

ON THE NATURAL Mn(II) EPR SIGNAL OF SWy-1 MONTMORILLONITE

In a recent paper published in *Clays and Clay Minerals* (Gehring *et al* 1993), the EPR signal indicating a Mn(II) impurity in Na-montmorillonite (SWy-1, Crook Co., Wyoming) was interpreted to arise from Mn^{2+} on exchange sites of the clay. However, the insensitivity of this signal to thermal dehydration (it did not change upon heating the clay from room temperature to 600°C) suggests that this Mn^{2+} was not hydrated at room temperature. Otherwise, the loss of hydration water would most likely have changed the ligand field of the Mn^{2+} , altering the EPR spectrum in the process, as observed by McBride *et al* (1975) for exchangeable Mn^{2+} on hectorite. A much more probable origin for the 6-line EPR signal can be suggested, as the room temperature spectrum presented in Figure 6 of Gehring *et al* (1993) is substantially the same as that for Mn^{2+} substituted in the structural sites of calcite, as shown in Figure 1a. Both spectra show the features characteristic of Mn^{2+} in an axially distorted site; that is, each of the 6 hyperfine lines ($m_I = 5/2, 3/2, \dots, -5/2$) is split into a doublet, and forbidden resonances ($\Delta m_I = 2$) appear as doublets between the main resonances (McBride 1990). The main difference between the Mn(II) spectrum of the montmorillonite and calcite is that the resonance lines of the latter are less broadened, so that the splitting of the main 6 lines is not obscured, even for the low-field ($m_I = 5/2$) line which has the smallest splitting. Similar spectra have been observed in soils known to contain calcite (Pacey 1984, McBride 1979).

Based on the similarity of the Mn(II) spectra in the montmorillonite and pure calcite, the Mn(II) EPR signal SWy-1 in montmorillonite is attributed to Mn^{2+} substituted isomorphically in calcite, which occurs as an impurity in this source clay (van Olphen and Fripiat 1979). As shown in Figure 2, almost all of the Mn(II) signal originates in the coarse ($>2 \mu m$) fraction of montmorillonite, proof that the signal does not arise from exchangeable Mn^{2+} on montmorillonite. The fact that this spectrum has broader resonance lines than that of Mn^{2+} in pure calcite (Figure 1a) could be due to relaxation effects from paramagnetic impurities (i.e., transition metals) in the natural calcite associated with montmorillonite, or to lower crystallinity of the natural calcite. The untreated montmorillonite sample contained 184 mg Mn/kg (Gehring *et al* 1993), and if all of this Mn were concentrated in the calcite impurity, then the Mn-Mn interatomic distances could be short enough to cause line broadening due to paramagnetic

relaxation. The spectrum of Mn^{2+} coprecipitated with Ca^{2+} in calcite (McBride 1990) has linewidths intermediate between that of the SWy-1 clay and the one shown in Figure 1a, suggesting that Mn^{2+} concentration in the solid affects spectral linewidths. In fact, for a range of Mn^{2+} concentrations co-precipitated into $CaCO_3$, the EPR linewidths increase with increasing concentration (McBride, unpublished data).

The fact that Gehring *et al* (1993) observed a marked change in the Mn(II) spectrum after heating the clay sample to 700°C can be attributed to thermal decomposition of $CaCO_3$ to CaO near this temperature. Figure 1b shows the spectrum of Mn(II) after heating pure calcite at 700°C for about 5 hours. The main spectrum consists of 6 hyperfine lines devoid of fine structure, indicative of Mn(II) in sites of cubic symmetry, which would be expected for the cubic CaO lattice (McBride 1990). Some $CaCO_3$ remains in the heated calcite, as

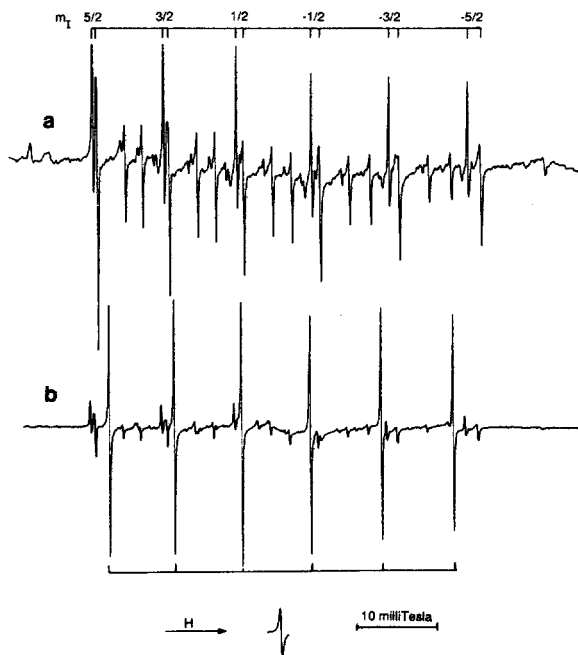


Figure 1. Room temperature ESR spectrum (x-band) of reagent-grade $CaCO_3$ powder (a) before heating and (b) after heating at 700°C for 5 hours. Positions of the six hyperfine lines with their respective nuclear quantum numbers (m_I) are marked. The $g = 2.00$ position is indicated by the strong pitch signal near the center of the spectrum.

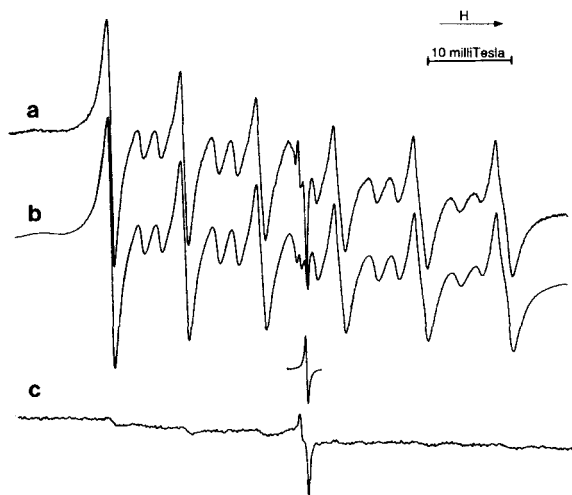


Figure 2. Room temperature ESR spectra (x-band) of SWy-1 Na⁺-montmorillonite powders with and without particle size separation: (a) whole sample (unfractionated), (b) >2 μm size fraction, (c) <2 μm size fraction. The gain for spectrum b was reduced by a factor of 12.5 relative to that of spectra a and c.

indicated by weak resonances at the field positions of the spectrum shown in Figure 1a.

It is interesting that a Mn(II) EPR spectrum not unlike that reported by Gehring *et al* has been observed after heating a Mg²⁺-hectorite (with some Mn²⁺ at exchange sites) to 215°C (McBride *et al* 1975). This spectrum may have arisen from Mn²⁺ in low-symmetry sites in hexagonal holes of the collapsed interlayer regions. However, this signal did not have a noticeable field-dependence of fine splitting in each of the main 6 hyperfine lines, suggesting a different degree of axial distortion of the Mn(II) site. Furthermore, the splitting in these lines varied depending upon the orientation of the silicate sheets of the hectorite relative to the applied magnetic field. Consequently, this EPR signal in the thermally dehydrated hectorite could be attributed with little question to Mn²⁺ coordinated to silicate oxygens of the clay itself.

In summary, there is strong evidence that the EPR spectrum of Mn(II) in Na-montmorillonite has been misassigned by Gehring *et al* (1993). It undoubtedly arises from Mn substituted into CaCO₃ impurities in this clay. There may be some exchangeable Mn²⁺ in this clay, but this form generates broader EPR lines which may not be detected under the more intense resonances of Mn²⁺ in calcite.

ACKNOWLEDGMENT

Appreciation is expressed to Dr. Colin Farmer for alerting the author to apparent inconsistencies of the EPR results with known reactions of smectites upon thermally-induced dehydroxylation.

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- (Received 9 May 1994; accepted 7 September 1994; Ms. 2505)