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Research Article

Formation of new low field signals in the EPR spectra of kaolin minerals

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Abstract

Kaolins are clay minerals that contain layers of SiO_4 tetrahedra bound to AlO_6 octahedra. They play important roles in environmental processes, and can be used in the preparation of novel products for use in various scientific industries. However, there is considerable variability in the physical and chemical properties of different samples, possibly caused by small amounts of impurity mineral phases, or isomorphous substitution of Fe^{3+} (and other cations) for Al in the structure. Fe^{3+} is paramagnetic and can be studied by electron paramagnetic resonance (EPR) spectroscopy. EPR spectra typically show a triplet and a singlet associated with structural Fe^{3+} with their relative intensities being related to structural order in the sample. Two additional singlet signals overlaying the conventional Fe^{3+} signal are now reported. One is formed by grinding, is stable to >300 °C, and is interpreted as arising from Fe^{3+} in a breakdown product from the aluminosilicate structure. The other is observed after irradiation and has low thermal stability; it is thought to correspond to a triplet state that results from the formation of two O^- centres in neighbouring sites in the aluminosilicate structure. Although we do not know the significance of these new centres, it is clear that interpretation of kaolin EPR spectra is more complex than is generally assumed.

Keywords: kaolin; EPR; Fe^{3+}; free radical

Introduction

The kaolins are aluminosilicate minerals with a 1:1 layer structure (Figure 1), in which layers are held together by hydrogen bonds between the octahedral and tetrahedral sheets of adjacent layers. The kaolins are actually 4 distinct minerals that are distinguished by the stacking order of these layers and whether or not there is water in the interlayer space. They exhibit isomorphous substitution of various di-, tri-, or tetravalent ions for Al at the octahedral sites, and possibly additional substitutions at the Si sites; overall, the kaolin minerals are amongst the most diverse in nature (Velde, 1995). Also, kaolin deposits often contain impurity minerals, notably quartz, illite, and various poorly crystalline oxides.

Although they are used extensively in the paper, ceramics, and paint industries, kaolin minerals have a wide range of additional uses that may be influenced considerably by the types and characteristics of their structural substitutions. They may also be used as starting materials for the preparation of other products (Goodman & Worasith, 2014), and along with 2:1 layer silicates, such as bentonites, may function as environmental barriers for the containment of

toxic and radioactive wastes. Understanding the factors responsible for the properties and stabilities of various kaolin deposits is, therefore, of considerable importance.

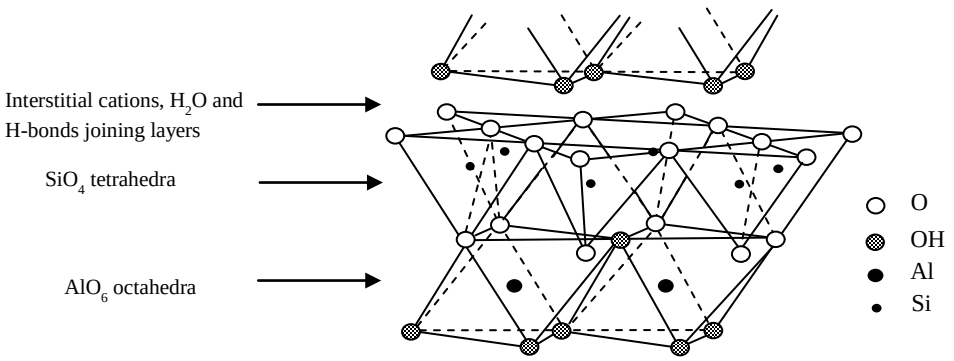

Figure 1. Diagrammatic representation of the structure of kaolin minerals

Apart from the various conventional methods that are used for evaluating mineral composition and properties, electron paramagnetic resonance (EPR) spectroscopy can be used to identify and understand the behavior of trace paramagnetic components that may have relatively high levels of reactivity, or function as markers of origin or environmental history of the minerals. Thus, ions such as Fe^{3+}, Mn^{2+}, Mn^{4+}, V^{4+}, and Cu^{2+} have been identified in kaolin samples, in addition to various free radical centres formed by exposure to ionizing radiation (Worasith & Goodman, 2012). However, interpretation of EPR results is not always straightforward, especially with natural samples. The present paper is based on a detailed investigation of the low field signals that are conventionally association with Fe^{3+}; an additional, previously undescribed signal is observed and its spectroscopic properties reported for ground, irradiated, and heated kaolin samples.

Materials and methods

The Ranong and Lampang kaolin samples were obtained from Had Som Pan, Part. and Lampang Kaolin Part., respectively, and sample preparation was as described in a previous report (Worasith et al., 2011). Irradiation was performed to a dose of 150 kGy using ^{60}Co in a Nordion *Gammacell 220 SN 189R*. EPR spectra were acquired as 1st or 2nd derivatives of the microwave absorption with a Bruker A300 spectrometer operating at X-band frequencies and equipped with a high sensitivity resonance cavity. Spectral analyses were performed using Bruker WinEPR software, and the intensity of the new feature was assessed as the distance between its maximum and minima in 2nd derivative recordings.

Results

The EPR spectra from natural and ground samples of Lampang and Ranong kaolins (Figure 2) show signals associated with Fe, Mn, and free radical centres. Resolution of the Fe^{3+} peaks in the low field regions has been related to the crystallinity of the samples (Mestdagh et al., 1980; Brindley et al., 1986), and on the basis of these results the structure of the Lampang sample is more disordered than that from Ranong. Also, with both minerals, the ground samples are more disordered than the natural samples. When the low field region was recorded

as 2nd derivatives of the microwave absorption, an additional sharp feature was observed (Figure 3) with greater intensity in the ground samples than in the natural samples. A similar signal was also observed in samples that had been exposed to γ-radiation (Figure 4), although with these samples the highest intensity was observed with the natural specimens. In fact, the ground Lampang sample showed little effect of radiation on the signal intensity [Figure 3(b) and 4(b)].

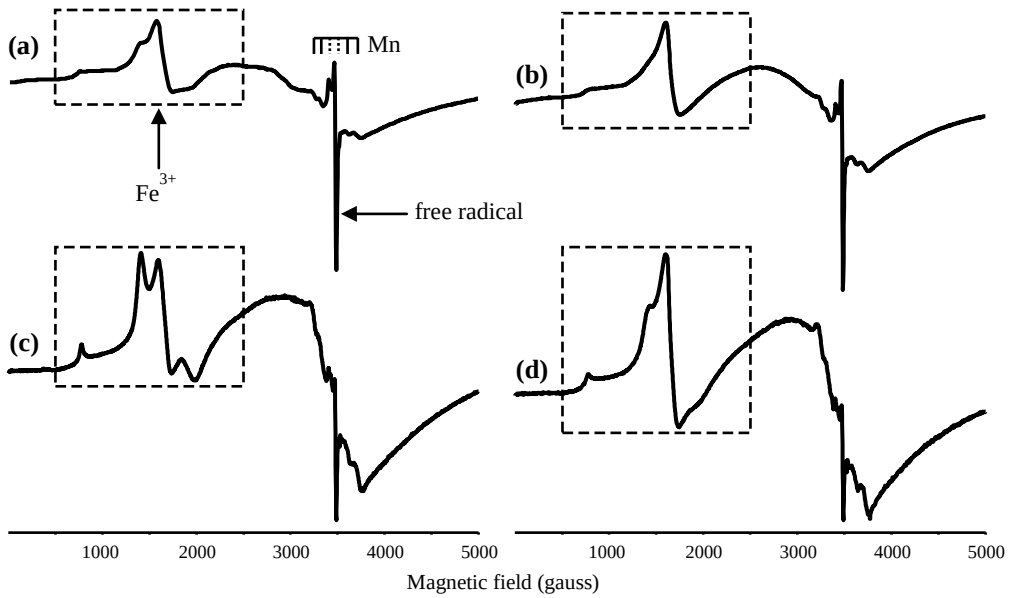

Figure 2. 1st derivative EPR spectra of natural (a) and ground (b) Lampang kaolin, and natural (c) and ground (d) Ranong kaolins. Dashed lines indicate the Fe^{3+} regions investigated in subsequent measurements.

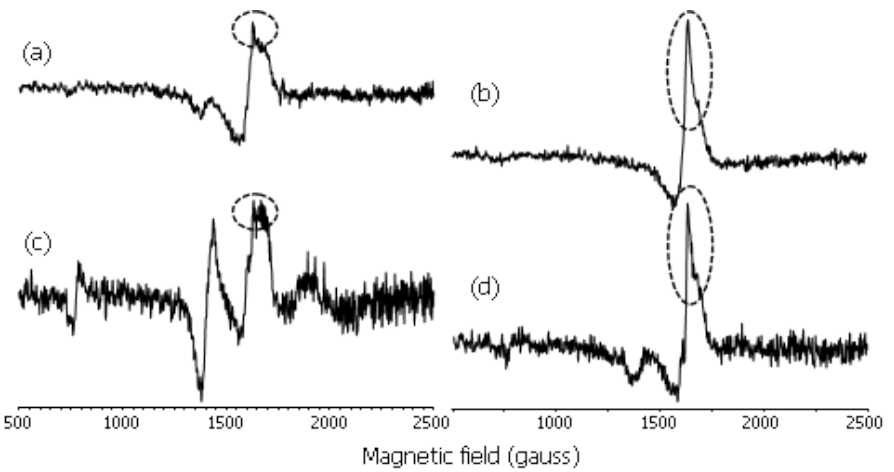

Figure 3. 2nd derivative EPR spectra of natural (a) and ground (b) Lampang kaolin ,and natural (c) and ground (d) Ranong kaolins. Dashed lines indicate the previously unreported resonance.

The stability to heat of this new sharp resonance was also influenced by the grinding history of the samples (Figure 5). For the irradiated natural samples, the sharp resonance at ~1630 gauss was almost completely lost from the natural samples after heating to 300 °C, whereas the intensity of the signal obtained from the ground samples actually increased slightly.

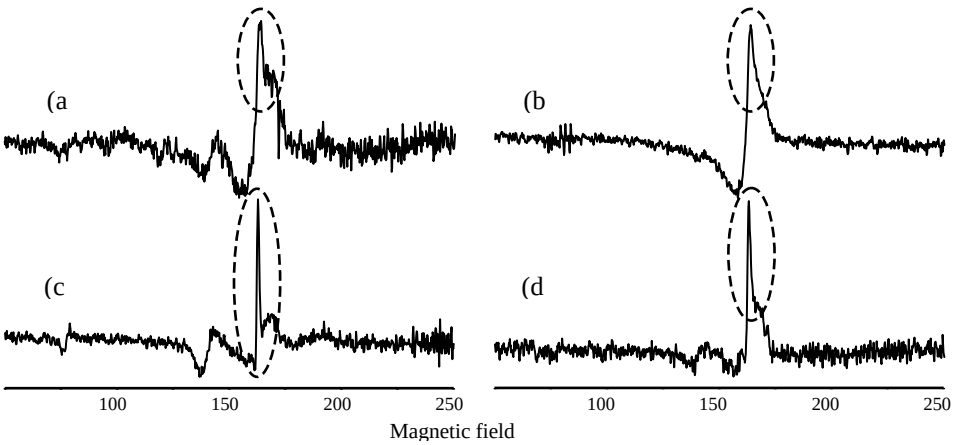

Figure 4. 2nd derivative EPR spectra of natural (a) and ground (b) Lampang kaolin and natural (c) and ground (d) Ranong kaolins after irradiation to a dose of 150 kGy. Dashed lines indicate the previously unreported resonance.

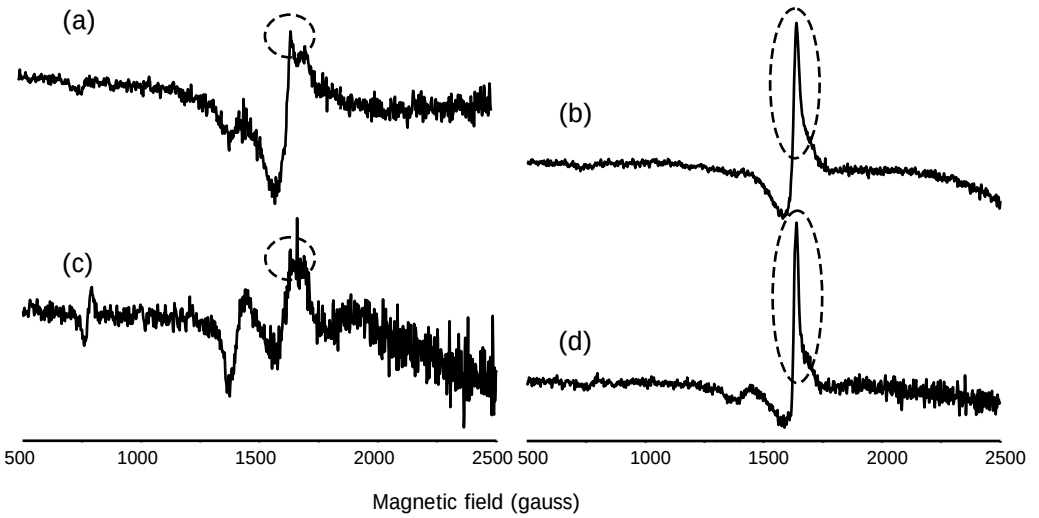

Figure 5. 2nd derivative EPR spectra of natural (a) and ground (b) Lampang kaolin and natural (c) and ground (d) Ranong kaolins after irradiation to a dose of 150 kGy, then heating to 300 °C for 1 h. Dashed lines indicate the previously unreported resonance.

Variation with temperature of the intensity of the new resonance in irradiated natural and ground Ranong samples is shown in more detail in Figure 6. With the natural sample 90%

of the intensity was lost between 80 and 160 °C, whereas with the ground sample the intensity doubled between 150 and 300 °C. It should be noted that the increase in EPR signal intensity between room temperature and 80 °C is probably the consequence of loss of water (and consequent improvement in spectral sensitivity) from the kaolin mineral which contains a high percentage of halloysite (Worasith et al 2011) (the kaolin mineral that has water in the interlayer space).

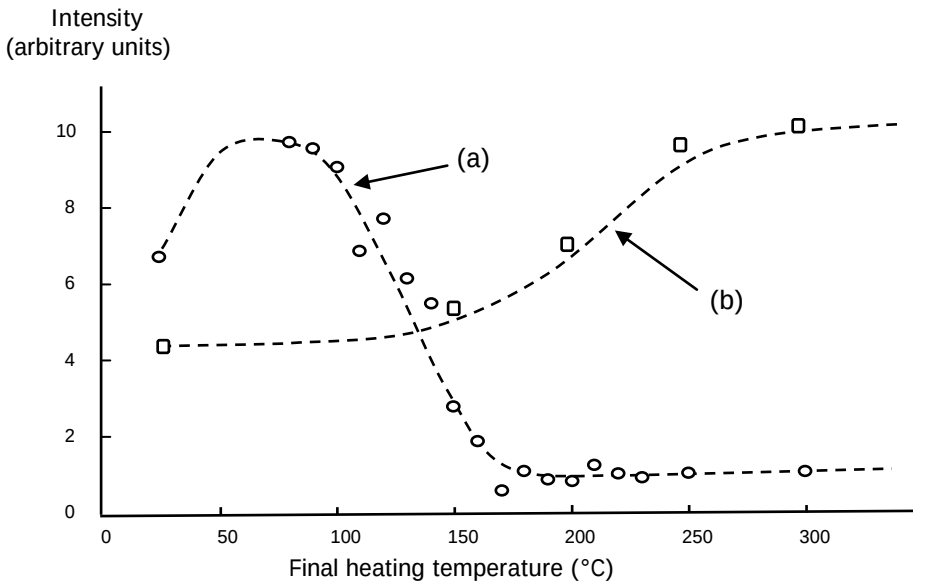

Figure 6. Effect of heating on the intensity of the narrow g = 4.3 peak in the (a) natural and (b) ground Ranong samples after irradiation to a dose of 150 kGy

Discussion

Kaolin minerals invariably show the presence of low field EPR features originating from Fe^{3+} substituting isomorphously for Al in the octahedral sites. These correspond to situations in which the metal experiences near rhombic symmetry (i.e. the zero field splitting parameters, D and E are described by E ~ D/3) and have a g-value ~4.27 (Aasa 1970). Analyses of the Fe^{3+} component in the EPR spectra of kaolin minerals have shown the presence of one singlet and one triplet feature in the spectra with relative intensities that are related to the crystallinity of the sample (Mestdagh et al., 1980; Brindley et al., 1986). In the present work, we have identified the presence of an additional sharp feature at ~1630 gauss (g = 4.28) superimposed on the singlet and central peak of the triplet resonances. This may be similar to a narrow radiation-induced signal in the g = 4.3 region of a kaolinite spectrum that was reported by Gaite et al., (1997), although these authors didn't discuss its identity. In the present work, the resolution of this feature was greatly improved by the use of 2nd derivative recordings which suppress the contributions of broader peaks relative to narrower ones.

Although as mentioned above, EPR peaks with g ~ 4.27 are conventionally associated with Fe^{3+} in rhombic symmetry (Aasa, 1970), this is not its only possible assignment, and a resonance in this position can also be observed for a $\Delta m_S = 2$ transition of a triplet state formed by combination of two S=½ centres (Smith & Pilbrow, 1974), which could result from the formation of O^- centres in neighbouring sites in the kaolin structure. This interpretation is supported by the radiation dose dependence of this signal in the unground Ranong sample (our

unpublished results), and its relatively low stability with respect to heating (Figure 6). Furthermore, the different stabilities with respect to temperature of the new signals with g = 4.28 in the irradiated natural and ground Ranong kaolin samples (Figure 6) are suggestive of different origins. Since grinding results in breakdown of the kaolin mineral structure (Makó et al., 2001), the EPR signal in the ground samples could be derived from a secondary phase, although the results with the unheated samples do not exclude a triplet state formed by damage to the mineral surface. However, the stability to heating to 300 °C combined with its insensitivity to irradiation are strong arguments against its assignment to a triplet state, and thus it most likely corresponds to Fe^{3+} expelled from the structure during the grinding process.

Conclusion

Although the broader implications of these research findings are still unclear, this work illustrates that previously unrecognized changes occur in kaolins as a result of grinding, heating, and/or irradiation, and the origins of their EPR spectra are more complex than is generally assumed. Indeed, it appears that the new resonance observed in the present work corresponds to different paramagnetic species in the natural and ground kaolin samples. Consequently, EPR spectra recorded in isolation can lead to inappropriate conclusions, and in order to fully understand the behavior of paramagnetic components in minerals such as the kaolins, it may be necessary to perform a comprehensive range of studies involving physical, chemical, and radiation treatments.

Acknowledgements

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