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RESIDUAL MANGANESE(II) ENTRAPPED IN SINGLE-LAYER-HYDRATE MONTMORILLONITE INTERLAYERS

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Abstract—Electron paramagnetic resonance (EPR) and Fourier transform infrared (FTIR) spectroscopy in combination with X-ray diffractometry and thermal methods were used to determine the coordination of residual exchangeable Mn(II) in an untreated sample of Wyoming montmorillonite. At room temperature, Mn(II) in a single-layer-hydrate interlayer was proposed to be coordinated directly with oxygen ions of the siloxane surface on one layer and to form water bridges to the oxygens on the siloxane surface of the opposite layer. Dehydration and collapse of the interlayer entrapped and thereby stabilized the partially solvated Mn(II) up to 600°C. A change to Mn(II) in highly symmetric coordination occurred during dehydroxylation of the montmorillonite structure between 600°C and 700°C. Manganese(II) remained coordinated at the surface but positioned in a bicapped trigonal antiprism formed by oxygens of the silicate structure. This coordination was metastable at 800°C when the structural decomposition of the clay mineral began.

Key words—Electron paramagnetic resonance, Mn(II) coordination, Montmorillonite.

INTRODUCTION

Manganese(II) is only weakly adsorbed by clay minerals and, therefore, is very mobile in temperate-zone environments. Drying and wetting of clays, however, can decrease the exchangeability of Mn(II). Either interlamellar entrapment or oxidation/precipitation reactions have been postulated to explain the increased retention (Reddy and Perkins, 1976). Manganese(II) entrapped in interlayers can be considered to be residual.

Electron paramagnetic resonance (EPR) spectroscopy is a powerful method for the study of Mn(II) in mineral samples at concentrations as low as 10 mg kg^{-1} (McBride, 1990). Characteristic EPR derivative spectra with a six-line hyperfine pattern arise from the interaction of the electron spin with the odd nuclear spin ($I = 5/2$) of ^{55}Mn (100% abundance in natural Mn). This spectrum can be characterized by two parameters, A and D, to yield direct information about the Mn(II) ligand field. The hyperfine coupling constant, A, determined from the spacing of the hyperfine lines, is a measure of the covalency of Mn-ligand bonds (Simánek and Müller, 1970). The axial distortion parameter, D, indicates the perturbation of the second-order crystal field, which depends on the departure of coordination from cubic symmetry. This latter parameter can be estimated from the difference in line widths of the first and sixth hyperfine components (Tikhomirova *et al.*, 1972).

McBride *et al.* (1975a, 1975b) used EPR spectroscopy to study the coordination of interlamellar Mn(II) doped into Na- and Mg-saturated smectites. A broad six-line spectrum was found in fully hydrated clays and attributed to the solvated $Mn(H_2O)_6^{2+}$ ion. The collapse of the interlayers after heating to 200°C yielded a well-resolved hyperfine splitting (HFS) spectrum characteristic for Mn(II) in the solid state. This spectral change was explained by postulating the migration of Mn^{2+} into hexagonal cavities of the siloxane surface, where it is coordinated with oxygen ions of the silicate structure (McBride *et al.*, 1975a).

Natural montmorillonite, however, yields well-resolved EPR spectra without interlayer collapse (Coyne and Banin, 1986). Recently, Gehring and co-workers (Gehring and Karthein, 1990; Gehring *et al.*, 1993) have developed a methodology to determine the coordination environment of paramagnetic cations [e.g., Fe(III), V(IV)] in clay minerals without chemical pretreatment. In this approach, spectroscopic methods [Fourier transform infrared (FTIR) and EPR] in conjunction with calorimetric and magnetic methods are used to monitor thermal conversion processes. The correlation of the changes in the EPR signal with the known thermal stability of clay mineral structures makes it possible to assign isomorphous substitutions involving paramagnetic ions to specific structural sites. The present study applies this approach to describe the coordination of naturally-occurring Mn(II) entrapped in the montmorillonite interlayer.

SAMPLES AND METHODS

The smectite (SWy-1), a Na-montmorillonite from Cook County, Wyoming, was obtained from the Source Clay Repository of The Clay Minerals Society. A com-

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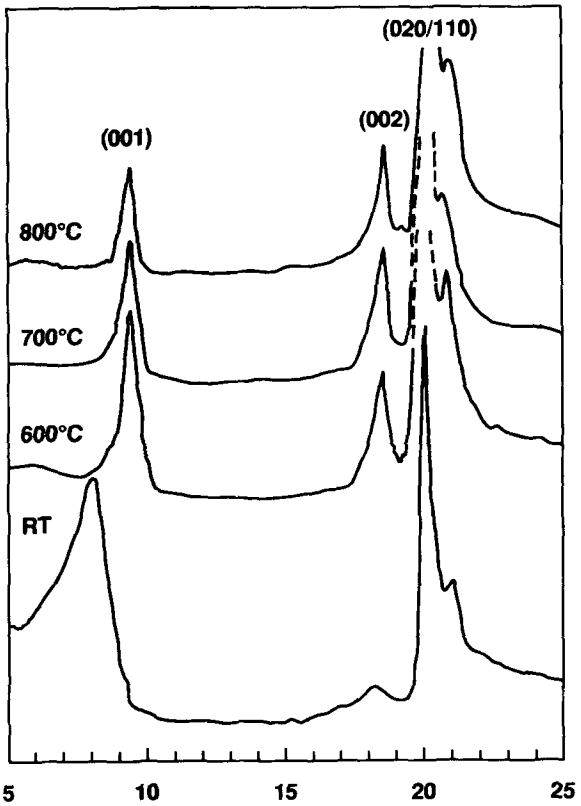


Figure 1. X-ray diffraction pattern of the untreated montmorillonite powder sample at RT and after stepwise heating to 600°, 700°, and 800°C.

pilation of the chemical and physical properties of this smectite has been published by van Olphen and Fripiat (1979). Untreated and thermally treated powder samples were analyzed by EPR and FTIR spectroscopy, as well as by X-ray diffractometry (XRD, Rigaku Geigerflex) using CuKα radiation. For the thermal experiments, samples were heated incrementally for 1 hr in 100°C steps between room temperature (RT) and 800°C in an oven. After each heating step, the mass loss of the sample was measured using a Mettler microbalance. In addition, untreated samples were annealed at 600° and 700°C for 24 hr. The total Mn concentration in the air-dried sample was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) following a hydrofluoric acid digestion (Bernas, 1968).

FTIR spectra in the wavenumber range 400–4000 cm^{-1} were recorded on a Mattson Cygnus 100 spectrometer. The FTIR spectra were obtained in absorbance mode on pellets containing 0.5 mg sample in a 50 mg KBr matrix. Electron paramagnetic resonance spectra were recorded at RT and 10 K on a Bruker 200ER spectrometer equipped with an Oxford Instruments ESR-900 cryostat and operating at X-band frequency with 100 kHz magnetic field modulation. The spectrometer settings were 0.1 mT modulation amplitude, 9.38 GHz frequency, and 2 mW microwave power. The EPR spectra were processed using computerscope programs from R.C. Electronics (Santa Barbara, California) to determine g-values (N,N-diphenylpicrylhydrazyl (DPPH) as reference for g-values) and hyperfine coupling constants (A).

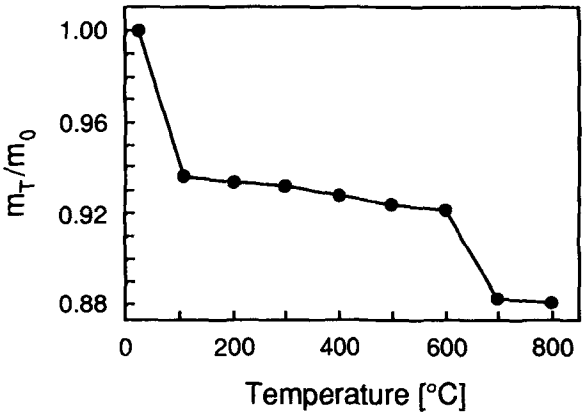


Figure 2. Relative mass loss of the untreated montmorillonite sample during stepwise heating to 800°C for 1 hr at each step.

RESULTS

The XRD pattern at RT was characteristic of montmorillonite powder samples, with a broad (001) line at 1.13 nm and strong non-basal diffraction peaks (020, 110) at 0.44 nm (Figure 1). After heating the sample to 200°C, the (001) peak shifted to 0.95 nm, the (002) peak became more pronounced, and the non-basal diffraction peak remained stable. This pattern persisted upon heating to 800°C (Figure 1). Thermal treatment of the sample up to 800°C revealed an overall mass loss of 11.79 ± 0.53 wt. % (Figure 2). Two major steps, with mass losses of 6.48 ± 0.13 wt. % and 3.92 ± 0.06 wt. %, were observed at 100°C and between 600° and 700°C, respectively (Figure 2).

The total Mn concentration in the untreated sample was 184 ± 3 mg kg^{-1}. The FTIR spectrum of untreated montmorillonite in the 3800–3000 cm^{-1} range (Figure 3) showed the characteristic stretching vibrations of structural OH at 3630 cm^{-1} and around 3400 cm^{-1} (Farmer, 1974). In the mid-infrared region, the untreated sample exhibited Si-O stretching (1119 and 1046 cm^{-1}), Si-O deformation and Al-O stretching (523 and 466 cm^{-1}), and OH deformation (920, 885, 850 cm^{-1}) bands (Farmer, 1974). Upon heating to 700°C, changes in the FTIR spectrum were observed (Figures 3 and 4). The absorption bands assigned to vibrations of the OH groups (3635, 3400, 920, 885, 850 cm^{-1}) disappeared. The Si-O stretching bands broadened and the shoulder at 1119 cm^{-1} shifted slightly to 1135 cm^{-1}.

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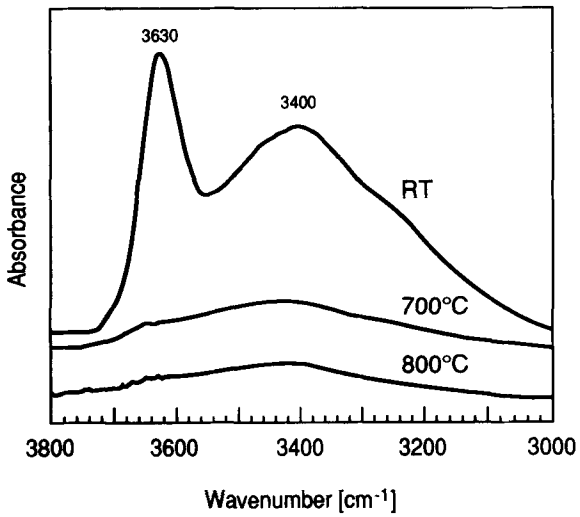


Figure 3. Near-infrared spectra of the untreated montmorillonite sample at RT and after stepwise heating to 600°, 700°, and 800°C.

A shift to higher wavenumber also was found for the Si-O deformation and Al-O stretching bands: New bands appeared at 566 and 481 cm^{-1} (Figure 4), respectively. Upon heating to 800°C, a drastic decrease in band intensity in the mid-infrared range was observed (Figure 4).

The EPR spectrum of montmorillonite at RT exhibited two principal resonances around g = 4.3 and g = 2 (Figure 5). The feature at g = 4.3, attributed to Fe(III) in a strongly distorted orthorhombic crystal field, has been described in detail for clay minerals (Hall, 1980). The resonance around g = 2 showed a six-line pattern overlaying a sharp, isotropic signal. This signal, which can be attributed to a stable free radical caused by structural defects or organic impurities (Cuttler, 1980), persists below 400°C (Figure 6). The remaining anisotropic six-line spectrum, with weaker doublets between the principal hyperfine components is characteristic for Mn(II). The weaker doublets, referred to as "forbidden transitions" ($\Delta m = \pm 1$), are caused by axial distortion of the crystal field (Wertz and Bolton, 1972). A g‖-value of 2.003 ± 0.001 and a parallel hyperfine coupling constant of A‖ = 9.53 ± 0.13 mT were calculated for this signal. The resolution of the spectrum for the powder sample did not allow a determination of the perpendicular spectral parameters (g⊥ and A⊥). An axial distortion parameter D ≈ 10 mT was estimated from the difference of the line widths of the first (ΔB_1 = 1.20 ± 0.01 mT) and the sixth (ΔB_6 = 2.36 ± 0.01 mT) HFS component (Figure 6), using data from Tikhomirova *et al.* (1972). Stepwise heating to 600°C as well as heat treatment at 600°C for 24 hr led to a decrease in signal intensity, but the spectral parameters A‖ and D remained constant.

Between 600° and 700°C, however, a drastic spectral change was observed. The newly formed spectrum was isotropic, with A = 8.80 ± 0.01 mT and a constant line width of 0.41 ± 0.03 mT for all the HFS components, which corresponds to D = 0 (Figure 6). This signal remained stable upon continued heating at 700°C for 24 hr. Upon heating to 800°C, the isotropic HFS signals disappeared and a broad asymmetric spectrum developed (Figure 5). This new spectrum broadened considerably upon cooling to 10 K.

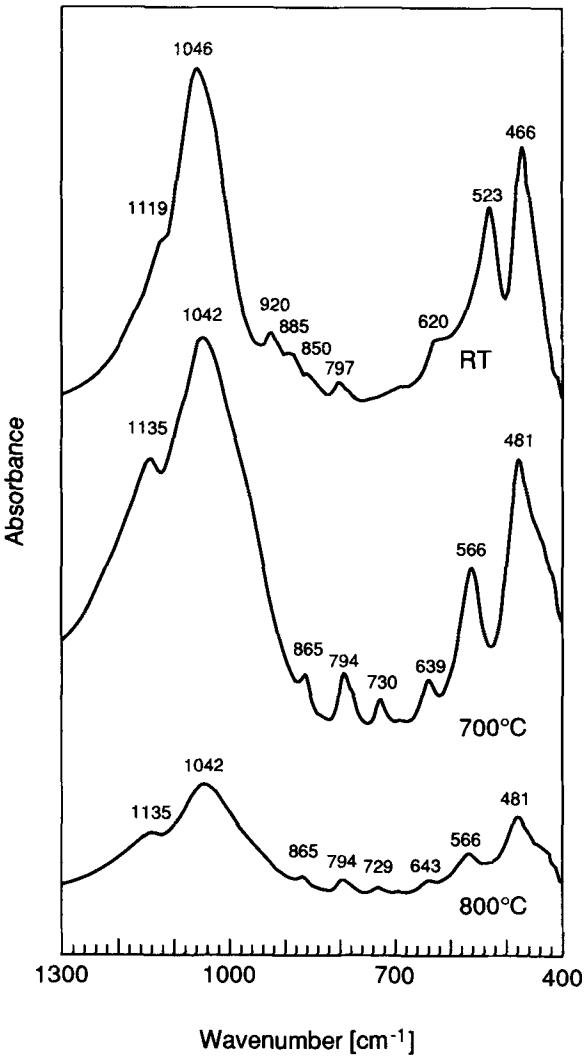


Figure 4. Mid-infrared spectra of the untreated montmorillonite sample at RT and after stepwise heating to 600°, 700°, and 800°C.

DISCUSSION

Manganese occurs as a trace element in the montmorillonite sample (total concentration of 184 mg kg^{-1}). Since Mn(II) is EPR-detectable, the HFS signals (Figures 5 and 6) represent a Mn(II) concentration ≤184 mg kg^{-1}. The good resolution of the six-line EPR spec-

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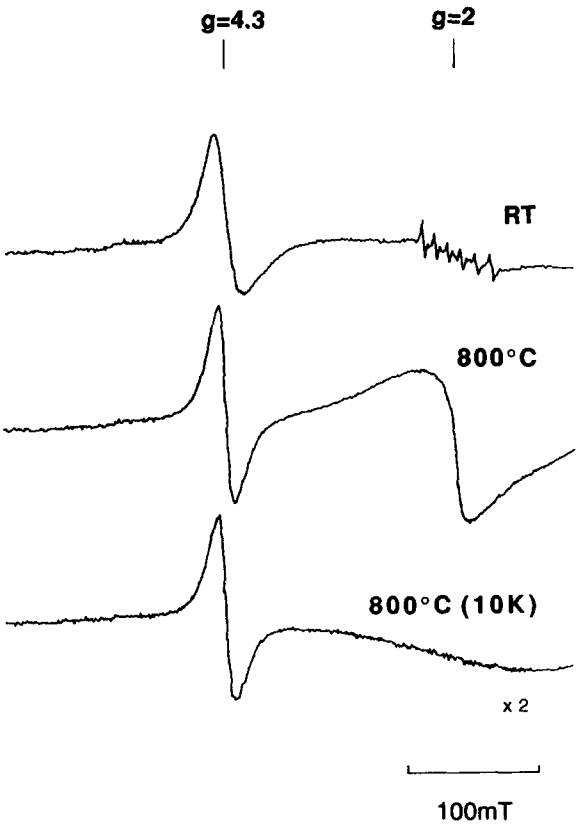


Figure 5. Wide-range EPR spectra of the untreated montmorillonite sample at RT, and after heating to 800°C, measured at RT and 10 K. The low-temperature signal is gain-reduced by a factor of 2.

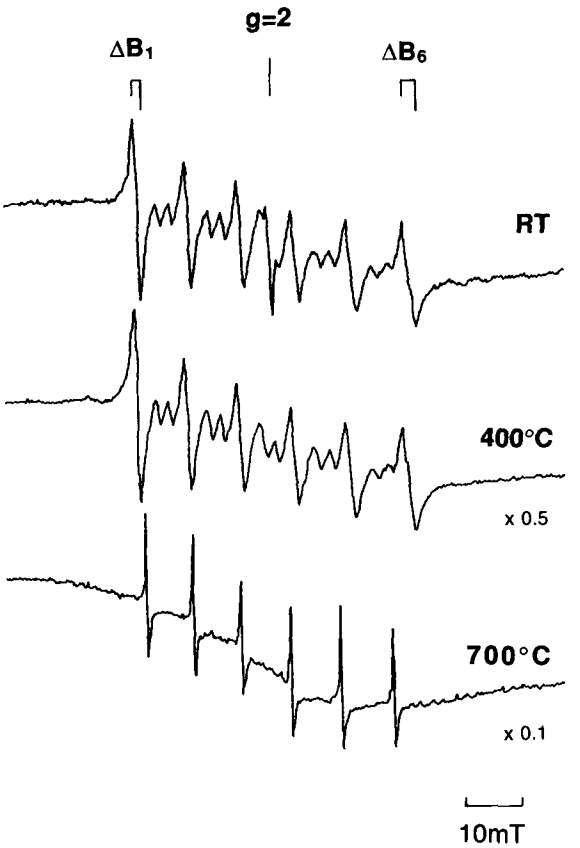


Figure 6. Narrow-range EPR spectra of the untreated montmorillonite sample at RT and after stepwise heating to 400° and 700°C. The spectra of the heat-treated samples are gain reduced by factors of 0.5 and 0.1, respectively.

trum at g = 2 indicates that Mn(II) is magnetically dilute, consistent with a low concentration of Mn(II) in the sample. Manganese (II) could yield HFS signals either as an isomorphically substituted species or as an adsorbed species on the clay mineral surface. The easy exchangeability of Mn(II) in SWy-1 montmorillonite (Coyne and Banin, 1986) is inconsistent with the presence of Mn(II) in a structural site. Therefore, the EPR spectra can be attributed to Mn(II) located in interlayers.

However, similar HFS signals have been described by McBride *et al.* (1975a, 1975b) in a thermally dehydrated hectorite. These signals were interpreted in terms of Mn(II) coordinated to silicate oxygens in the hexagonal cavities. Exchangeable Mn(II) must be at least partially solvated (Sposito and Prost, 1982). The basal plane spacing of about 1.24 nm suggests the presence of single-layer-hydrate interlayers within the untreated montmorillonite (Figure 1). Therefore, it can be proposed that residual interlamellar Mn(II) is coordinated directly with oxygen ions of the siloxane surface on one layer but forms water bridges to the oxygens on the siloxane surface of the opposite layer. A similar coordination environment has been suggested for Na(I) in single-layer-hydrate interlayers (Farmer, 1968).

Annealing at 200°C led to dehydration and collapse of the interlayers (Figures 1 and 2) but did not perturb the coordination of Mn(II) as indicated by the EPR spectra. The persistence of partially solvated Mn(II) after dehydration of the montmorillonite samples suggests that Mn(II) is entrapped within the interlayer and protected from complete dehydration and oxidation. Incomplete dehydration of Mn(II) during thermal treatment at 200°C also has been observed for Na(I) hectorite (McBride *et al.*, 1975b). This effect was explained by an incongruent collapse of the interlayer region resulting from the fact that monovalent cations desolvate more readily than bivalent cations.

The decrease of the EPR signal intensity upon stepwise heating to 600°C indicates that not all of the entrapped Mn(II) is protected from oxidation. Given a uniform distribution of the Mn(II) sites, it can be argued that those with easier access to oxygen (e.g., sites at layer edges) are more easily oxidized. Moreover, the best-protected sites (stable up to 600°C) are expected to be deep within the interlayers. Comparison of the

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XRD and FTIR data indicates that the layer structure of montmorillonite persists to 800°C despite dehydroxylation between 600° and 700°C (Figures 1, 3, and 4).

The change of the HFS spectrum upon heating to 700°C (Figure 6) reveals that Mn(II) associated with the dehydroxylated montmorillonite is in a new coordination environment. The isotropic EPR signal, with spectral parameters A = 8.8 mT and D = 0, indicates that Mn(II) has six-fold coordination in an undistorted ligand field. It can be assumed that, after annealing at 700°C, the EPR signal arises from dehydrated Mn(II). Moreover, the new spectrum, with the six sharp HFS components (ΔB = 0.4 mT) and no forbidden transitions, suggests that Mn(II) is coordinated in a cubic symmetry that is expected only for solids. This high symmetry excludes the possibility that Mn(II) has migrated into a vacant octahedral site. Since the change in the FTIR spectra indicates that dehydroxylation leads to a distortion of the silicate framework (Shimoda and Brydon, 1971), it is unlikely that the Mn(II) is located in an undistorted site within a hexagonal cavity. Therefore, Mn(II) must remain at the surface coordinated with six oxygens. Such interlamellar Mn(II) is then most likely positioned in the center of a highly symmetric, bicapped trigonal antiprism.

These sites, sandwiched between dehydroxylated montmorillonite layers, are unstable upon heating to 800°C when the residual Mn(II) becomes oxidized. The broad signal around g = 2 (Figure 5) at 800°C points to the release of Fe from the montmorillonite structure and the formation of an Fe oxide phase. The shape and the temperature-dependence of the new signal argues in favor of hematite (α-Fe_2O_3) or magnetite (Fe_3O_4) (Gehring *et al.*, 1990). The release of Fe and the subsequent formation of an Fe oxide phase thus marks the beginning of the structural decomposition of the montmorillonite.

CONCLUSIONS

The use of combined spectroscopic and thermal methods to investigate Mn(II) in an untreated montmorillonite led to the following conclusions:

1) Residual Mn(II) in a single-layer-hydrate interlayer is coordinated in a distorted ligand field to three oxygen ions of the siloxane surface and three water molecules bridging to the oxygens of the siloxane surface of the opposite layer. During dehydration, the partially solvated Mn(II) becomes entrapped and stabilized against oxidation in the interlayers.
2) Structural changes during dehydroxylation of the montmorillonite between 600° and 700°C led to Mn(II) positioned in highly symmetric, bicapped trigonal antiprism sites formed by structural oxygens at the basal plane surfaces of the montmorillonite.
3) Manganese(II) in these latter sites is unstable at 800°C, when the structural decomposition of montmorillonite begins.

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