant in the Georgia samples was relatively insoluble in Tamm's solution.

For samples which had been treated by this method no measurable changes were identified in their XRD patterns. For the Georgia kaolins the treatment had no
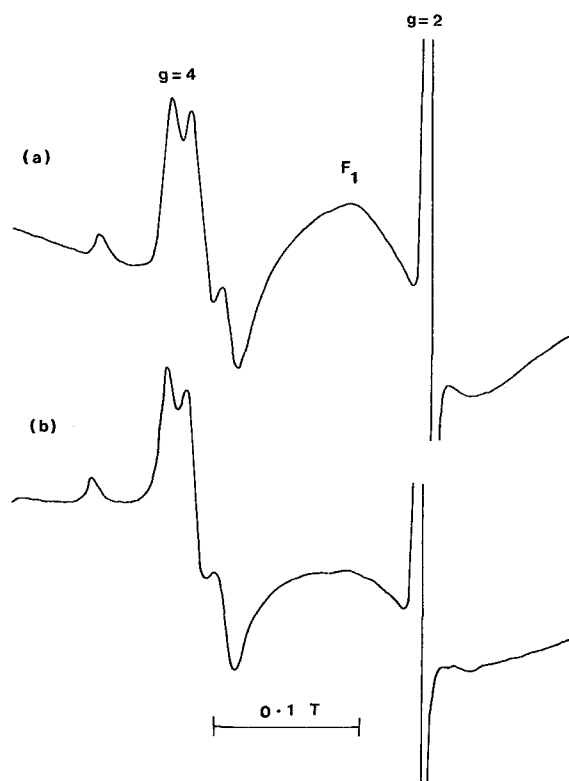
Fig. 4. ESR spectra (recorded at room temperature) of: a) untreated English kaolin; b) English kaolin deferrified using de Endredy's method.
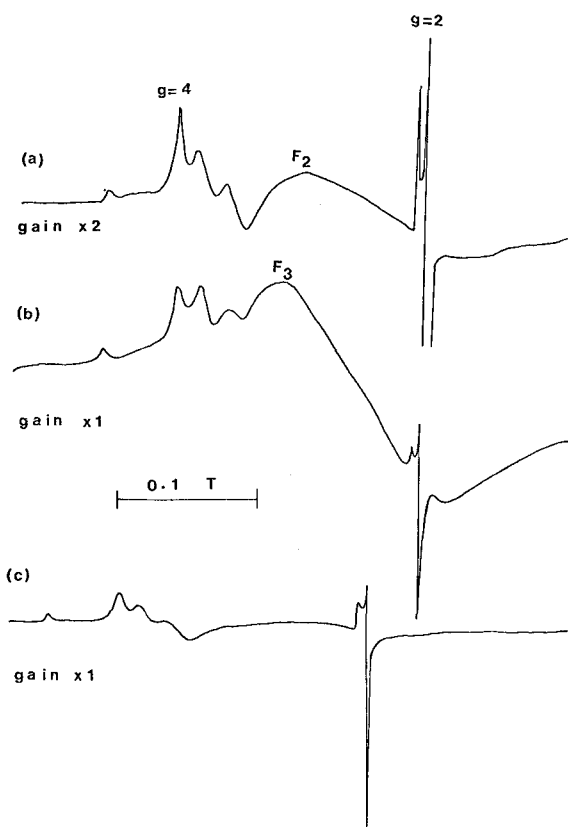

Fig. 5. ESR spectra (recorded at room temperature) of Blackpool kaolin: a) heated at 400°C for 1 hr in hydrogen; b) heated at 450°C for 1 hr in hydrogen; c) heated at 450°C for 1 hr in hydrogen followed by treatment with hydrochloric acid.

effect on resonance F_1. For the English samples the intensity of the resonance was reduced, but not completely removed (Figure 4).

Resonance F_2 was not reproduced in any of the samples which had been chemically treated and heated in air at 400°C for 1 hr. In addition, it was found that F_2 induced in the English samples by heating could be removed by de Endredy's treatment. To summarize, therefore, both the English and Georgia kaolins probably had surface iron contaminants associated with them which did not produce significant ESR signals. The effect of heating the English kaolins at 400°C for 1 hr in air was a change in the iron oxide contaminant which then produced an intense broad resonance at g = 2.0. However, the same effects were not produced in the Georgia kaolins. The iron oxides on English kaolins seemed to be different in nature from those on Georgia kaolins and were more soluble in UV-irradiated Tamm's solution.

THE EFFECT OF THERMAL TREATMENT IN ATMOSPHERES OF OXYGEN, NITROGEN AND HYDROGEN

In their study of the source of ferromagnetism in zircon, Lewis and Seftle (1966) heated zircon specimens in reducing and in oxidizing atmospheres at 500°C and followed the reactions by magnetization measurements. They interpreted the results in terms of an iron oxide coating which consisted mainly of hematite together with some maghemite and/or magnetite.

In this work, the effect of similar treatments on the Georgia and English kaolins was examined with the intention of possibly identifying the surface oxides. Samples were heated in oxygen, nitrogen, and hydrogen for 1 hr at temperatures ranging from 200 to 600°C. All the samples when heated for 1 hr in oxygen or nitrogen at 500°C produced results similar to those obtained for samples heated in air. Treatment in hydrogen produced further interesting results. For the English kaolins, resonance F_2 developed at temperatures below 400°C (Figure 5a), but, at this temperature, a more intense resonance (which will be referred to as F_3) was observed centered at about g = 2.4. The intensity of resonance F_3 reached a maximum value following heating in hydrogen at 500°C (see Figure 5b) and then remained constant up to temperatures of 600°C. Georgia kaolins also exhibited a similar intense resonance on heating in hydrogen (see Figure 6a), though the signal did not develop below 500°C for some of the samples (Figure 6b).

It was found that resonance F_3 was readily removed from both English and Georgia kaolins by warming the samples in hydrochloric acid for 2 min, centrifuging and washing until chloride free (Figure 5c, and Figure 6c). Kaolins from which free iron oxides have been removed by the method of de Endredy (1963) also were heated in hydrogen at 500°C for 1 hr. It was found that resonance F_3 did not develop in English kaolins, but was produced by the Georgia samples, even after magnetic refining. The very marked difference in the behavior of English and Georgia kaolins following hydrogen treatment at 500°C combined with chemical treatment by de Endredy's method provided more evidence that there were probably different types of iron oxide impurities associated with the two groups of kaolins.

It was noted that for all of the Georgia kaolins, which had been heated for 1 hr at 500°C in hydrogen, resonance A had decreased in intensity, while resonance D and the isotropic line of resonance C had increased in intensity. No reduction of resonance A was noted in English kaolins which had been treated similarly, although further heating at 500°C in hydrogen resulted in a decrease in resonance A with resonance C remaining unaltered. These effects (except for the change in resonance C in Georgia kaolins) were not observed in the samples when they were heated at similar temperatures in air.

STUDIES OF PRECIPITATED IRON HYDROXIDES ON KAOLINITE SURFACES

With a view to identifying the different iron phases present on English and Georgia kaolins, various kaolinites—iron hydroxide complexes—were synthesized. Samples of English kaolin from Blackpool pit, St. Austell, were treated by the method of de Endredy (1963) to remove free iron oxides. The samples were then coated with different iron hydroxides using three methods described by Greenland and Oades (1968). These methods involved: a) precipitation of goethite at pH 8; b) precipitation of lepidocrocite at pH 3; and c) precipitation of amorphous hydroxides at pH 3, 5, and
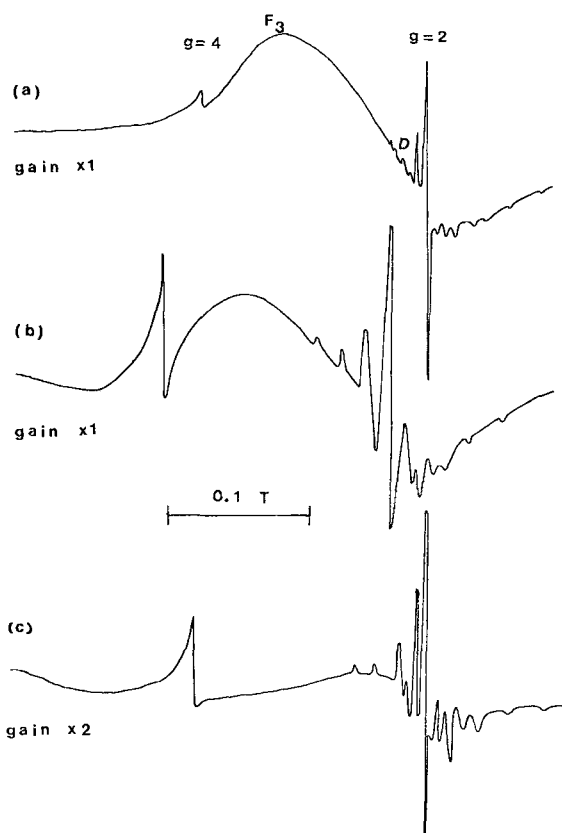

Fig. 6. ESR spectra (recorded at room temperature) of: a) Mine 11 kaolin heated at 450°C in hydrogen for 1 hr; b) Mine 15 kaolin heated at 500°C in hydrogen for 1 hr; c) Mine 11 kaolin heated at 500°C in hydrogen for 1 hr., then treated with hydrochloric acid.

7. The kaolinite-hydroxide complexes were studied using identical methods to those described previously. The results are summarized in Table 1.

Unfortunately, the initial iron hydroxide coatings were not identifiable by XRD. However, it was clear from the ESR results that kaolinites coated with hydroxides precipitated at low pH produced resonances similar to those observed previously from natural English kaolins. In contrast, kaolins coated with hydroxides precipitated at higher pH produced results similar to those obtained from natural Georgia kaolins.

STUDIES OF NATURALLY OCCURRING IRON OXIDES AND HYDROXIDES

The magnetic properties of naturally occurring iron oxides and hydroxides are summarized in Table 2 where it can be seen that species detectable by ESR at room temperature are amorphous oxides, maghemite, lepidocrocite, magnetite, and possibly hematite.

Since resonance F_2 was observed to be either ferromagnetic or ferrimagnetic in nature and its line width increased with decreasing temperature, it may be assigned to only maghemite or hematite. Resonance F_2

Table 1. Relative intensity of broad resonances at g = 2.0 observed for iron hydroxides precipitated on Blackpool kaolin.

Coating Treatment	Goethite	Lepidocrocite	Amorphous Hydroxides		
			pH 3	pH 5	pH 7
Untreated	Weak[+]	Medium	Medium[+]	Weak[+]	Weak[+]
400° C 1 hour	Weak[+]	Very Intense[+]	Intense[+]	Medium[+]	Weak
500° C 1 hour in hydrogen	Very Intense[o]	Very Intense[o]	Very Intense[o]	-	-

Key: [+] kaolinite only detected by XRD

[o] in addition to kaolinite, hematite and magnetite detected by XRD

Table 2. Magnetic properties of naturally occurring iron oxides and hydroxides.

Name	Formula	Magnetic Properties
Amorphous Oxides	–	Paramagnetic (Towe and Bradley, 1967).
Hematite	$\alpha-Fe_2O_3$	Weakly ferromagnetic above $-10°$ C (Tebble and Craik, 1969). Controversy in literature as to observance by ESR at X-band at room temperature (Weeks et al., 1973; Tsay et al., 1973).
Goethite	$\alpha-FeOOH$	Antiferromagnetic with Neel temperature of $120°$ C (Tsay et al., 1973).
Akaganite	$\beta-FeOOH$	Antiferromagnetic with Neel temperature of $20°$ C.
Maghemite	$\gamma-Fe_2O_3$	Ferrimagnetic (Tebble and Craik, 1969).
Lepidocrocite	$\gamma-FeOOH$	Antiferromagnetic with Neel temperature of $-200°$ C.
Magnetite	Fe_3O_4	Ferrimagnetic (Tebble and Craik, 1969). ESR line width decreases with decreasing temperature to $-143°$ C.

is produced when English kaolins are heated at 400°C in air and maghemite is known to be transformed into hematite at this temperature. It seems reasonable, therefore, to attribute F_2 to hematite. However, there is a divergence of opinion in the literature (Tsay et al., 1973b; Weeks et al., 1973) as to whether hematite would be detectable at room temperature by ESR.

To clarify the situation a study was made of some available iron oxides and hydroxides. Samples of naturally occurring magnetite and hematite were obtained from the Department of Geology, Plymouth Polytechnic, and synthetic goethite and lepidocrocite were kindly donated by Professor U. Schwertmann of Technische Hochschule, Munich. The results are summarized in Table 3.

It was found that hematite exhibited a broad resonance, but not with sufficient intensity to account for resonance F_2 in kaolins. However, lepidocrocite produced an intense broad resonance on heating both in air and in hydrogen, a behavior pattern which is similar to that observed in the English kaolins.

In contrast, the ESR spectra of both goethite and hematite were unaffected by heating in air at 400°C, but an intense broad resonance developed on heating in hydrogen—a behavior pattern which resembles that of Georgia kaolins. Therefore, it may be reasonable to infer that English kaolins are associated with a lepidocrocitelike phase, while Georgia kaolins are associated with a goethite- hematitelike phase. The results are considered in more detail in the discussion.

SUMMARY AND DISCUSSION

The various heat treatments applied to the kaolins used in this work produced significant changes in the ESR features associated with substituted defects, as well as interesting results with regard to surface iron oxides. Previous work (Angel et al., 1975) has shown that the resonance at $g = 4.0$ in natural kaolins is composite and can be unequivocably assigned to two Fe^{3+} species in different sites and resonance A may be attributed to a defect which can be produced by X-irradiation and stabilized by Mg^{2+} or Fe^{2+}. Resonance D, which is common only to the Georgia kaolins, is attributable to V^{4+} and is the subject of a separate publication (Vincent and Angel, 1978). In all kaolins containing the A-center resonance, it is found that by expanding the spectrum it is possible to identify additional paramagnetic species which have become known as B-centers and produce weak resonance peaks between the two main lines of the A-center resonance.

Heating the Georgia kaolins in hydrogen at 500°C produced a significant increase in the intensity of resonance D, but oxygen had no effect. Since neither V^{5+} nor V^{3+} is detectable at room temperature and only heating in hydrogen caused an increase in the concentration of V^{4+}, it is logical to conclude that the Georgia kaolins probably contain mainly V^{4+} ions, a smaller number of V^{5+} ions and no detectable V^{3+} ions. The possible situation of the vanadium ions either on the surface or within the structure of kaolinite forms the basis of a separate paper (Vincent and Angel, 1978).

It is known (Angel and Hall, 1972) that resonance A in natural kaolinites normally collapses if samples are heated in air at 550°C when dehydroxylation occurs. For samples heated in hydrogen, resonance A collapsed at temperatures of 500°C, but it was not possible to detect any dehydroxylation effects by X-ray powder diffraction. Furthermore, it was found in this work that resonance A could only be reformed in samples which had been treated in hydrogen provided that prior to X-irradiation and annealing they were evacuated to remove any occluded hydrogen. It is known (Angel et al., 1975; Jones et al., 1974) that at least X-ray energies are required to produce defect A and ultraviolet radiation is ineffective. On the basis, therefore, of recoil energies involved in an elastic collision, it is reasonable to suspect that the defect is formed by removal of a proton or a hydrogen atom. The results from the hydrogen treated samples support this hypothesis on the basis that occluded hydrogen prevents the defect reforming.

In his previous work on the A-center, Jones (1974) suggested models for the defect which involved either the formation of $(O_2)^-$ created by the initial removal of hydrogen atoms through X-irradiation or alternatively the production of trapped holes. Although it may be argued that removal of protons or hydrogen atoms might conceivably lead to the formation of trapped holes, the results obtained here indicated the importance of hydrogen in the formation and annealing of resonance A and, therefore, support an explanation in terms of formation of $(O_2)^-$.

In the Georgia kaolins, it was also noted that the effect of heating in hydrogen at 500°C not only removed resonance A, but also caused the isotropic line at $g =$

Table 3.   Relative intensities of broad resonances near g = 2.0 observed for iron oxides and hydroxides.

Treatment/ Sample	Goethite	Lepidocrocite	Hematite	Magnetite
Untreated	Weak	Medium	Medium	Intense
400° C 1 hour	Weak[h]	Very Intense[a,b,h]	Medium[h]	Intense[h,a]
500° C 1 hour	Very Intense[h,a,f]	Very Intense[h,a,f]	Intense[h,a,f]	Intense[h,a,f]

Key: a – magnetite;   b – maghemite;   f – iron;   h – hematite

4.0 to increase in intensity. It is tempting, therefore, to assume that changes in the resonance at g = 4.0 are related to annealing of the defect responsible for resonance A. Indeed, if resonance A were attributable to a defect stabilized by Fe^{2+} substituting for Al^{3+} and the defects were annealed, one might expect Fe^{2+} to be converted to Fe^{3+}, which would account for the observed change in the g = 4.0 resonance. However, for English kaolins heated in hydrogen, no corresponding change in the g = 4.0 resonance was observed when resonance A collapsed. Considering the chemical analysis of the samples, it might be argued that, in the English kaolins, Mg^{2+}, as opposed to Fe^{2+}, acts as the precenter and, therefore, does not create more Fe^{3+} and a change in the g = 4.0 signal. However, in contrast to English kaolins in which no changes were observed, an increase in the isotropic line at g = 4.0 was noted for the Georgia kaolins heated in air at 500°C, but with no corresponding decrease in resonance A. These results suggest that changes in the Fe^{3+} distribution are independent of any Fe^{2+}, which stabilizes the A-centers.

It is known (Angel and Hall, 1972) that dehydroxylation of some kaolins at 500°C causes an increase in the isotropic resonance at g = 4.0 accompanied by a decrease in resonance A. However, as XRD spectra of Georgia kaolins heated at 500°C in air were found to be identical to those of untreated samples and as resonance A had not been reduced in intensity, it was assumed that dehydroxylation had not occurred. To date, no satisfactory explanation has been found for the change in the resonance at g = 4.0 observed on heating Georgia kaolins below their dehydroxylation temperatures.

The preliminary ESR studies of English and Georgia kaolins established that all samples exhibited a broad resonance, F_1, to varying extents. On heating at 400°C for 1 hr in air, oxygen or nitrogen, English kaolins produced a more intense broad resonance, F_2. Resonance F_2 was also found in two of the Georgia samples, but separate studies using magnetic filtration and XRD

analysis showed that resonance F_2 in these samples was associated with anatase impurities and not the kaolinite fraction. Magnetically refining samples also demonstrated that resonance F_2 in English kaolins was common to both the kaolinite fraction and the mica impurities. Both Georgia and English kaolins, however, produced an intense broad resonance, F_3, when they were heated in hydrogen at 500°C.

Since deferrification by de Endredy's method had a negligible effect on resonance F_1 in Georgia kaolins, and reduced but did not remove it completely in the English samples, it was concluded that resonance F_1 could not be attributed wholly to surface iron oxides associated with the kaolins. However, it was found that English kaolins, which had been deferrified, produced neither resonance F_2 on heating at 400°C in air nor resonance F_3 following hydrogen treatment at 500°C. Therefore, it was deduced that resonance F_2 and F_3 in English kaolins were due to iron oxides, which could be removed by deferrification. In contrast, it was found that Georgia kaolins, which had been deferrified, continued to produce resonance F_3. This being so, it was clear that iron oxides associated with Georgia kaolins were not effectively removed by the deferrification process used, and were probably different from those in the English kaolins.

By using kaolins selectively coated with hydroxides at different pH values, it was possible to produce similar behavior patterns to those found in the naturally occurring kaolins, although it was not possible to identify positively the true nature of the oxide coating. However, the conclusions which might have been drawn from these experiments were substantiated by the results obtained from the samples of raw oxides. Combining the two sets of results, it seems reasonable to conclude that the iron oxide associated with the English kaolins is very similar, if not identical, to lepidocrocite. On a similar basis, goethite or hematite is associated with the Georgia kaolins.

It is generally accepted that deferrification by the

method of de Endredy (1963) consists of dissolution in Tamm's solution involving a chemical reaction which is photosensitive to UV and de Endredy (1963) has claimed that his method removed both the crystalline and the amorphous oxides of iron. However, it has been found more recently that only amorphous and poorly crystalline iron oxides are soluble in Tamm's solution in the dark (Schwertmann et al., 1968).

Samples of lepidocrocite, goethite and hematite treated by de Endredy's method in this laboratory showed that lepidocrocite dissolved in about 2 hr, while the others persisted even after 24 hr. These results provide further evidence in support of the suggestion that the English kaolins are coated with a lepidocrocitelike phase, which is removed on deferrification, whereas the Georgia kaolins are coated with a goethite- or hematitelike phase, which is less readily extracted.

The main difficulty which arises from the above conclusions, bearing in mind the known transformations of the oxides and hydroxides of iron, is that upon heating at 400°C in air, both lepidocrocite and goethite are known to be transformed to hematite.

It is not clear, therefore, why lepidocrocite at 400°C should produce resonance F_2 while goethite and hematite do not. However, XRD studies of lepidocrocite heated at 400°C for 1 hr in air showed the presence of magnetite or maghemite in addition to hematite, and both of these oxides (being ferrimagnetic) could account for resonance F_2. Owing to the broadness and relatively low intensity of the peaks, it was not possible to distinguish between magnetite and maghemite by XRD. However, it was deduced that the oxide was more probably maghemite for the following reasons: a) the line width of resonance F_2 was found to increase with decreasing temperature, whereas it is known that the line width of the magnetite resonance decreases with decreasing temperature; b) magnetite would not be expected to be formed from the other oxides at temperatures below 400°C in air (Cotton and Wilkinson, 1967). On the other hand, it is not clear why maghemite should remain stable at 400°C when it might be expected to have been converted to hematite.

With regard to resonance F_1 which, in English kaolins is partially reduced in intensity on deferrification, the removed component can be attributed to the lepidocrocitelike phase, which would be extracted by de Endredy's treatment and which is known to be paramagnetic at temperatures above 200°C. It must be emphasized that a paramagnetic resonance is approximately three orders of magnitude less intense than a ferrimagnetic resonance for the same number of spins (Tsay et al., 1973a). The difference accounts for the much greater intensity of resonance F_2, which has been attributed to a ferrimagnetic phase. In Georgia kaolins, resonance F_1 was not affected by de Endredy's treatment, so this resonance and part of resonance F_1 in English kaolins is probably due to the interaction between adjacent Fe^{3+} ions, which are known to be substituted in the kaolinite structure (Angel et al., 1975; Jones et al., 1974).

Resonance F_3 is formed by all of the kaolinites on heating in hydrogen at 500°C. Kaolinites coated with amorphous iron hydroxides and naturally occurring iron oxides and hydroxides thus treated show the presence of hematite, magnetite, and iron. Resonance F_3 is, therefore, attributed to magnetite and/or iron.

Isolated lepidocrocite is normally metastable and readily transforms to its stable polymorph, goethite. However, lepidocrocite is known to occur as a stable compound in soils (particularly in humid, temperate regions) (Schwertmann and Taylor, 1972). The relative stability of lepidocrocite in soils has been studied in detail and has been shown to be dependent on the amount of organic matter (Schwertmann et al., 1968) and the concentration of silicon cations (Schwertmann and Taylor, 1972) which might be present. The chemical analyses of the samples indicate that the English Kaolins contain more silica than the Georgia kaolins. Also, organic matter is generally more abundant in English kaolins. It seems reasonable, therefore, to suggest that English kaolins in a temperate climate are associated with an iron oxide which is similar to lepidocrocite. Hematite rarely occurs in soils of temperate regions, but mixtures of hematite and goethite are common in warmer regions (Fischer and Schwertmann, 1975). It is reasonable, therefore, to assume that the Georgia kaolins are associated with hematite- or goethitelike phases.

During the course of the ESR studies of the English and Georgia kaolins, the effects of the various physical and chemical treatments on the brightness values of the samples were examined. It was found that deferrification improved the brightness of all the English kaolins, but produced no measurable effect in the Georgia samples. This behavior pattern is expected as iron oxide impurities are known to form one of the major nonwhite components of kaolins. Deferrification using de Endredy's treatment was shown by the ESR studies to be effective only for the English kaolins. Organic material is also thought to have a deleterious effect on the brightness of clays. However, in this work, removal of organic impurities by hydrogen peroxide treatment had a negligible effect on the brightness values of the kaolins studied. It was noted that the brightness of all the kaolins decreased appreciably following thermal treatment at 400°C for 1 hr. Moreover, the heated samples were found to have significantly lower brightness values when the heating had been preceded by chemical treatment. This result was most unexpected and was not readily explained. The only change in the ESR spectrum, which was exhibited by all the samples on heating at 400°C, was the collapse of the resonance attributed to B-centers. It is known that B-centers can be reformed on X-irradiation, but in this work no accom-

panying increase in brightness was observed. It can only be assumed that the effect of heating on the brightness of kaolinite is related in some way to the surface of kaolinite. To date, the surface chemistry of kaolinite is not fully understood. In this respect, it is hoped that the results presented in this paper may be of assistance.

Further information regarding the iron oxide phases associated with English and Georgia kaolinites might be found by comparing magnetic susceptibility measurements for samples following chemical and thermal treatments. Also, an investigation of the effect of other methods of iron oxide removal, in particular the dithionite–citrate–bicarbonate method of Mehra and Jackson (1960) on the Georgia kaolins might prove useful.

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Резюме- Различные типы фаз окиси железа,приуроченные к поверхностям двух свит каолина,развитых в Джорджии,С.Ш.А.,и на Юго-западном полуострове Англии,были определены с помощью спектроскопического метода резонанса электронного спина/РЭС/в сочетании с магнитно-фильтрационной,тепловой и химической обработками. Было показано,что каолины из Англии покрыты фазой подобной лепидокрокиту,который легко удаляется методом дефферизации де Ендреди,в то время как каолины из Джорджии покрыты фазами подобными гематиту или гетиту, которые не снимаются этой обработкой. В течение этих исследований были изучены эффекты разных физических и химических обработок на интенсивность осветления каолинов.

Kurzreferat- Die verschiedenen Arten von Eisenoxydphasen, verbunden mit
der Oberfläche zweier verwandter Kaolins, von Georgia, USA und von der Süd-
West Halbinsel Englands, wurden durch "electron spin resonance" (ESR),kom-
biniert mit magnetischer Filtration, thermischer und chemischer Behandlung,
identifiziert. Es wurde gezeigt, daß die englischen Kaoline mit einer Lepi-
dokrokit-artigen Phase bedeckt sind, die leicht mittels der de Endredy Me-
thode des Eisenentfernens beseitigt werden kann, wohingegen die Georgia
Kaoline mit einer Hematit-oder Goethit-artigen Phase überzogen sind, welche
nicht durch diese Behandlung entfernt werden kann. Im Verlauf dieser Unter-
suchung, wurden die Effekte verschiedener physikalischer und chemischer Be-
handlungen auf die Glanz-Werte der Kaoline untersucht.

Résumé-Les différentes espèces de phases d'oxide de fer associées avec les
surfaces de 2 suites de kaolins de Géorgie,U.S.A. et de la Péninsule Sud-
Ouest de l'Angleterre ont été identifiées utilisant la spectroscopie de spin
(E S R) combinée avec des traitements thermiques,chimiques,et de filtration
magnétique.Il a été démontré que les kaolins anglais sont recouverts d'une
phase ressemblant à la lépidocrocite qui est facilement retirée par la mé-
thode de déferrification de de Endredy,tandis que les kaolins de Géorgie
sont recouverts d'une phase ressemblant à l'hématite ou à la goethite qui
ne peut pas être retirée par ce traitement.Au cours de cette étude,les ef-
fets des traitements physiques et chimiques sur les valeurs de l'éclat des
kaolins ont été examinés.