

## SYNTHETIC KAOLINITES DOPED WITH $\text{Fe}^{2+}$ AND $\text{Fe}^{3+}$ IONS

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**Abstract**—Previous studies by Electron Spin Resonance (ESR) have established the substitution of  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$  in the kaolinite structure. It is shown that  $\text{Fe}^{2+}$  can substitute in kaolinite and stabilize defects which are detectable by ESR in a manner identical to  $\text{Mg}^{2+}$ . The development of methods of preparing a synthetic kaolinite doped with  $\text{Fe}^{2+}$  is described in detail. It is shown that the main ESR signals, which occur at  $g = 2.0$  in natural kaolinites and which previously have been interpreted in terms of iron and magnesium, can be attributed to iron alone.

### INTRODUCTION

The general ESR characteristics of naturally occurring kaolinites were first examined in this laboratory in 1968 (Hall, 1973) and a survey of a large number of samples established, without exception, the existence of fairly intense signals. The ESR spectra usually contained two main groups of resonance lines centred at about  $g = 2.0$  and  $g = 4.0$ , respectively (Figure 1). However, some samples exhibited only one of the main groups of resonances either at  $g = 2.0$  or at  $g = 4.0$ . On this basis, it seemed reasonable to suggest that the paramagnetic species responsible for the two groups of signals were not necessarily related or connected in any way and could exist as separate entities.

A series of experiments was carried out to establish that the ESR signals associated with kaolinite could be attributed to impurities substituted within the crystal structure and not to mineralogical impurities or surface contaminants (Angel and Hall, 1972). For the signal at  $g = 2.0$  it was clear that, with the exception of ball clays which contain relatively high concentrations of organic matter, there was no measurable

contribution from the organic fraction (Hall *et al.*, 1974). This being so, it seemed feasible to seek the source of the resonances from comparisons of the chemical analysis of natural samples with the known structure of kaolinite and the results indicated that iron was most probably responsible. Castner *et al.* (1960) have shown that glass doped with iron produces intense resonance signals at  $g = 4.0$  and it has been shown by Angel *et al.* (1974) using iron doped synthetic kaolinites that the  $g = 4.0$  resonance in kaolinite can be assigned to iron substituted in the structure. However, the signals at  $g = 2.0$  are less easily attributed to iron.

### THE $g = 2.0$ RESONANCE

The resonance at  $g = 2.0$  is stable at temperatures up to about  $400^\circ\text{C}$ . The collapse of the signal on dehydroxylation suggests that the paramagnetic species is more closely associated with the octahedral layer than the tetrahedral layer, which is virtually unchanged by dehydroxylation. Furthermore, Angel *et al.* (1974) found that intercalation of kaolinite with

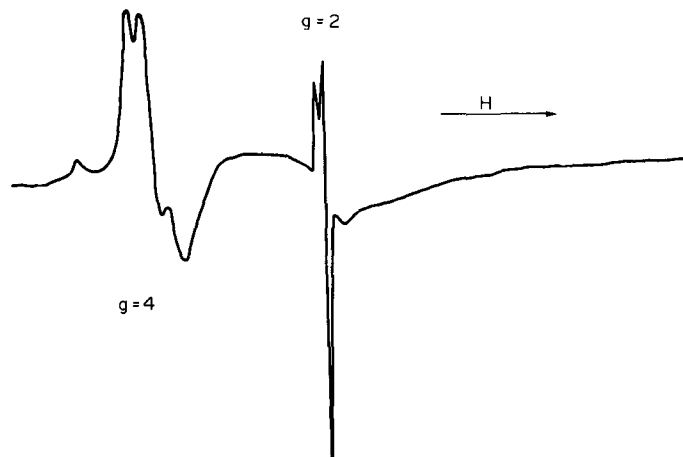


Figure 1. ESR spectrum of a typical natural kaolinite 0-0.6T.

dimethylsulphoxide leaves the  $g = 2.0$  signal unaffected, which indicates that the signal is not due to an interlayer defect.

The spin relaxation time of  $\text{Fe}^{2+}$  is extremely short (Orton, 1968) and liquid helium temperatures are required to detect it directly by ESR. Hence it would seem unlikely that  $\text{Fe}^{2+}$  could be responsible for a signal at  $g = 2.0$  at room temperature. It is also difficult to attribute this resonance to  $\text{Fe}^{3+}$  substitution. The five unpaired electrons associated with the free ferric ion, either through spin orbit coupling or interaction of surrounding ligands or both, can be shown to stabilize in a number of different ways, depending on the relative strengths of the interactions and the geometry of the crystal field. At room temperature, either groups of lines at  $g = 4.0$  are observed or at least five lines at  $g = 2.0$ . However, in kaolinite, only two lines are present at  $g = 2.0$ , which is indicative of a paramagnetic system with an effective spin  $S = \frac{1}{2}$  and in axial symmetry. It is difficult to see how much such a resonance could be produced directly by iron.

A considerable volume of literature is available describing the various defects which have been identified in minerals (Griffiths *et al.*, 1955; Joffe, 1967; Marfunin *et al.*, 1970). In particular, it has been suggested that the production of a stable paramagnetic center (such as that which might account for the  $g = 2.0$  signal in kaolinite) usually requires the presence of some sort of "pre-center" which, when irradiated, subsequently traps a hole or an electron. The pre-center often takes the form of a foreign ion substituting within the crystal structure and requiring charge compensation. For kaolinite, divalent magnesium or divalent iron substituting for trivalent aluminium might provide the necessary pre-center for the production of a stable defect.

To test this hypothesis, kaolinites doped with magnesium were synthesized. These samples did not exhibit ESR signals, but when irradiated by X-rays with a dose of the order of 1 Mrad a fairly intense broad resonance around  $g = 2.0$  with a positive  $g$ -shift was observed. By annealing the samples at 200°C for 2 hr the majority of the resonance disappeared to leave a signal at  $g = 2.0$  identical to that observed in natural kaolinites.

These results suggested that  $\text{Fe}^{2+}$  might be able to perform the same function as  $\text{Mg}^{2+}$  and it now seemed possible that both groups of resonances at  $g = 4.0$  and at  $g = 2.0$  might be caused by iron impurities. Clearly, evidence for  $\text{Fe}^{2+}$  producing the  $g = 2.0$  signal in kaolinite could be obtained from a synthetic sample which was known to contain a reasonable amount of substituted ferrous iron.

In order that  $\text{Fe}^{2+}$  could be detected directly in kaolinite samples, Mössbauer spectroscopy was used. The Mössbauer technique has the advantage that both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  can be detected and easily distinguished at room temperatures. The main disadvantage of this method is that only the  $^{57}\text{Fe}$  isotope, which is 2.24% abundant, is detectable. A typical clay,

which might contain up to 2% total impurity, will therefore contain a relatively small amount of  $^{57}\text{Fe}$  and consequently the statistics of results obtained from past studies on natural clays have placed restraint on their interpretation. Therefore, it was decided to attempt the synthesis of a kaolinite doped with  $^{57}\text{Fe}$ . Although from previous work it was thought that the iron would substitute predominantly as  $\text{Fe}^{3+}$ , it was anticipated that sufficient  $\text{Fe}^{2+}$  also would be present to provide a kaolinite suitable for detailed Mössbauer studies.

#### SYNTHESIS OF $^{57}\text{Fe}^{2+}$ -DOPED KAOLINITES; RESULTS AND DISCUSSION

In doping a kaolinite with  $^{57}\text{Fe}$ , a number of practical difficulties arise. In their experiments, Angel *et al.* (1975) adopted a method of doping with iron using commercially available ferric chloride from which ferric benzoate was prepared. This was dissolved in dimethylformamide and could be added to the mixture of aluminium isopropoxide and tetraethylsilicate prior to hydrolysis. Reaction of the gels so formed produced  $\text{Fe}^{3+}$  doped kaolinite with resonances at  $g = 4.0$ .

To repeat the process in an identical manner with  $^{57}\text{Fe}$  is more difficult. First, it should be noted that  $^{57}\text{Fe}$  is very expensive (approximately £10<sup>6</sup>/kilo) and so only small amounts could be used. Second,  $^{57}\text{Fe}$  is available only in the form of metallic filings or chips. Therefore, a method had to be devised to produce ferric benzoate from a few mg of metallic iron. Initially, a method was established using natural iron. The iron was dissolved in concentrated hydrochloric acid and then oxidized by the addition of a small quantity of nitric acid. The pH of the solution was raised to a value of 5 with sodium acetate before adding ammonium benzoate solution. The precipitation of ferric benzoate formed was filtered, washed with sodium acetate solution and distilled water, and dried at 50°C. Although the ESR spectra of  $\text{Fe}^{3+}$  in the kaolinites produced were fairly weak compared with those kaolinites produced from commercially available ferric chloride, the technique was sufficiently refined to initiate experiments with  $^{57}\text{Fe}$ . Accordingly, a sample of kaolinite was grown and doped with  $^{57}\text{Fe}$ . Most surprisingly, the Mössbauer spectrum (Figure 2) showed that the iron was substituted in the kaolinite structure as  $\text{Fe}^{2+}$  with very little indication of  $\text{Fe}^{3+}$ . Although a fairly weak  $g = 4.0$  resonance could be identified in the sample by ESR, it should be noted that the ESR technique is probably at least an order of magnitude more sensitive than Mössbauer spectroscopy.

It seemed, therefore, that during the course of the preparation of the  $^{57}\text{Fe}$ -doped kaolinite, the iron had been reduced to the ferrous state. In an attempt to ensure complete oxidation of the iron in the gel prior to hydrothermal reaction to form kaolinite, some of the  $^{57}\text{Fe}$ -doped gel was heated in oxygen to 1400°C.

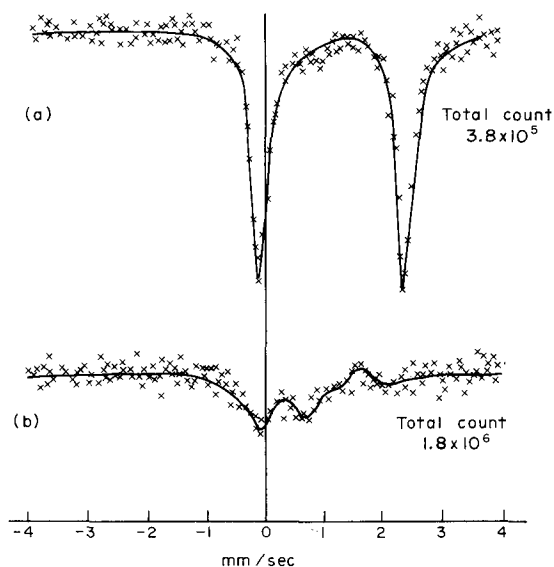


Figure 2. Mössbauer spectra of (a)  $^{57}\text{Fe}^{2+}$ -doped kaolinite (b) a typical natural kaolinite.

However, it was found that the kaolinite produced still contained an abundance of  $\text{Fe}^{2+}$  with very little  $\text{Fe}^{3+}$ .

An intriguing situation presented itself. The ESR signals at  $g = 4.0$  and  $g = 2.0$  in kaolinites had so far been attributed to  $\text{Fe}^{3+}$  and a defect stabilized by  $\text{Mg}^{2+}$ , respectively. Now a sample had been produced which, from the Mössbauer study, was known to contain iron, predominantly in the ferrous state. This kaolinite was therefore irradiated and annealed in a manner identical to that which had been used previously for samples doped with  $\text{Mg}^{2+}$ . It was found to exhibit a  $g = 2.0$  resonance identical to that observed in natural kaolinites. Hence, a synthetic kaolinite had been produced doped only with iron,

but exhibiting both the  $g = 2.0$  and the  $g = 4.0$  signals in natural samples. It must be emphasized, however, that, for the  $g = 2.0$  signal, substituted  $\text{Fe}^{2+}$  does not in itself produce the signal, but acts as a center for the paramagnetic defect which is produced on irradiation.

The availability of an  $^{57}\text{Fe}^{2+}$ -doped kaolinite has provided a facility whereby the Mössbauer spectrum of  $\text{Fe}^{2+}$  in natural clays has been interpreted in more detail. The results of this study are to be presented in a separate paper.

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